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Micro-Structured $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ Catalysts for Oxidative Coupling of Methane

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$Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS), a ceramic material showing great activity and selectivity to oxidative coupling of methane (OCM), has been fabricated into catalyst rings (i.e., capillary tubes) with a plurality of self-organized radial microchannels. The unique microchannels inside such BYS catalyst rings allow easier access of reactants, as well as increased the surface area, which potentially contributes to higher reaction efficiencies due to improved mass transfer. The micro-structured BYS catalyst rings were investigated systematically via two types of reactors; (1) randomly packed fixed bed reactor and (2) monolithic-like structured reactor. These two reactor designs have different flow patterns of reactants, that is, non-ideal and ideal flows, which can significantly affect the final OCM performance. A remarkable improvement in C_{2+} yield ($Y_{C2+} > 20\%$) was obtained in the monolith-like structured reactor, in contrast to randomly packed powder and micro-structured rings ($Y_{C2+} < 15\%$), which proves the advantages of using a micro-structured catalyst with an ideal flow in the feed for OCM. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 3451–3458, 2015

Keywords: oxidative coupling methane, micro-structured catalyst, fixed bed reactor, monolith-like reactor

Introduction

Recent developments in shale gas are generating much excitement around the world, as it has been foreseen as an opportunity to gradually shift toward the use of natural gas (methane) as the feedstock producing a wide range of valuable chemicals due to its abundant supply at a lower price over petroleum.[1–3] The state-of-the-art process of methane conversion can be roughly divided into direct and indirect routes.[4] Among those methane conversion processes available, oxidative coupling of methane (OCM) has been considered as an attractive route for more efficient utilization of natural gas, as it offers a direct conversion of methane to C_{2+} products [ethane (C_2H_6) and ethylene (C_2H_4)]. However, due to a number of scientific and technique challenges, indirect conversions of methane via syngas are more widely considered for industrial applications. Major challenges that still constrain the commercial exploitations of OCM include (1) high operating temperatures (700–900°C) in order to achieve high C_{2+} yield; (2) C_{2+} products are more reactive than methane, resulting in deep oxidation of the C_{2+} products to CO_x especially at high temperatures; and (3) higher conversion is normally accompanied with lowered selectivity, making the achievement of high C_{2+} yield extremely difficult. However, with the recent soaring exploration of shale gas, once again, OCM is becoming an interest research topic, which has been well reflected by the increasing number of related publications since 2010. The OCM reactions for C_{2+} formation are shown below

$$2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O\,(\Delta H = -175.6\,\mathrm{kJ/mol}) \quad (1)$$

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O\,(\Delta H = -280.8\,\mathrm{kJ/mol}) \quad (2)$$

Besides the two selective reactions above, there are several side-reactions that generate CO_x, which can reduce the C_{2+} yields, with examples given below

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O\,(\Delta H = -890.4\,\mathrm{kJ/mol}) \quad (3)$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O\,(\Delta H = -1411.17\,\mathrm{kJ/mol}) \quad (4)$$

As a result, an ideal OCM catalyst should allow high initiation rate of methyl radical, which usually occurs on the catalyst surface, and most importantly can suppress the non-selective oxidation of CH_4 and C_{2+} products to CO_x.[5] Since the pioneering work on OCM catalyst by Keller and Bhasin[6] in 1980s, remarkable progress in developing highly efficient and selective OCM catalysts have been achieved. Nevertheless, the C_{2+} yields obtained are still below the 30% threshold value expected for the purpose of commercialization.[7]

Mixed metal oxides with adjustable solid-state properties have been known with impressive catalytic properties toward OCM, when compared to the single metal oxide catalysts.[5] Among the mixed metal oxide catalysts investigated for OCM, $Bi_{1.5}\,Y_{0.3}Sm_{0.2}\,O_{3-\delta}$ (BYS) of a fluorite structure, which was reported by Zeng et al.[8] and Akin and Lin,[9] shows a promising performance. This material appears to be not only oxygen permeable but also catalytic active for OCM, a reaction with both heterogeneous and homogeneous reaction mechanisms.[9–12] In addition, BYS is mechanically and chemically stable for OCM reaction, making it suitable to be used as OCM catalyst. Interestingly, when this BYS powder was used to make a tubular dense membrane reactor, a 35% of C_{2+} yield was achieved at 900°C,[9] exceeding the C_{2+} yield of its powder form (~20%).[8]

