



Contents lists available at [www.sciencedirect.com](http://www.sciencedirect.com)

## Journal of the European Ceramic Society

journal homepage: [www.elsevier.com/locate/jeurceramsoc](http://www.elsevier.com/locate/jeurceramsoc)



# Compact hollow fibre reactors for efficient methane conversion

Nicholaus Prasetya<sup>a,b</sup>, Zhentao Wu<sup>c</sup>, Ana Gouveia Gil<sup>a,b</sup>, K. Li<sup>a,b,\*</sup>

<sup>a</sup> Barrer Centre, Imperial College London, South Kensington, SW7 2AZ, London, UK

<sup>b</sup> Department of Chemical Engineering, Imperial College London, South Kensington, SW7 2AZ, London, UK

<sup>c</sup> Aston Institute of Materials Research, School of Engineering and Applied Science, Aston University, Birmingham, B4 7ET, UK

### ARTICLE INFO

#### Article history:

Received 31 January 2017

Received in revised form 30 March 2017

Accepted 4 April 2017

Available online xxx

#### Keywords:

Membrane reactor  
Catalytic hollow fiber  
Rhodium  
Catalyst  
Methane conversion

### ABSTRACT

In this study, a micro-structured catalytic hollow fiber membrane reactor (CHFMR) has been prepared, characterized and evaluated for performing steam methane reforming (SMR) reaction, using Rh/CeO<sub>2</sub> as the catalyst and a palladium membrane for separating hydrogen from the reaction. Preliminary studies on a catalytic hollow fiber (CHF), a porous membrane reactor configuration without the palladium membrane, revealed that stable methane conversions reaching equilibrium values can be achieved, using approximately 36 mg of 2 wt.%Rh/CeO<sub>2</sub> catalyst incorporated inside the micro-channels of alumina hollow fibre substrates (around 7 cm long in the reaction zone). This proves the advantages of efficiently utilizing catalysts in such a way, such as significantly reduced external mass transfer resistance when compared with conventional packed bed reactors. It is interesting to observe catalyst deactivation in CHF when the quantity of catalyst incorporated is less than 36 mg, although the Rh/CeO<sub>2</sub> catalyst supposes to be quite resistant against carbon formation. The “shift” phenomenon expected in CHFMR was not observed by using 100 mg of 2 wt.%Rh/CeO<sub>2</sub> catalyst, mainly due to the less desired catalyst packing at the presence of the dense Pd separating layer. Problems of this type were solved by using 100 mg of 4 wt.% Rh/CeO<sub>2</sub> as the catalyst in CHFMR, resulting in methane conversion surpassing the equilibrium conversions and no detectable deactivation of the catalyst. As a result, the improved methodology of incorporating catalyst into the micro-channels of CHFMR is the key to a more efficient membrane reactor design of this type, for both the SMR in this study and the other catalytic reforming reactions.

Crown Copyright © 2017 Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Hydrogen plays crucial roles in terms of producing and processing chemicals at industrial scales [1], and has been widely acknowledged as an efficient and clean energy carrier [2]. In addition to increasingly larger global demands, how to produce hydrogen in a more energy-efficient and environment-benign way has driven various researches across different areas, from catalyst formulation, reactor configuration to process integration. To date, steam methane reforming (SMR) coupled with water gas shift (WGS) reaction is still the main route producing hydrogen from methane at an industrial scale [3]. It has also been considered as an energy intensive process, mainly due to the high operating temperatures (750–900 °C) and pressures (1.4–4 MPa) [4], as well as the complicated separation processes.

Among various technologies and processes for efficient productions of hydrogen from SMR, membrane reactor (MR) distinguishes itself by combining the reaction and separation into a single unit, with the “on-site” separation of hydrogen driving the unique “shift” of the reaction towards the product side, thus being able to surpass the equilibrium conversions applied commonly to other technologies. In despite of various challenges for scaling-out membrane reactors towards industrial deployment, the advantages aforementioned keep propelling new researches to be performed in this area, particularly by adopting and combining the latest achievements in material, membrane technology and catalysis etc.

MR for reforming reactions normally consists of a thin Pd-based membrane supported by an inorganic substrate, with a selected catalyst located on the reaction side. The recent progresses in fabricating micro-structured ceramic hollow fibres (HFs) via a phase-inversion assisted process, particularly the HFs with open-ended micro-channels, have generated new opportunities of developing efficient and compact MR designs [5–8]. In general, the thin outer sponge-like layer of HFs has the average pore size of around 0.2 μm, and thus allows the direct formation of a Pd-based separating layer of several microns in thickness, leading to

\* Corresponding author at: Barrer Centre, Imperial College London, South Kensington, SW7 2AZ, London, UK.

E-mail address: [kang.li@imperial.ac.uk](mailto:kang.li@imperial.ac.uk) (K. Li).

efficient separation/removal of hydrogen from SMR. Meanwhile, the selected catalyst can be “accommodated” inside the radial micro-channels, offering greater contacting areas and reduced mass transfer resistance for the SMR to proceed. Moreover, such a unique substrate microstructure significantly reduces the permeation resistance, facilitating the transfer of hydrogen from the reaction side to the permeate side of the MR, which is expected to further promote the “shift” phenomenon, reduce the quantity of catalyst needed, and lower the operating temperatures.

