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Compact hollow fibre reactors for efficient methane conversion

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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/CeO₂ 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/CeO₂ 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/CeO₂ 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/CeO₂ 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/CeO₂ 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.

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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

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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/CeO₂ 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/CeO₂ 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/CeO₂ 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% Al₂O₃ 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⁻¹, 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 CeO₂ was used as the catalyst support. Rhodium chloride (RhCl₃.xH₂O, Sigma-Aldrich) and CeO₂ (Alfa Aesar) were used as the precursor materials. Catalysts were fabricated through a wet impregnation method, in which 2 wt% Rh/CeO₂ was prepared by mixing 1.084 g of rhodium chloride solution and 2 g of CeO₂. For 4 wt% Rh/CeO₂, the amount of nano-sized CeO₂ 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⁻¹. After dwelling for 4 h, it was cooled down to room temperature at 1 °C min⁻¹. 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 (SnCl₂·2H₂O, Sigma-Aldrich), de-ionized water and palladium chloride (PdCl₂, 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(NH₃)₄Cl₂·H₂O, 99.99% metal-bases, Sigma-Aldrich), sodium hydroxide (NaOH, 28% in H₂O, 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/CeO₂ 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

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