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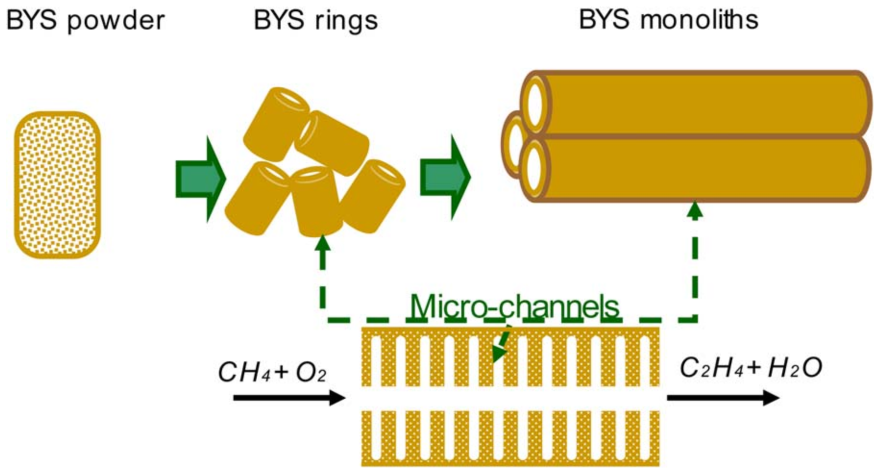

Figure 1. Schematic representation between BYS powder, micro-structured BYS rings, and micro-structured BYS monoliths.

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This suggests that apart from the catalytic properties of the metal oxides, the OCM performance can be improved by designing the catalyst structure and reactor configuration.

Most of the catalysts investigated in laboratory were in a powder form as it is much easier and faster to prepare. While for larger scale operations, catalyst pellets (or rings) are much preferred due to less clogging and great mechanical strength. Fixed bed reactor (FBR) is one of the established reactors that have been extensively used in industry as it generally shows low cost and easy maintenance.[13] The packing of catalyst inside the FBR is normally irregular and lack of ordered patterns, which can lead to a nonuniform flow of reactants and subsequently hot spots/thermal runaway, especially for a highly exothermic reaction such as OCM. In contrast to the FBR, a structured catalytic reactor offers a more organized flow of reactants (i.e., an ideal flow), which could reduce pressure drop across the reactor while maximizing the access to the active sites of catalysts. This type of catalytic reactor can contain either "normal' catalyst particles that are in a structured arrangement or "structured catalyst" in which catalyst and reactor are in the same entities.[14]

In this study, a new design of BYS catalyst rings, which have significant self-organized microchannels opening from the inner surface, has been developed using a viscous fingering-induced phase inversion process. This technique has been widely used in the fabrication of micro-structured ceramic hollow fiber membrane as it offers great flexibility in tailoring both the macrostructure and microstructure.[15,16] To understand the role of catalyst structure in affecting OCM, a systematic comparison between BYS powder, micro-structured rings and micro-structured monolith was designed as shown in Figure 1. Two types of reactors, that is, randomly packed reactor and structured reactor, have been used in this study to evaluate the performance of micro-structured BYS rings and monoliths. The use of BYS powder serves as a comparison on the OCM activity of this material.

Experimental

Chemicals and materials

$Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) was purchased from PIDC. Dimethyl sulfoxide (DMSO, VWR), Hypermer KD-1 (Croda), and polyethersulfone (PESf, Radal A300, Ameco Performance) were used as the solvent, dispersant, and polymer binder for spinning suspensions, respectively. DMSO and tap water were used as a bore fluid and external coagulant, respectively.

Fabrication of micro-structured BYS catalyst rings for OCM

A BYS spinning suspension was first prepared by dispersing 68 wt % of BYS powder into a mixture of solvent and dispersant. The mixture was then roll milled for at least 3 days before adding the polymer binder. The milling was then continued for another 3–5 days to ensure a homogeneous spinning suspension. Prior to the spinning process, the suspension was degassed by stirring under vacuum to remove air bubbles. The degassed spinning suspension was then transferred into a 200-mL stainless steel syringe controlled by Harvard PHD 22/2000 Hpsi syringe pump.

The micro-structured BYS rings (or capillary tubes) were fabricated using a viscous fingering-induced phase inversion process, the details of which have been described elsewhere.[15,17] In this process, the spinning suspension was extruded through the spinneret, which was positioned inside the coagulation bath, with a stream of solvent as the bore fluid flowing through the central bore of spinneret, forming a capillary tube configuration. The extruded tube precursors were rinsed with water and left in a water bath overnight to complete the phase inversion process, before being cut into a specific length prior to calcination. The calcination process was carried out between 920–1080°C for 12 h. The calcined tubes

Table 1. Fabrication Conditions of Micro-Structured BYS Catalyst Rings (Capillary Tubes)

Experimental Parameters	Values
Composition of spinning suspension	
Ceramic powder	68 wt %
Polymer, PESf	6.8 wt %
Solvent, DMSO	22.2 wt %
Dispersant, KD1	3 wt %
Spinning parameter	
Bore fluid	DMSO
Air gap	0 cm
Flow rate of spinning suspension	7 mL/min
Flow rate of bore fluid	5 mL/min
External coagulant	Tap water