However, using such CHFMRs for reforming reactions, such as SMR, does not always present the “shift” phenomenon, although good recovery of hydrogen at the permeate side can be achieved. One reason previously reported is the difficulty in assembling the CHFMR, i.e. using available procedure and methodology without sacrificing the integrality, quality and formulation of the Pd separating layer and catalysts [5]. This can affect the overall reactor performance in terms of methane conversion, sometimes to a level even worse than a catalytic hollow fibre (without the Pd membrane). Another important and interesting reason is that, although the catalyst incorporated inside the HF substrate “works harder”, under the same space velocity as a packed bed reactor, such catalyst is subject to easier coke-formation and consequent deactivation, particularly for Ni-based catalyst when hydrogen is removed via the Pd membrane. In an earlier study [5], an elevated “kicking-off” temperature was suggested. Starting the SMR reaction at a higher operating temperature contributes to a greater supply of hydrogen from the reaction (reaction rate increases with the increasing temperature), thus being able to maintain the stability of the Ni-based catalyst inside the CHFMR.

In this work, Rh/CeO<sub>2</sub> catalysts, which were reported with less tendency to coke formation in reforming reactions, were prepared, and incorporated inside a ceramic hollow fibre substrate with open-ended micro-channels to obtain CHF for SMR. CHFMR was further prepared by forming a Pd membrane on the outer surface of HF substrates. In contrast to previous studies, this work employed Rh/CeO<sub>2</sub> as the more coke-resistant catalyst mainly to: 1) investigate how a more robust precious metal catalyst would perform inside micro-channels of the HF substrate, e.g. catalytic hollow fibre (CHF), or in another word how the unique micro-structure of the HF would help to reduce the use of precious metal catalyst; 2) investigate if such a coke-resistant catalyst will behave differently from the Ni-based counterparts, and as thus avoiding the higher starting up temperature previously used and as thus widening the operating temperature window. Another difference from previous studies is that, Rh/CeO<sub>2</sub> catalyst was prepared prior to being incorporated inside the HF substrate, which is more similar to the way of producing supported catalyst at an industrial scale, such as wash-coating 3-way catalyst onto ceramic monoliths.

## 2. Experiment

### 2.1. Fabrication of alumina hollow fiber

Alumina hollow fibers for CHF and CHFMR were prepared as described previously [5], using a phase-inversion assisted process. Generally, a uniform suspension consisting of approximately 55 wt% Al<sub>2</sub>O<sub>3</sub> powder (1 μm, Alfa Aesar) 39.1 wt% dimethylsulfoxide (DMSO, VWR), and 0.39 wt% dispersant and 5.5 wt% polyethersulfone (PESf, Ameco Performance) was prepared via ball milling. After degassing, the ceramic suspension was transferred into a 200 ml stainless steel syringe. The ceramic suspension and a solvent-based bore fluid were co-extruded through a tube-in-orifice spinneret (OD 3.5 mm, ID 1.2 mm), at the same flow rate of 15 ml min<sup>-1</sup>, into a coagulation bath containing DI water with no air gap (0 cm). The hollow fibre precursors were kept in the coag-

ulation bath to complete the phase inversion. After straightening and drying, the precursor fibres were sintered in a tubular furnace (Elite TSH17/75/450) at 1400 °C for 4 h. Prior to the incorporating catalyst and preparing the Pd membrane, the outer surface of the sintered hollow fibre were coated with a gas-tight glaze layer by a thermal-treatment at 900 °C for 1 h, with the exception of the central 7 cm for electroless plating of Pd membrane.

### 2.2. Catalyst fabrication and incorporation

Rhodium was used as the active phase of the catalyst for SMR and CeO<sub>2</sub> was used as the catalyst support. Rhodium chloride (RhCl<sub>3</sub>.xH<sub>2</sub>O, Sigma-Aldrich) and CeO<sub>2</sub> (Alfa Aesar) were used as the precursor materials. Catalysts were fabricated through a wet impregnation method, in which 2 wt% Rh/CeO<sub>2</sub> was prepared by mixing 1.084 g of rhodium chloride solution and 2 g of CeO<sub>2</sub>. For 4 wt% Rh/CeO<sub>2</sub>, the amount of nano-sized CeO<sub>2</sub> was halved. The mixture was then diluted with ethanol absolute (VWR) in a flask. Wet impregnation method was completed by evaporating the ethanol via a rotary evaporator and leaving the catalyst particles inside the flask. The evaporation process was repeated for three times, before putting the flask in a high vacuum system to remove the ethanol completely. Afterwards, the catalyst underwent calcination in a temperature-programmed furnace. The temperature was first raised up from room temperature to 550 °C at a heating rate 1 °C min<sup>-1</sup>. After dwelling for 4 h, it was cooled down to room temperature at 1 °C min<sup>-1</sup>. With regard to catalyst incorporation, the prepared catalyst was mixed with ethanol to form a uniform mixture, which was directed through the lumen of the hollow fibre substrates under a low pressure, which is very similar to a conventional wash-coating process. The samples were put inside an oven overnight to remove the ethanol (at 40 °C), with the amount of catalyst measured based on the weight gains of the samples.

