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Hierarchically structured NiO/CeO_2 nanocatalysts templated by eggshell membranes for methane steam reforming

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ABSTRACT

A template synthesis process has been studied to prepare hierarchically structured NiO/CeO_2 nanocatalysts by using eggshell membranes as a template. The templated catalyst is constructed by interwoven ceramic fibres, and the fibres have a nanoporous structure with NiO nanoparticles supported on a CeO_2 scaffold. The effects of immersion time and calcination temperature on catalyst microstructure were investigated using SEM, XRD, TGA and TPR techniques. The catalyst prepared with an immersion time of 3 h has a robust structure that is able to resist internal thermal stresses caused by cooling down after calcination. Calcination temperature greatly affected the performance of steam reforming via catalyst microstructure. Both particle size and the interaction between NiO and CeO_2 determined the reforming performance. The catalyst calcined at 950 °C achieved the highest and most stable methane conversion owing to the optimized microstructure. The strong NiO–CeO_2 interaction is critical to achieve coking-resistance. The three-dimensional structure of the fibrous catalyst ensured the high thermal stability of the nanocatalyst in terms of high reisstance to catalyst sintering.

1. Introduction

Of all fossil fuels, natural gas is relatively clean in terms of the emission of greenhouse gases and other pollutants. Unfortunately, abundant reserves of natural gas are located in remote areas. Natural gas cannot be transported efficiently to highly populated regions where there are high energy demands. The efficient conversion of these stranded natural gas resources into easily transportable liquid fuels and chemicals is therefore of great social, economic and environmental significance [1]. Natural gas reforming is the first step in the conversion of natural gas into valuable liquid fuels and chemicals. Once methane, the dominant component of natural gas, is reformed into syngas (a mixture of H_2 and CO), a variety of liquid fuels and chemicals can be synthesized, for example via the Fischer–Tropsch process [2].

Catalysts play an important role in methane reforming. Stable methane molecules are activated on the catalyst surface to form radicals, which are then oxidized into CO or CO_2 by oxygen species derived from oxidants such as O_2, CO_2 or steam [3]. Noble metal catalysts such as Pt and Pd have high catalytic activity and coking-resistance, while high prices and low availability limit their practical applications [4]. Transition metals such as Ni and Fe are considered to be good alternatives for noble metal catalysts. However, Fe catalyst has low catalytic activity and Ni catalyst readily causes coke formation due to its high catalytic activity in methane activation [5]. The coke formation can be restrained by reducing the Ni particle size and enhancing the interaction between catalyst and support [6,7]. Therefore, the catalyst/support structure (or morphology) greatly affects the reforming performance.

The catalyst/support structure is mainly determined by the catalyst preparation methods. Supported catalysts are generally prepared by either wet-impregnation or one-pot synthesis. Wet-impregnation has been widely used to prepare catalysts for industrial applications because of the high thermal stability of the supports and high efficiency of catalyst utilization [8]. Catalysts, noble metals or transition metals, are impregnated into porous supports such as ceramic monoliths and ceramic powders [8,9]. Nevertheless, supports occupy the major volume of catalyst beds in reactors, and catalyst loadings are restricted by catalyst aggregation. The one-pot synthesis of catalyst and support is mainly used in laboratories to investigate catalyst activity, including sol–gel, combustion and homogenous precipitation processes [10–12]. High loadings of catalysts can be readily

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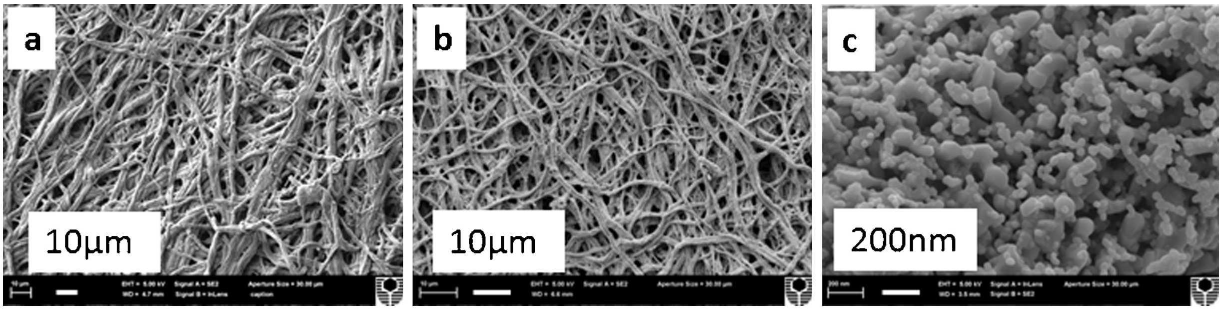

Fig. 1. SEM images of template and the hierarchical structure of templated nanocatalyst: ESM template (a), ESM-templated NiO/CeO_2 nanocatalyst (b) and nanoporous catalyst fibre (c).

achieved by adjusting the composition of the catalyst precursors. However, catalyst sintering during the reforming at 700–900 °C incurs the decay of reforming performances because catalysts are normally calcined at low temperatures (below 700 °C) to retain high the surface areas of catalysts [10].