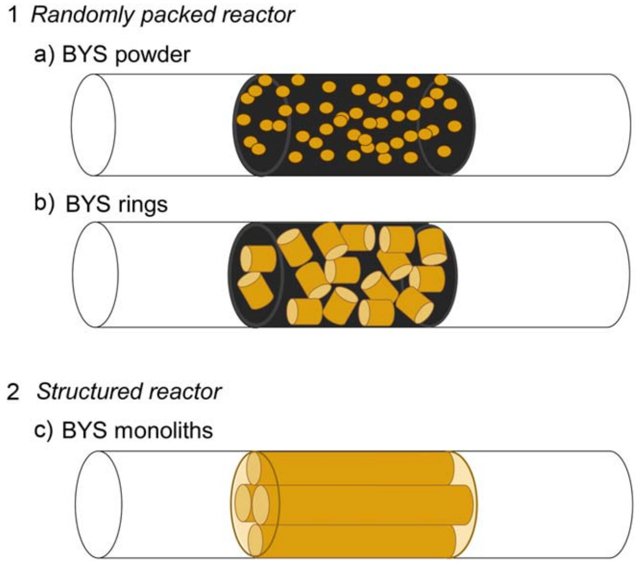

Figure 2. Reactor designs investigated in this study; (1) randomly packed reactor and (2) structured reactor.

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are then cut into rings (short tubes) or assembled as monoliths (long tubes and then bundled together) for OCM reaction. The fabrication conditions of the micro-structured BYS catalysts are shown in Table 1.

Characterizations

X-ray diffraction (XRD) analysis was used to characterize the structure of BYS upon heat treatment. The XRD patterns were obtained with an X'celerator detector (X'Pert PRO) using Cu-Kα as the radiation source. The XRD scans were carried out in a 2θ range from 10° to 80° using a step width of 0.05°. The equipment voltage and current were set at 40 kV and 40 mA, respectively.

A JEOL JSM-5610LV scanning electron microscope (SEM) was used to observe the catalyst structures. The samples were coated with gold under vacuum using an SEM sputter coater before being viewed. Bunauer–Emmett–Teller (BET) analysis was performed using nitrogen to measure the specific surface areas of BYS powders upon different calcination temperatures. Prior to the analysis, the samples were dried and degassed at 120°C for 4 h.

Oxidative coupling of methane

Two types of the reactor designs, that is, randomly packed and structured (i.e., monolith-like) reactors were investigated in this study, as shown in Figure 2. A randomly packed FBR of BYS powder (2.0 g) was prepared by mixing a predetermined amount of BYS powder with silica carbide. The mixture was then placed at the center of a dense ceramic tube (internal diameter = 6 mm), giving a catalyst zone of 5 cm in length (Figure 2a). Quartz wool was used to fix the catalyst bed in the middle of the reactor. For the BYS rings, 2.0 g of the rings (0.5–0.7 cm in length) was randomly packed in the middle of the reactor using similar procedure as described for powder (Figure 2b), forming a fixed bed of 5 cm in length. For the structured reactor, four long BYS capillary tubes of 5 cm in length with a total weight of 2.0 g were arranged as a monolith (Figure 2c), with the gaps between the BYS tubes being sealed using ceramic sealant to provide organized reactant flows.

The experimental setup for OCM reaction is shown in Figure 3. The prepared reactor was positioned horizontally in a tubular furnace (uniform heating length of 5 cm) and heated up to the desired reaction temperature in argon. The setting temperature of the furnace was referred as the operating temperature of the reaction. The flow rates of the reactants were controlled using mass flow controllers (Brooks Instrument, model 0154) and monitored by a bubble flow meter. All gas flows were at the standard temperature and pressure. Once the

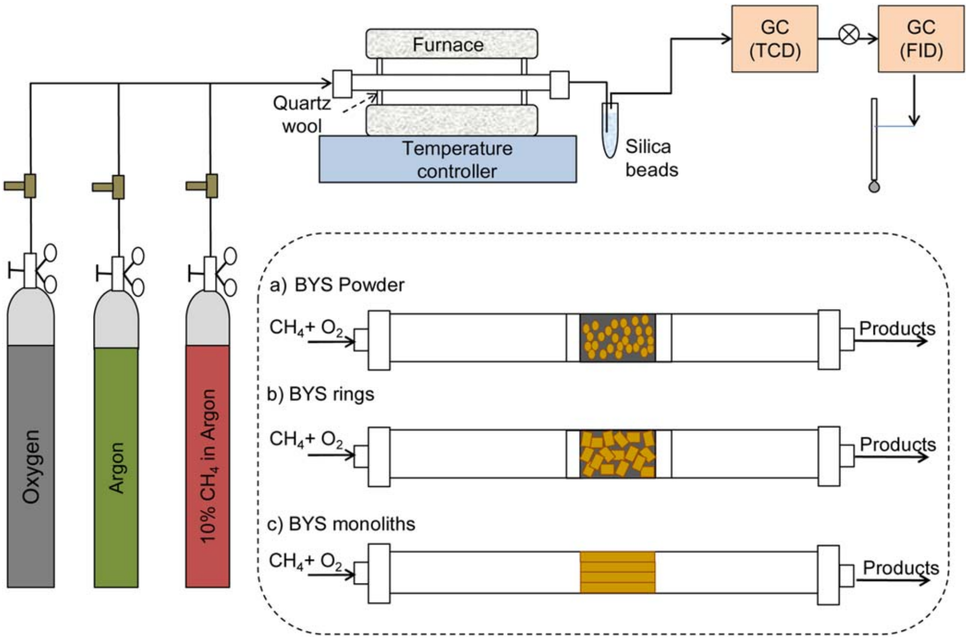

Figure 3. Schematic diagram of OCM experimental setup.