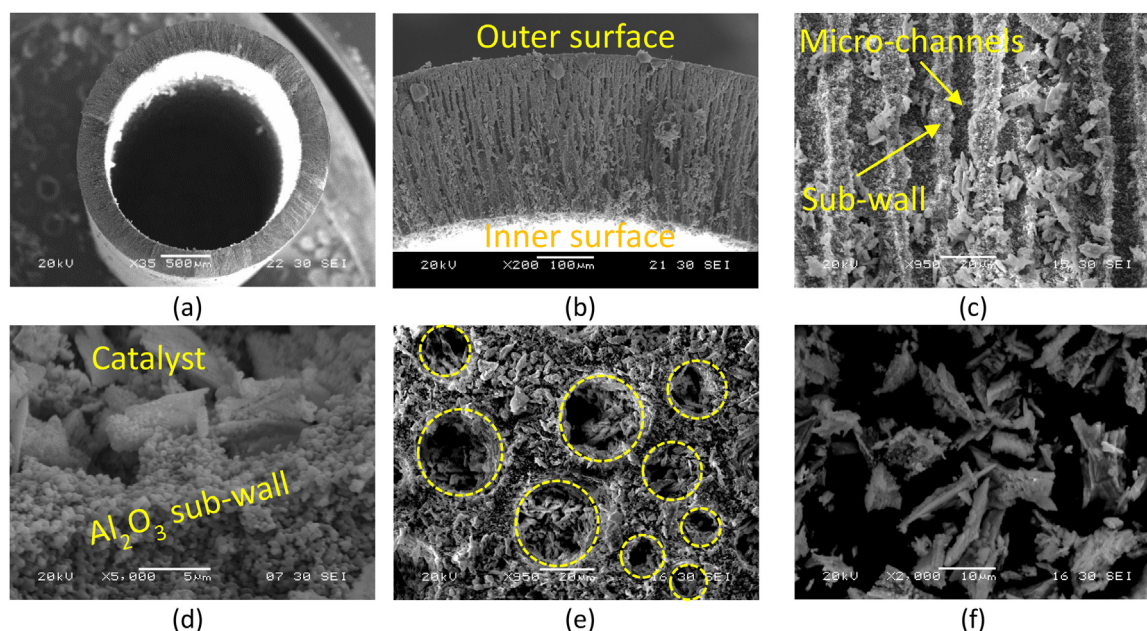
### 2.3. Electroless plating of Pd membranes

Electroless-plating was conducted through two subsequent steps: activation and plating. Activation was performed by subsequently immersing hollow fiber in tin chloride solution (SnCl<sub>2</sub>·2H<sub>2</sub>O, Sigma-Aldrich), de-ionized water and palladium chloride (PdCl<sub>2</sub>, 99.999%, Sigma-Aldrich) for 5 min each. Afterwards, the fibers were immersed in 0.01 M HCl solution for 2 min, followed by re-immersing in de-ionized water for 3 min. All of these steps were repeated for eight times in order to obtain sufficient Pd seeds on the outer surface of the hollow fiber substrate. In each step, air bubble was introduced to promote the bath homogeneity. Thereafter, plating was conducted by immersing the activated hollow fiber into a plating bath containing palladium plating solution at 60 °C. The plating solution was prepared by mixing tetraaminepalladium (II) chloride monohydrate (Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>·H<sub>2</sub>O, 99.99% metal-bases, Sigma-Aldrich), sodium hydroxide (NaOH, 28% in H<sub>2</sub>O, Sigma-Aldrich), EDTA (IDRANAL III, Riedel-deHaen), and hydrazine hydrate (Sigma-Aldrich). When fabricating the CHFMR, the Pd membrane was formed before the incorporation of Rh/CeO<sub>2</sub> catalyst, to avoid the change in catalyst compositions.

### 2.4. Characterizations

The morphology of all alumina hollow fibre substrates and catalyst was characterized by scanning electron microscopy (SEM, JEOL JSM-5610LV and LEO Gemini 1525 FEGSEM). Prior to SEM analysis, the samples were gold coated in a vacuum chamber (EMITECH Model K550) for 2 min at 20 mA and brush painted with silver.

The catalytic performance of the different reactor configurations, i.e. CHF and CHFMR, was evaluated using an experimental



**Fig. 1.** SEM images of catalytic hollow fibres (CHFs), (a) whole view, (b) cross-section, (c) a higher magnification image of cross-section, (d) catalyst inside micro-channels, (e) inner surface, (f) catalyst particles.

apparatus described previously [5]. The flow rates of the reactants and sweep gas (Ar) were controlled by individual mass flow controllers (Brooks Instrument, model 5800) with a collective reader (Brooks Instrument, model 0254). A syringe pump (ChemixN5000) was used to feed liquid water into a heating coil (1/16" stainless steel tube), which was connected to the reactor. The inlet and outlet pressures were monitored using a digital pressure gauge (Sick, 10 bar). The temperature of the tubular furnace (Vecstar SP HVT) was controlled by a temperature controller (CAL 9400) and monitored by a thermocouple located at the central position of the uniform heating zone (7 cm). The outlet stream was analyzed online by a gas chromatograph (Varian3900), using a packed column (shincarbon, part nbr 19,808) and the flow rate monitored by a bubble flow meter. Methane (5 ml/min) balanced with the carrier gas (Ar, 45 ml/min) and water (gas, 10 ml/min) were feed to the lumen of both CHF and CHFMR. This gives a space velocity (GHSV) value of  $18,148 \text{ h}^{-1}$  (based on  $0.2 \text{ cm}^3$  reactor volume). For CHFMR, the sweep gas flow rate of 50 ml/min was maintained the same throughout the tests.