Template synthesis is an effective way to control material structure through selecting suitable templates [13,14]. Green and easily available eggshell membranes are constructed of interwoven protein fibres. Utilizing the strong bonding between metal ions and protein, we have templated three-dimensional catalytic ceramics as cathodes of solid oxide fuel cells [15,16], and the three-dimensional structure ensured high thermal stability owing to a high resistance to sintering. Recently, we used the method to prepare fibrous NiO/CeO_2 nanocatalysts [17]. High catalyst loadings (up to 59.2%) were achieved, while no obvious aggregation of nanocatalysts was found after being heated at 1000 °C, which is higher than the temperatures of methane reforming. As a result, high syngas yields were obtained during the partial oxidation of methane at microsecond contact times. We also found that the interaction between catalyst and support greatly affected carbon formation during dry reforming of methane [18]. In this study, as a recently-developed method, the preparation parameters such as immersion time and calcination temperature will be investigated as factors influencing catalyst structure and in turn performance in steam reforming of methane.

2. Experimental

2.1. Catalyst preparation

As described in our previous study [17], eggshell membrane (ESM) was used as a template to prepare catalysts. Typically, $Ni(NO_3)_2·6H_2O$ (>99.99%) and $Ce(NO_3)_3·6H_2O$ (>99.9%) were dissolved in deionized water to obtain 0.5 M metal ion ($Ni^{2+} + Ce^{3+}$) solutions with the Ni^{2+}/Ce^{3+} molar ratio of 4:1. The eggshell derived from commercial eggs was immersed into 1 M nitric acid solution for 5–10 min, followed by peeling protein membrane from $CaCO_3$ shell. Then, the ESM was washed with deionized water to remove egg white, and subsequently dried in an oven at 95 °C for 2 h. Next, the fibrous catalyst was prepared by one step template process. 1 g of the dried ESM was immersed into 100 ml of the above nitrate solution at room temperature for 1, 3, 5 and 9 h respectively, where the adsorption of metal ions within protein fibres occurred. After taking the ESM from the solution, the excessive solution on the ESM surface was removed by rinsing with deionized water. Finally, the ESM with adsorbed catalyst precursors was dried at 95 °C for 2 h, and then calcined at 900, 950, 1000 and 1050 °C for 2 h in air respectively to remove protein fibres and crystallize catalysts. All chemicals were purchased from Sigma Aldrich Australia, and used without further treatment.

2.2. Catalyst charaterization

Thermogravimetric analysis (TGA) of the ESM–metal composites was conducted on a thermogravimetric analyzer (Q5000, TA instruments). The microstructures of the catalysts were observed by a scanning electron microscope (Zeiss Neon 40EsB FIBSEM). X-Ray diffraction patterns of catalysts were tested by using CuKα radiation with a Bruker D8 Advance diffractometer equipped with a LynxEye detector (Bruker-AXS, Karlsruhe, Germany) at a scan rate of 2°/min and a step size of 0.02°. Temperature-programmed reduction (TPR) was performed on a ChemBET3000 machine (Quantachrome Instruments). 0.03 g of NiO/CeO_2 catalyst was put into a U-tube and held by quartz wool. The U-tube was purged with nitrogen to expel the air in the lines, and then heated to 250 °C for 30 min in N_2 atmosphere with a flow rate of 40 ml/min in order to remove the moisture and impurities on the catalyst surface. After that, it was cooled to room temperature. Next, a gas mixture (5% H_2 in N_2) replaced the nitrogen to conduct TPR. The catalyst was heated up to 900 °C at a ramp rate of 10 °C/min. The H_2 consumption by the catalyst reduction as a function of temperature was detected using thermal conductivity detector (TCD), and the data were analyzed by TPRWin™ software.

2.3. Steam reforming test

The templated NiO/CeO_2 catalysts were firstly crushed into flakes with the sizes of 1–2 mm. Then, 0.04 g of the flake catalyst was put on a quartz filter that was set in the middle of a quartz tube reactor with an inner diameter of 10 mm. The reactor was heated using a tubular furnace, and the temperature on the surface of the catalyst bed was measured by a K-type thermocouple. The NiO/CeO_2 catalyst was reduced by a mixed gas of 20 vol% H_2/Ar at 750 °C for 1 h, and then a gas mixture of $40Ar:20CH_4:40H_2O$ (volume) was introduced into the reactor to conduct steam reforming at 800 °C. The gas flow rate was adjusted by mass flow controllers (AALBORG). Steam was fed by an HPLC pump (M626, AllTech) through a preheating tube. The exit gas from the reactor was ventilated to air through extraction. The components of the exit gas from the reactor were analyzed by an gas chromatography (GC, Agilent 6890). According to gas volume and CH_4 concentration, CH_4 conversion was calculated as follows:

$$CH_4 \text{ conversion} = \frac{CH_{4,\text{in}} - CH_{4,\text{out}}}{CH_{4,\text{in}}}$$

3. Results and discussion

3.1. Hierarchically structured NiO/CeO_2 nanocatalyst

Eggshell membrane (ESM) exhibits a structure of interwoven protein fibres, as shown in Fig. 1a, and the structure has been