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Table 2. Specific Surface Areas of BYS Powder at Different Calcination Temperatures

Calcination Temperature	Specific Surface Area (m^2/g)
Fresh powder	0.22
920°C	0.20
1040°C	0.17
1080°C	0.14

furnace temperature reached 600°C, argon was replaced with a mixture of 10% methane in argon to activate the catalyst. Then, the furnace was further heated up to desired reaction temperatures (700–900°C).

The analyses of the reactor effluents were performed online by gas chromatography (GC), after the reaction temperature was stabilized for 1 h. Before entering the GC, the effluent gas was passed through a silica gel for removal of water. Two types of GC (Varian 3900) were used in the analysis; that is, thermal conductivity detector for permanent gasses (hydrogen, CO, CO_2, etc.) and flame ionization detector for light hydrocarbons (CH_4, C_2H_4, etc.). The OCM performance was evaluated based on the CH_4 conversion (X_{CH_4}) as well as selectivity (S_j) of C_{2+} and CO_x using the equations below

$$X_{CH_4}=\frac{\left(F_{CH_4\,\mathrm{inlet}}-F_{CH_4\,\mathrm{outlet}}\right)}{F_{CH_4\,\mathrm{inlet}}}\times 100\% \tag{5}$$

$$S_j=\frac{\sum n_jF_j}{\left(F_{CH_4\,\mathrm{inlet}}-F_{CH_4\,\mathrm{outlet}}\right)}\times 100\% \tag{6}$$

$$C_{2+}\,\mathrm{Yield}=X_{CH_4}\times S_{C2+} \tag{7}$$

where n_j is the number of carbon atom in the carbon-containing product j, F_{CH_4} and F_j are the flow rates of methane and product j in mol/min. The C_{2+} yield was then calculated by multiplying the methane conversion with selectivity. The productivity rate (Y_j) was calculated by taking into account the mass of BYS (M_{cat}) used in the reactor, as shown in the equation below

$$Y_j=\frac{\sum n_jF_j}{M_{cat}}\times 100\% \tag{8}$$

Results and Discussion

Physical properties of BYS catalyst powders

Fabrication of BYS capillary tubes and the subsequent OCM reactions involves high operating temperatures, which can cause the sintering of BYS that affects its activity. As a result, the effects of sintering temperature toward the OCM performance were first investigated. The BYS powder was heat-treated at various temperatures between the maximum operating temperatures of OCM (900°C) and melting points of BYS (~1100°C). Table 2 shows the BET surface area of BYS powder before and after heat treatment. It can be seen that in general, the surface area values of fresh and calcined BYS powders are relatively small (<1.0 m^2/g), similar to a previous study.[18] Also, the effect of sintering temperature on the change of the specific surface area was noticeable, but was not significant. The effect of calcination temperature toward the change of BYS crystal structures is shown in Figure 4. From the XRD patterns, it can be seen that the calcined BYS was still of the fluorite structure, which is consistent with the fresh powder, up to 1040°C. At 1080°C, a small amount of impurity phase (°) was observed, which is likely due to the change in BYS crystal structure when the calcination temperature approached the melting point of BYS. The intensity of the XRD peaks was observed to increase with the heat treatment temperatures, which indicates the increase in crystal size of BYS.

Fabrication of micro-structured BYS catalysts using a viscous fingering-induced phase inversion

Figure 5 shows the SEM images of precursor of micro-structured BYS capillary tubes fabricated via a viscous fingering-induced phase inversion process, using DMSO as the bore fluid. The outer diameter of the precursor is approximately 2.36 mm, with a wall thickness about 0.50 mm. From the SEM images, it can be seen that the use of DMSO as the bore fluid helps to delay the phase inversion at the inner surface, allowing the microchannels initiated from the outer surface to grow continuously across the tube wall, forming open microchannels at the inner surface of the tube. This type of microchannels offers great advantages in enhancing the accessible surface area, reducing the intraparticle mass-transfer resistance, and thus providing easier access of the reactant to the active sites of the catalyst.

Figure 6 shows the SEM images of micro-structured capillary tubes calcined at different temperatures. The outer diameter of the tube calcined at 920°C is approximately at 2.25 mm, and decreases to 1.70 mm when the calcination temperature was increased to 1040°C. It can be seen that lower calcination temperature gives a more porous tube (Figure 6a), while a denser tube (Figure 6b) was obtained when the calcination temperature