### 3. Results and discussion

#### 3.1. Micro-structures of catalytic hollow fibres (CHFs)

Catalytic hollow fibres (CHFs) were prepared by incorporating Rh/CeO<sub>2</sub> catalyst particles inside the micro-structured alumina hollow fibre (HF) substrates, with their microstructures shown in Fig. 1. The OD and ID of CHF/HF substrate were measured at approximately 2482 and 1929  $\mu\text{m}$ , respectively (Fig. 1(a)). In addition, there is a large number of radial micro-channels self-distributed in the cross-section of HF substrate, which differentiates it from other ceramic substrate counterparts. Such HF substrates have a smooth and skin-like layer on the outer surface allowing the direct formation of Pd separating layer, and micro-channels with open ends on the inner surface facilitating the incorporation of catalyst particles. As can be seen in Fig. 1(b)–(d), Rh/CeO<sub>2</sub> catalyst particles can be found deeply into the micro-channels, without reaching the outer surface due to the decreasing width of micro-channels close to the outer surface. As a result, more catalyst particles were located in the region near to the inner surface (Fig. 1(b)). The micro-channels

were separated by porous sub-walls with average pore sizes much smaller than the catalyst particles (Fig. 1(c)–(d)), which retain the catalyst particles inside the micro-channels. As a result, each micro-channel with catalyst particles packed inside can be considered as an individual micro-reactor with greater mass transfer efficiency that can benefit various catalytic reactions. After catalyst incorporation, the open ends of the micro-channels are still visible on the inner surface (Fig. 1(e)), which significantly reduces the transport resistances for both reactants and products. The rest part of inner surface is covered by a thin layer of catalyst, which is due to the methodology employed for incorporating catalysts. Meanwhile, the length and width of Rh/CeO<sub>2</sub> catalyst particles are typically less than 15  $\mu\text{m}$  (Fig. 1(f)), which enables easy incorporation of such catalyst particles into the porous HF substrates.

#### 3.2. Catalytic performance of CHFs

In addition to accommodating catalyst and reducing transport resistance, the unique radial micro-channels substantially enlarging the surface area for the catalytic reactions to proceed, which contributes to the reducing amount of catalyst needed. As a result, the catalytic performance of CHFs was evaluated with different amounts of 2 wt.% Rh/CeO<sub>2</sub> catalyst (within the reaction zone of 7 cm in length), in order to outline the quantity of catalyst needed for such a reactor configuration.

Fig. 2 presents the methane conversion of the CHFs at temperatures between 400 °C and 550 °C, using approximately 28 mg of 2 wt.% Rh/CeO<sub>2</sub>. As can be seen, methane conversions are lower than the equilibrium values within the range of testing temperatures, with the difference becoming more significant at higher temperatures. Meanwhile, methane conversions decline slightly with time between 400 and 450 °C, and decrease in a much quicker way at 500 °C, although the methane conversion still climbs up when the temperature is increased from 400 °C to 500 °C. At 550 °C, methane conversion is even lower than the one at 500 °C, in addition to a quick drop against time. All these indicate catalyst deactivation, which will be further discussed in the following sections.



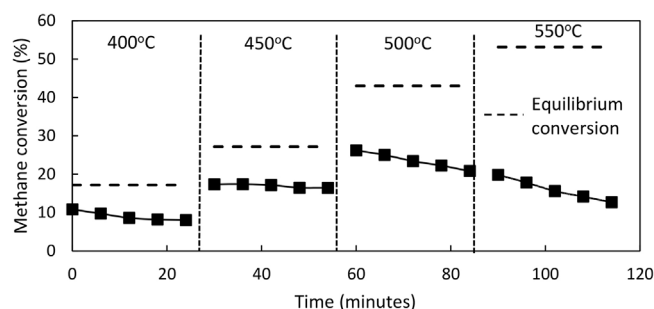


Fig. 2. CH<sub>4</sub> conversion of CHFMs with 28 mg of 2 wt% Rh/CeO<sub>2</sub> catalyst.

The same test was then performed by using approximately 36 mg of 2 wt% Rh/CeO<sub>2</sub>, which represents nearly 30% increase of the catalyst. As can be seen in Fig. 3(a), methane conversion quickly reaches the equilibrium values for the temperatures above 400 °C. Moreover, no signs of decreasing methane conversion were observed during the whole course of testing, which indicates little or even no catalyst deactivation that is completely different from the CHFMs using 28 mg of 2 wt% Rh/CeO<sub>2</sub> (Fig. 2).

Despite of being acknowledged with good catalytic stability, deactivation of rhodium-based catalysts has been reported for some applications, such as jet fuel steam reforming [9], ethane partial oxidation [10], methane dry reforming [11], as well as steam methane reforming [12]. The actual deactivation mechanisms can be complicated and are linked to various factors, with poisoning, thermal degradation and fouling considered as the main causes for SMR reaction [13]. By comparing Figs. 2 and 3(a), poisoning and thermal degradation can be excluded, due to the stable methane conversion at equilibrium values obtained when 36 mg of 2 wt% Rh/CeO<sub>2</sub> was used (Fig. 3(a)).

Catalyst fouling for SMR is normally related to carbon formation, such as encapsulating carbon, whisker-like structure carbon and carbon formed due to pyrolysis etc. [14]. For instance, whisker-like and amorphous carbon can be formed due to methane decomposition in the combined dry reforming and partial oxidation [15]. Since methane activation on rhodium surface can be independent of the types of co-reactants used in the reaction [16], it is reasonable to infer that catalyst deactivation in this experiment is caused by carbon formation.

Faster carbon formation can occur at increased reaction temperatures. In a previous study on jet-fuel pre-reforming reaction using Rh/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [17], the heaviest carbon formation occurred at the temperature of around 510 °C, which is in line with Fig. 2. Using ceria in catalyst supports helps to reduce coke formation, due to the enhanced water dissociation that provides oxygen species to oxidize carbonaceous compounds normally formed on the catalyst active site [18,19]. However, the strong metal support interaction (SMSI) can be impaired by the whisker-like carbon [14], and consequently deactivating the catalyst, which is another possibility for the quick deactivation shown in Fig. 2. By increasing the amount of catalyst inside the CHF to 36 mg, the higher methane conversion results in more hydrogen being produced, leading to a more reducing environment that helps to suppress carbon formation, which agrees with our previous studies [5]. As a result, no catalyst deactivation was observed in Fig. 3(a), and a “threshold” amount of 2 wt% Rh/CeO<sub>2</sub> of around 36 mg is thus needed for the CHFMs for SMR reaction. Below this value, insufficient hydrogen inside the micro-channels, which is due to relatively low methane conversion, can affect the catalyst stability.

CO<sub>2</sub> selectivity in Fig. 3(b) starts at a high value (nearly 97%) at 400 °C, and keeps decreasing with the increasing temperature, which is due to the exothermic nature of WGS reaction. Meanwhile, the hydrogen yield keeps increasing at higher temperatures, mainly

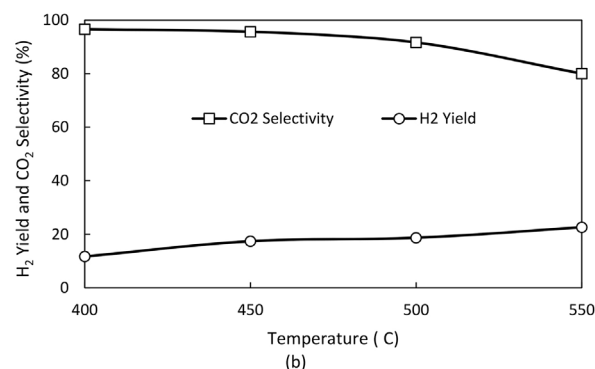
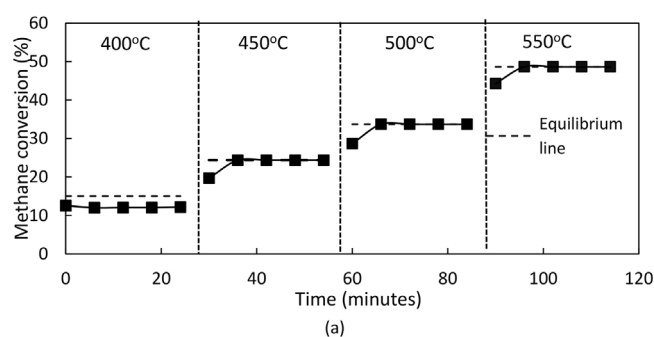


Fig. 3. Catalytic performance of CHFMs using 36 mg of 2 wt% Rh/CeO<sub>2</sub> catalyst (a) CH<sub>4</sub> conversion, and (b) H<sub>2</sub> yield and CO<sub>2</sub> selectivity.

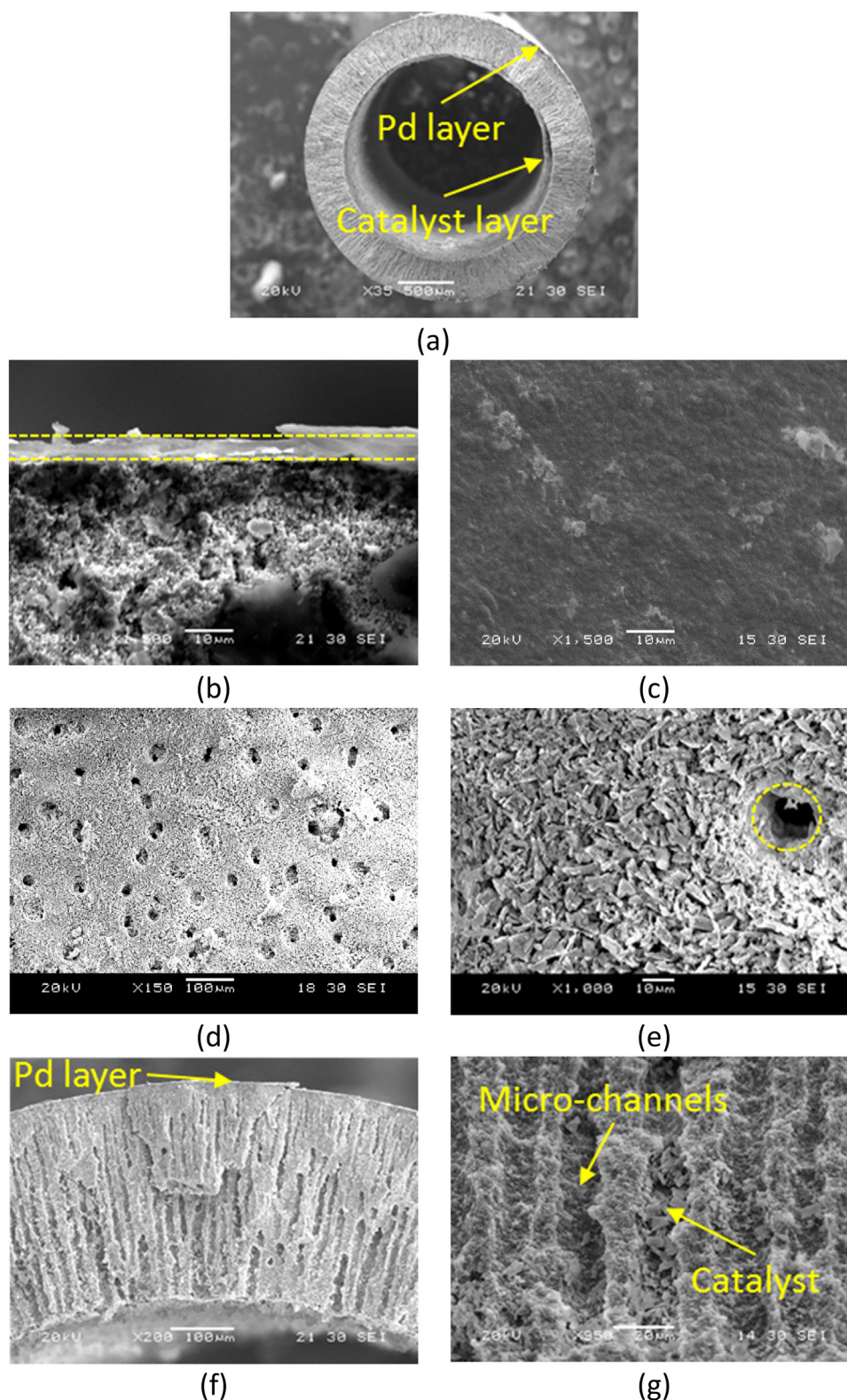
due to the enhanced methane conversion, despite of reduced contribution from WGS reaction.