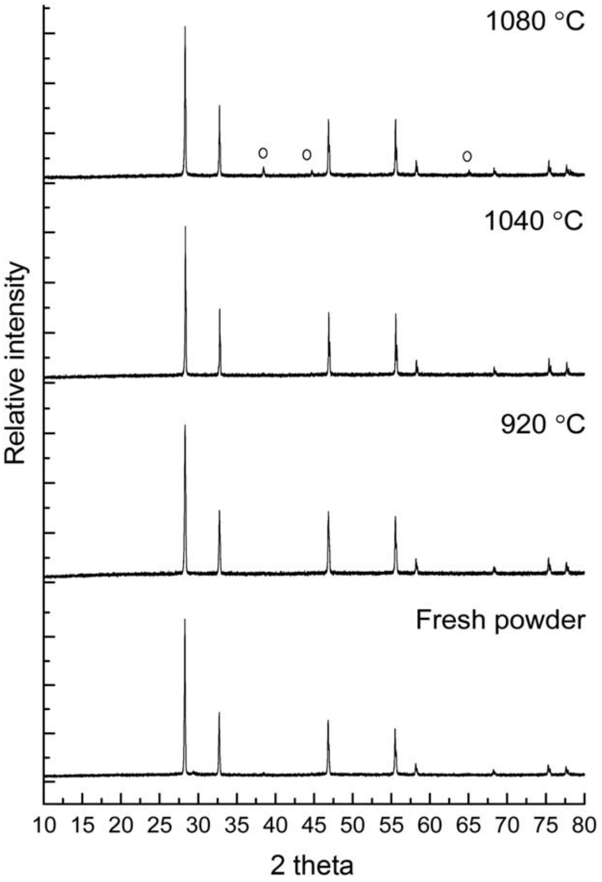

Figure 4. XRD patterns of the heat-treated BYS powder. (○) indicate the presence of foreign phases.

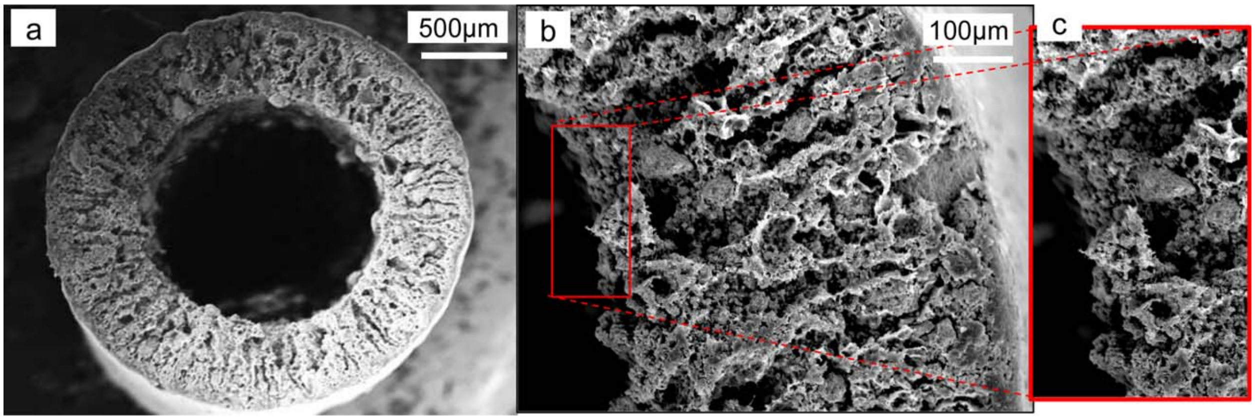

Figure 5. SEM images of precursor micro-structured BYS capillary tubes; (a) overall view, (b) cross-section, and (c) higher magnification of the cross-section.

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of 1040°C was used. It can also be seen from the SEM image of the inner surface of the tube as shown in Figure 6c that the microchannels opening on the inner surface are well retained even after the high calcination temperature was used.

Effects of catalyst designs in randomly FBR on OCM performance

Figure 7 compares the effects of catalyst designs (i.e., micro-structured BYS rings) in a randomly FBR with that of fresh BYS powder. The BYS rings were calcined at two temperatures, 920 and 1040°C, in order to ensure that they remain in fcc fluorite structure. From Figures 7a, b, it can be seen that the methane conversion and C_{2+} selectivity of the BYS micro-structured rings are higher than that of the powder. The improved methane conversion and C_{2+} selectivity may be linked to better flow characteristics of the reactor packed with catalyst rings and less mass-transfer resistance to the reactants within the catalyst due to the presence of the significant micro-channels (Figures 5 and 6).[17,19,20] Moreover, the unique microchannels enhance the geometric surface area of BYS rings, which further contributes to greater interaction between the BYS catalyst and the reactants.