### 3.3. Micro-structure of catalytic hollow fibre membrane reactors (CHFMRs)

Catalytic hollow fibre membrane reactors (Fig. 4(a)) were assembled by electroless plating a thin and dense Pd membrane (Fig. 4(b)–(c)) onto the outer surface of HF substrate, prior to incorporating Rh/CeO<sub>2</sub> catalysts. In contrast to the highly porous CHFMs, catalyst incorporation is less efficient mainly due to the presence of the dense Pd separating layer. This leads to the formation of a thin catalyst layer on the inner surface of CHFMR (Fig. 4(a)) that blocks a significant number of the openings on the inner surface (Fig. 4(d)). This catalyst layer is quite thin and highly porous (Fig. 4(e)), and would not generate significant mass transfer resistance under the testing conditions used for CHF (Fig. 2). However, incorporating catalyst throughout the micro-structured hollow fibres has been reported with higher reaction efficiencies when compared with such a catalyst layer, especially at very high space velocities [20]. Also due to the presence of the Pd separating layer, only a very limited amount of the catalyst particles is found inside the radial micro-channels (Fig. 4(f)–(g)), which is not desired and is very different from CHFMs.

### 3.4. Catalytic performance for CHFMRs

Preliminary evaluations were carried out by testing CHFMRs with approximately 25 mg of 2 wt% Rh/CeO<sub>2</sub> catalyst, a very similar amount of catalyst as the CHF with methane conversions shown in Fig. 2. However, almost no methane conversion can be observed throughout the operating temperatures between 400 °C and 550 °C. This is in line with our previous studies [5,21] that removing hydrogen from catalytic reactions can speed up catalyst deactivations, mainly due to the faster or more serious carbon formation. As a result, a significantly higher amount of catalyst, i.e. 100 mg of 2 wt%



**Fig. 4.** SEM images of catalytic hollow fibre membrane reactor (a) whole view, (b) cross-section view of Pd layer, (c) top-view of the Pd layer, (d) inner surface of the reactor, (e) higher magnification of inner surface, (f) cross-section view of the reactor, (g) higher magnification image (f).

Rh/CeO<sub>2</sub> catalyst or 100 mg of 4 wt.% Rh/CeO<sub>2</sub> catalyst, was incorporated inside the CHFMRs for SMR. It should be noted here that, further increasing the weight of the catalyst can block the reactor lumen, and was thus not involved in this study.

Benefit from the higher amount of catalyst used, no deactivation was observed during the course of performance tests. As can be seen in Fig. 5(a), methane conversion keeps increasing with the elevated temperatures for both 2 wt.% Rh/CeO<sub>2</sub> and 4 wt.% Rh/CeO<sub>2</sub> catalyst. However, 100 mg of 2 wt.% Rh/CeO<sub>2</sub> catalyst, which formed a cat-

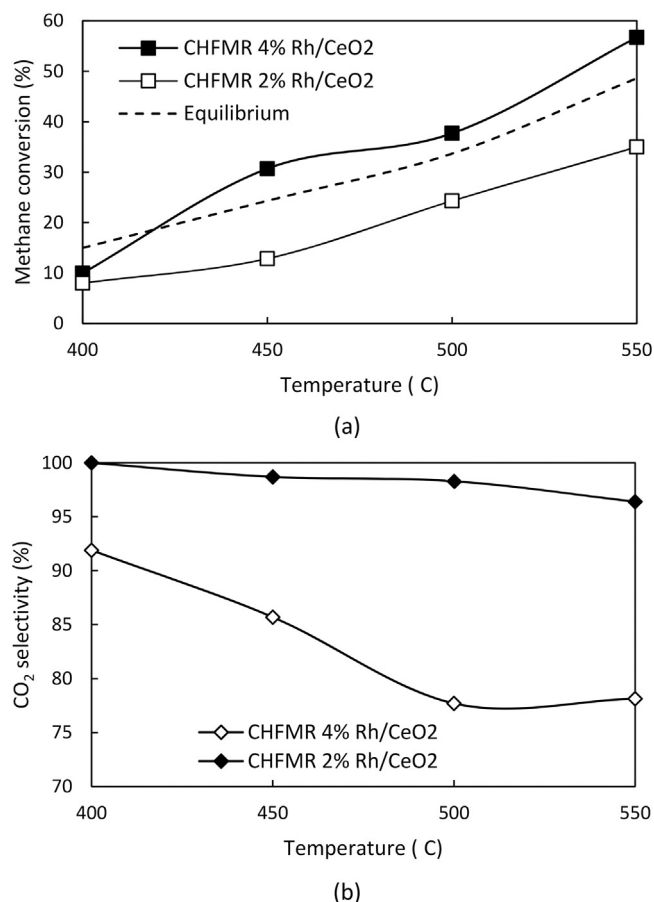


Fig. 5. Catalytic performance of CHFMRs with 100 mg of Rh/CeO<sub>2</sub> catalysts (a) methane conversion, and (b) CO<sub>2</sub> selectivity.