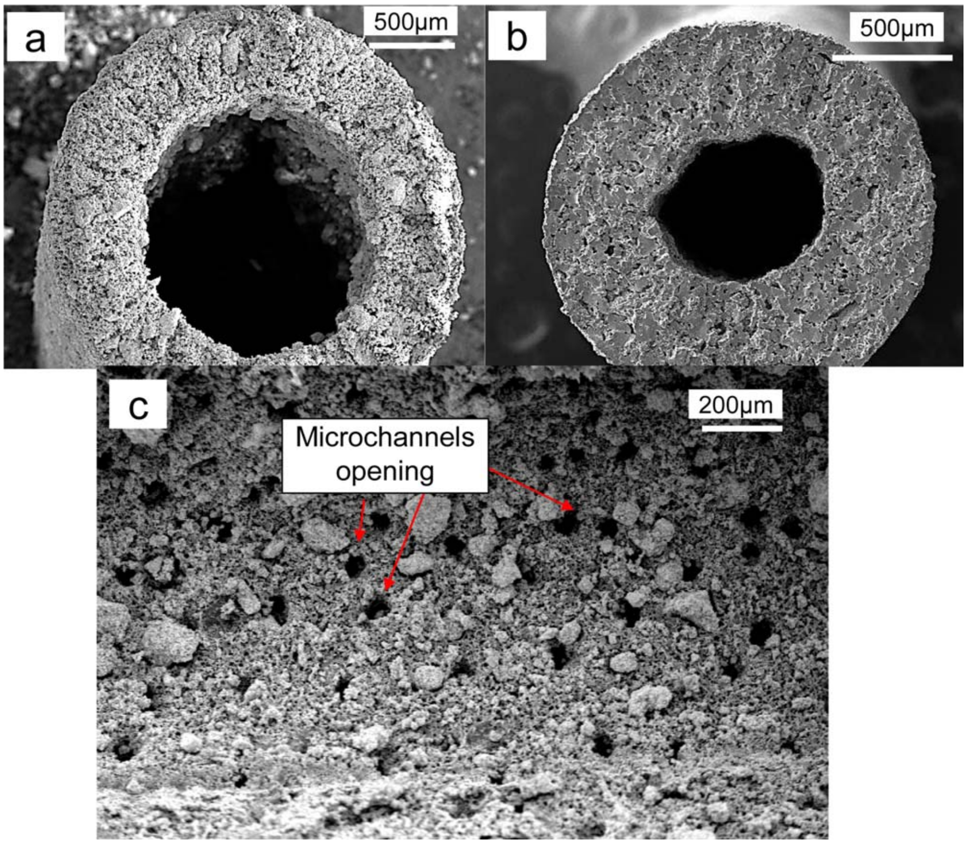

Figure 6. SEM images of micro-structured BYS capillary tubes calcined at different temperatures; (a) cross-section at 920°C, (b) cross-section at 1040°C, and (c) inner surface at 1040°C.

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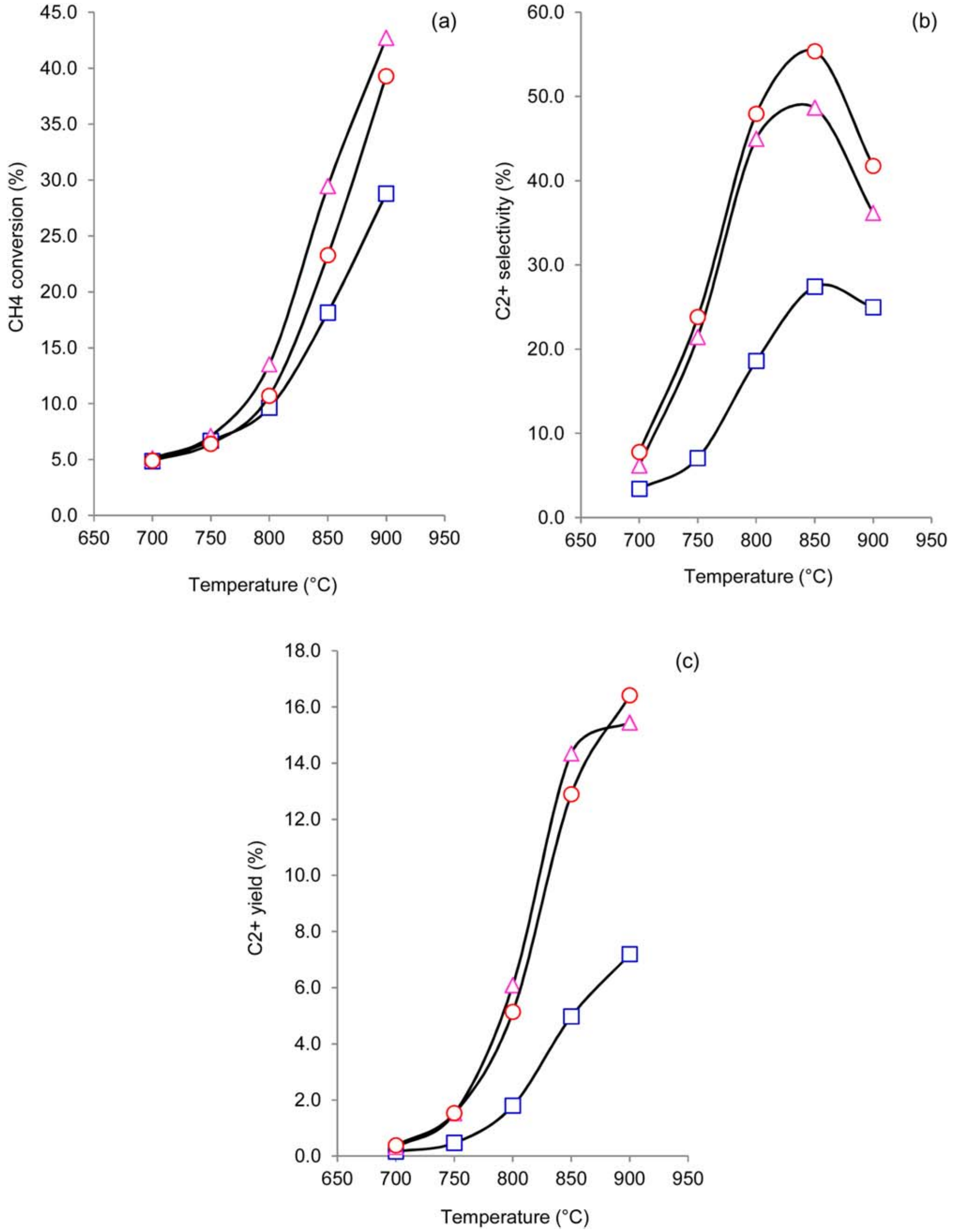