alyst layer along the reaction zone of approximately 7 cm (instead of being inside the micro-channels of the alumina hollow fibre as CHF), cannot exceed the equilibrium values, despite of the fact that hydrogen was continuously removed by the Pd membrane. Moreover, the methane conversion is even lower than the CHF without Pd membrane and using approximately 36 mg of 2 wt.% Rh/CeO<sub>2</sub> catalyst (Fig. 3(a)), which further proves the importance of incorporating catalysts inside the micro-channels. By “doubling” the loading of Rh, the CHFMR with 100 mg of 4 wt.% Rh/CeO<sub>2</sub> catalyst managed to exceed the equilibrium conversions at temperatures above 450 °C, but at the cost of more catalyst required. As thus,

how to incorporate catalyst inside the micro-channels of CHFMR will be the key step of improving the reactor performance at the use of less amount of catalyst.

CO<sub>2</sub> selectivity of the two CHFMRs keeps dropping with the increasing temperatures (Fig. 5(b)), which is mainly due to the exothermic nature of the WGS reaction. CHFMR with 4 wt.% Rh/CeO<sub>2</sub> catalyst has a slightly lower CO<sub>2</sub> selectivity, which indicates that for higher methane conversions (Fig. 5(a)), WGS is less significant in terms of converting CO produced from SMR into CO<sub>2</sub>. Moreover, it is interesting to see a slight increase in CO<sub>2</sub> selectivity for this reactor at 550 °C. Such a phenomenon was also observed in one of our previous studies between 550 °C and 575 °C [5], in which a similar membrane reactor was investigated using Ni-based catalysts. This indicates that removing hydrogen via the Pd membrane not only promotes the overall conversion of methane, but also affects the formation of CO (due to SMR) and CO<sub>2</sub> (due to WGS), leading to this type of change in CO<sub>2</sub> selectivity at temperatures around 550 °C.

In addition to promoting reactant conversions, another key advantage of a membrane reactor is to separating hydrogen as an important energy carrier when the catalytic reaction proceeds. As can be seen in Fig. 6, hydrogen permeation rates keep increasing with the increasing operating temperatures. The higher methane conversion of CHFMR (100 mg of 4 wt.% Rh/CeO<sub>2</sub> catalyst) leads to the hydrogen permeation rate of around twice the value of the other one using 100 mg of 2 wt.% Rh/CeO<sub>2</sub> catalyst. Despite of the higher permeation rates at elevated temperatures, hydrogen recovery keeps dropping slightly, which is due to the decreasing hydrogen partial pressure on the permeate side (shell), since the flow rate of sweep gas in shell is maintained at a constant value. For the similar reason, the hydrogen recovery of the CHFMR using 100 mg of 4 wt.% Rh/CeO<sub>2</sub> catalyst is slightly lower. Both hydrogen permeation rate and recovery can be further increased by using a high flow rate of the sweep gas or vacuum that is more feasible to obtain highly pure hydrogen as the product [8].

#### 4. Conclusions and future work

In this study, Rh/CeO<sub>2</sub> catalysts were prepared and incorporated inside micro-structured alumina hollow fibres, in order to develop two types of reactors, i.e. catalytic hollow fibre (CHF) and catalytic hollow fibre membrane reactor (CHFMR), for methane conversion.

Most of Rh/CeO<sub>2</sub> catalyst particles were successfully deposited inside the radial micro-channels of porous CHFs. This leads to an efficient methane conversion process, with the equilibrium conversions achieved by using approximately 36 mg of 2 wt.%Rh/CeO<sub>2</sub> catalyst (within 7 cm length of the reaction zone), and for the

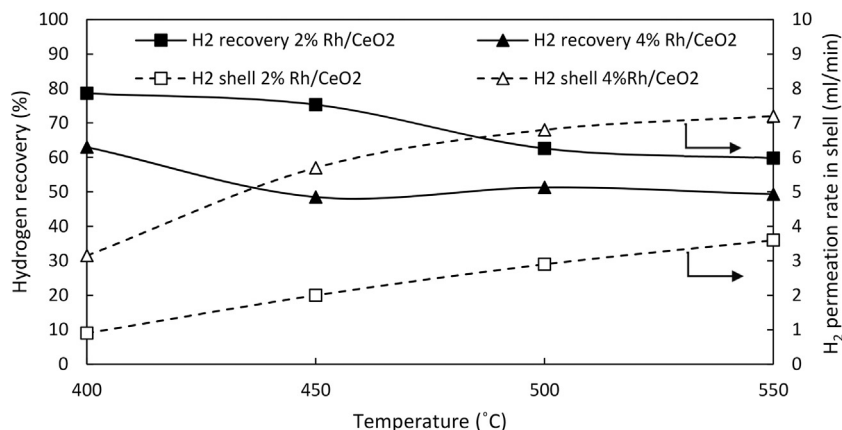


Fig. 6. Hydrogen recovery and permeation rate in CHFMRs with 100 mg of Rh/CeO<sub>2</sub> catalysts.



operating temperatures above 450 °C. Catalyst deactivation, which is mainly due to carbon formation, occurred when the 28 mg of the same catalyst was employed. This indicates that a “threshold” amount of the catalyst is needed for such a reactor design.

Catalyst incorporation inside CHFMRs was less efficient, due to the earlier step of forming a dense Pd membrane. This results in a very porous catalyst layer on the inner surface of the hollow fibre substrates, with a large portion of micro-channel openings covered. For the CHFMR with 100 mg of 2 wt.%Rh/CeO<sub>2</sub> catalyst and hydrogen continuously removed by the Pd membrane, the methane conversion is lower than the CHF with 36 mg of 2 wt.%Rh/CeO<sub>2</sub> catalyst, which highlights the advantage of depositing catalysts inside the micro-channels. Methane conversions exceeding the equilibrium values can be achieved when 100 mg of 4 wt.%Rh/CeO<sub>2</sub> catalyst was used, with no catalyst deactivation observed. Hydrogen recovery of the CHFMRs keeps decreasing with the increasing temperatures, together with the enhanced hydrogen permeation rate. Further improvements in hydrogen recovery can be achieved by using higher sweep gas flow rates or vacuum.

In order for further improved performance of CHFMRs, alternative methodology in terms of assembling the reactor needs to be addressed, in order to avoid the formation of the catalyst layer in this study. From this point of view, electroless plating of Pd membranes need to be modified or even be replaced by another technology, which allows catalyst incorporation to proceed prior to Pd membrane formation, with the catalyst composition and properties not being changed during the membrane formation. This is, unfortunately, still an outstanding dilemma of current researches related to CHFMR.

## Acknowledgment

Nicholaus Prasetya would like to acknowledge the master-degree scholarship granted by Indonesia Endowment Fund for Education when he was undertaking this study. K. Li would like to acknowledge the research funding provided by EPSRC in the United Kingdom (Grant no EP/J014974/1).

## References

- [1] J.-P. Lange, Methanol synthesis: a short review of technology improvements, *Catal. Today* 64 (1) (2001) 3–8.
- [2] A. Iulianelli, et al., Methanol steam reforming for hydrogen generation via conventional and membrane reactors: a review, *Renew. Sustain. Energy Rev.* 29 (2014) 355–368.
- [3] A. Boyano, et al., Exergoenvironmental analysis of a steam methane reforming process for hydrogen production, *Energy* 36 (4) (2011) 2202–2214.
- [4] M. De Jong, et al., Optimizing a steam-methane reformer for hydrogen production, *Int. J. Hydrogen Energy* 34 (1) (2009) 285–292.
- [5] A.G. Gil, et al., A catalytic hollow fibre membrane reactor for combined steam methane reforming and water gas shift reaction, *Chem. Eng. Sci.* 137 (2015) 364–372.
- [6] F. García-García, et al., Dry reforming of methane using Pd-based membrane reactors fabricated from different substrates, *J. Membr. Sci.* 435 (2013) 218–225.
- [7] F. García-García, et al., A novel catalytic membrane microreactor for CO<sub>x</sub> free H<sub>2</sub> production, *Catal. Commun.* 12 (3) (2010) 161–164.
- [8] M.A. Rahman, F.R. García-García, K. Li, Development of a catalytic hollow fibre membrane microreactor as a microreformer unit for automotive application, *J. Membr. Sci.* 390 (2012) 68–75.
- [9] J.J. Stroh, J. Zheng, C. Song, Low-temperature steam reforming of jet fuel in the absence and presence of sulfur over Rh and Rh?Ni catalysts for fuel cells, *J. Catal.* 238 (2) (2006) 309–320.
- [10] S. Cimino, L. Lisi, G. Russo, Effect of sulphur during the catalytic partial oxidation of ethane over Rh and Pt honeycomb catalysts, *Int. J. Hydrogen Energy* 37 (14) (2012) 10680–10689.
- [11] H. Wang, E. Ruckenstein, Carbon dioxide reforming of methane to synthesis gas over supported rhodium catalysts: the effect of support, *Appl. Catal. A: Gen.* 204 (1) (2000) 143–152.
- [12] R. Duarte, F. Krumeich, J. van Bokhoven, Structure: activity, and stability of atomically dispersed Rh in methane steam reforming, *ACS Catal.* 4 (5) (2014) 1279–1286.
- [13] J.A. Moulijn, A. Van Diepen, F. Kapteijn, Catalyst deactivation: is it predictable?: What to do? *Appl. Catal. A: Gen.* 212 (1) (2001) 3–16.
- [14] C.H. Bartholomew, Mechanisms of catalyst deactivation, *Appl. Catal. A: Gen.* 212 (1) (2001) 17–60.
- [15] B. Nematollahi, M. Rezaei, M. Khajenoori, Combined dry reforming and partial oxidation of methane to synthesis gas on noble metal catalysts, *Int. J. Hydrogen Energy* 36 (4) (2011) 2969–2978.
- [16] J. Wei, E. Iglesia, Structural requirements and reaction pathways in methane activation and chemical conversion catalyzed by rhodium, *J. Catal.* 225 (1) (2004) 116–127.
- [17] J. Stroh, J. Zheng, C. Song, Temperature effects on the formation of carbon during pre-reforming of logistic fuels over noble metal catalysts for SOFC applications, in: *Abstracts Of Papers Of The American Chemical Society*, American Chemical Soc, 1155 16th St, NW, Washington, DC 20036 USA, 2003.
- [18] R. Duarte, et al., Transient mechanistic studies of methane steam reforming over ceria-Promoted Rh/Al<sub>2</sub>O<sub>3</sub> catalysts, *ChemCatChem* 6 (10) (2014) 2898–2903.
- [19] M. Halabi, et al., Low temperature catalytic methane steam reforming over ceria–zirconia supported rhodium, *Appl. Catal. A: Gen.* 389 (1) (2010) 68–79.
- [20] B. Kingsbury, et al., Advanced Ceramic Substrate with Ordered and Designed Micro-Structure for Applications in Automotive Catalysis, *SAE Technical Paper*, 2014.
- [21] Z. Wu, et al., A novel inorganic hollow fiber membrane reactor for catalytic dehydrogenation of propane, *AIChE J.* 55 (9) (2009) 2389–2398.