Figure 7. Comparison of (a) methane conversion, (b) C_{2+} selectivity, and (c) C_{2+} yield of powder catalyst (□), micro-structured rings calcined at 920°C (△), and micro-structured rings calcined at 1040°C (○).

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A C_{2+} selectivity as high as 55.4% was achieved by micro-structured rings calcined at 1040–850°C, but as the OCM operating temperature was increased to 900°C, the selectivity decreases, which is due to the deep oxidation of C_{2+} products. The C_{2+} yield obtained for the micro-structured rings were much higher than that of the powder form, as shown in Figure 7c. It was also observed that the micro-structured BYS rings prepared in this study has not only benefited the selectivity, but also methane conversion and C_{2+} yield. These results are in contrast to the study given by Zeng and Lin,[21] where the C_{2+} yield of pellets (without microchannels) was much lower than that of the powder catalyst, although the selectivity was improved due to low methane conversions from the pellets. The high methane conversion and C_{2+} yield obtained in our study is thus more likely related with the unique microchannels inside the BYS rings, allowing easier access of reactants to the active sites of the catalysts and as well as less resistance for the heat transfer due to the existence of microchannels.

Effects of reactor designs on OCM performance

As OCM mechanism involves complex interactions between the gas phase and catalytic surface, catalyst geometries and packing are expected to affect the reactor performance. Figure 8 compares the methane conversion, C_{2+} selectivity, C_{2+} yield, and C_2H_4/C_2H_6 ratio of different reactor designs as a function of operating temperature. From Figure 8a, it is evident that methane conversion was strongly affected by the reactor design, in which the conversion of monolith-like structured reactor is far better than that of the randomly packed BYS rings, although the residence time of the monolith-like structured reactor is seven times shorter. This is believed to be related to the more organized flow of the

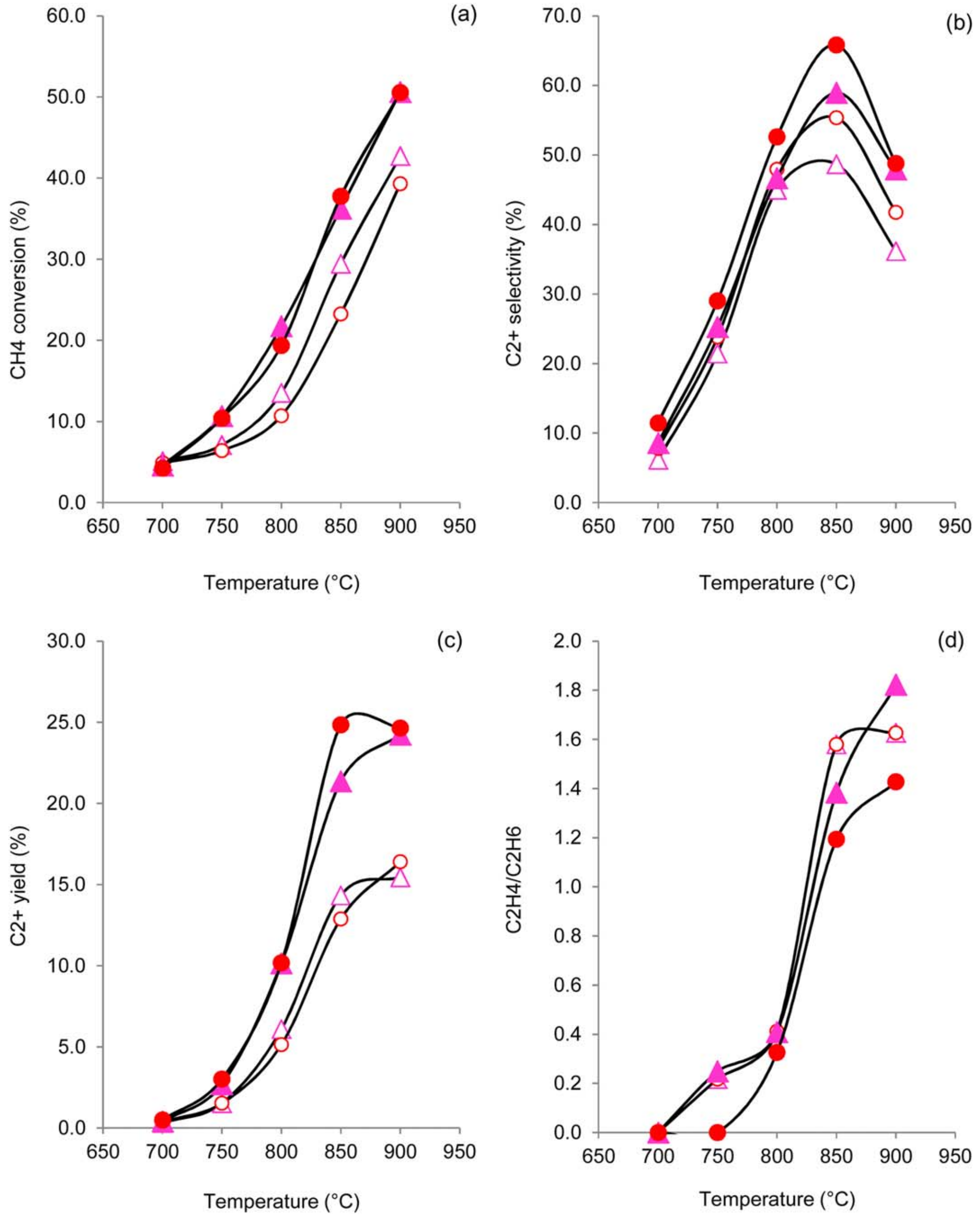

Figure 8. Comparison of (a) methane conversion, (b) C_{2+} selectivity, (c) C_{2+} yield, and (d) C_2H_4/C_2H_6 of different micro-structured reactor designs ([△]: rings calcined at 920°C; [▲]: monoliths calcined at 920°C; [○]: rings calcined at 1040°C; and [●]: monoliths calcined at 1040°C).

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reactants inside the micro-structured monolith reactor, when compared to the FBR, leading to more efficient interaction between the reactants and BYS catalyst at the presence of the microchannels. This agrees with our previous study,[17] in which BYS dispersed uniformly inside the microchannels of a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) hollow fiber membrane resulted in improved OCM performance of the membrane reactor. In addition, the irregular type of packing in the FBR could increase the pressure drop inside the reactor and further abolishes the uniformity of temperature and concentration profile, thus, leading to a decrease in reactor performance.

Similarly to methane conversion, the C_{2+} selectivity of monolith-like reactor was found to be considerably higher as shown in Figure 8b, which we believe is closely related to the more organized flow and greater mass and heat transfer due to the unique microstructures. Apart from higher methane conversion and C_{2+} selectivity, the C_{2+} yield obtained in monolith-like reactor was also better, achieving 20–25% at temperatures above 850°C. Comparing the performances between the monoliths that were calcined at 920 and 1040°C, it was observed that the C_{2+} yield of both monolith reactors was similar, except at 850°C (Figure 7c). The small difference in C_{2+} yield may be caused by the difference in C_{2+} selectivity as methane conversion of these reactors were almost similar. This seems to imply that the denser structure (i.e., sintered at 1040°C) of monolith-like micro-structured reactor can contribute to a higher C_{2+} selectivity because of less nonselective oxidation of C_{2+} products into CO_x in the catalyst.

There was no C_2H_4 observed at temperature below 750°C, but the C_2H_4/C_2H_6 increased gradually from 750 to 800°C as shown in Figure 8d. The increase of C_2H_4/C_2H_6 ratio with the reaction temperature can be the results of several side reactions depending on the amount of excessive oxygen as well as other factors, and may suggest that the conversion of ethane to ethylene can be more favored at higher temperatures. The formation of ethylene in this study is mostly due to the thermal cracking of ethane, which is consistent with the appearance of hydrogen after C_2H_4 was formed during the reaction. However, the high C_2H_4/C_2H_6 observed in the randomly packed rings reactor also indicates that the oxidative dehydrogenation of C_2H_6 on catalyst surface can also occur as a result of longer residence time. These results further confirmed that the OCM reaction in this study proceeds in combination of heterogeneous and homogeneous reaction.

Moreover, the C_{2+} productivity rate of the monolith-like reactor design (81.34 μmol/min/g) is observed to be 130% higher over the randomly packed configuration, which further proves the importance of organized flow in improving the efficiencies of catalytic reactions such as OCM.

Conclusions

A catalyst ring (i.e., short capillary tube) with a plurality of self-organized radial microchannels has been developed in this study for OCM using a viscous fingering-induced phase inversion process. An improvement in OCM performance was observed when the BYS powder was fabricated into micro-structured catalyst rings. This is linked to better mass and heat transfer in the catalyst rings, due to the presence of the significant and unique microchannels. In addition, higher C_{2+} yield was obtained when monolith-like structured reactor was used compared to the randomly packed reactor, which proves the advantages of using a micro-structured catalyst with an ideal feed flow in the reactor for OCM.

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