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Free-standing NiO–MgO nanosheets in-situ controllably composited on Ni-foam as monolithic catalyst for catalytic oxy-methane reforming

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ABSTRACT

Free-standing NiO–MgO composite nanosheet catalysts to be used for catalytic oxy-methane reforming (COMR) have been developed by in-situ growing onto the Ni-foam struts under hydrothermal condition followed by calcination treatment. Among them, the NiO–MgO/Ni-foam consisting of 1.0% MgO, 18.7% NiO and nickel-foam-strut balance is the best structured catalyst engineered from nano- to macro-scale, being capable of converting 82.9% CH_4 into syngas at selectivity of 94.7% to H_2 and of 89.9% to CO for a feed of $CH_4/O_2=2/1$ (vol/vol), at 700 °C and a high gas hourly space velocity of 100 L g^{-1} h^{-1}. Nevertheless, improvement of their carbon resistance and textural stability is particularly desirable.

1. Introduction

Methane, which is both the largest constituent of natural gas and one of the most available and affordable feedstocks for the synthesis of fuels and chemicals, can be converted into value-added products by either direct or indirect routes [1,2]. The direct routes are less viable from a commercialization viewpoint due to the limited product-yields originated from the higher product-reactivities than methane; while the indirect routes, with the syngas production process as the prerequisite operation in the indirect methane conversion, are commercially promising because syngas can be efficiently converted into various valuable products [3]. However, the well-established methane stream reforming is very energy-intensive and costly because the reaction is highly endothermic and H_2/CO ratio of 3 is too high for Fischer-Tropch synthesis. Therefore, the cost-effective process for syngas production from methane is particularly desirable but remains challenging, which have aroused the considerable scientific and technological interests [4]. Catalytic oxy-methane reforming (COMR) is an attractive method for the syngas production owing to the compact reactor, high energy-efficiency and favorable H_2/CO ratio for the downstream processes such as methanol and Fischer-Tropsch synthesis [5].

Ni-based catalysts with moderate cost and excellent performance are commonly recognized to be the most promising candidates for high-throughput COMR process [6–9]. It is urgent but still significantly challenging to delicately design a catalyst with a unique combination of excellent activity, satisfying carbon resistance, distinguished robustness, high thermal conductivity and high permeability for lowering pressure drop. Recently, as the process intensification gradually known, the metal-foam-structured catalysts have attracted ever-increasing interest [10]. Our previous efforts have demonstrated successful applications of the Ni-foam in developing high-performance structured catalysts for COMR [11], syngas methanation [12] and coalbed methane catalytic deoxygenation [13]. It is thus exceptionally worthwhile to develop foam-structured catalyst for such exothermic and high-throughput COMR reaction process [14].

Herein, we demonstrate a monolithic Ni-foam-structured catalyst engineering from micro- to macro-scale, which was obtained by in-situ growing NiO–MgO composite nanosheets on the Ni-foam strut surface via hydrothermal reaction followed by calcination treatment. This is a promising approach to provide a unique combination of the attractive ability of the MgO promoter for suppressing carbon formation and the high permeability and enhanced heat/mass transfer stemmed from Ni-foam.

2. Experimental

The catalysts were typically prepared by hydrothermal treatment

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of Ni-foam using aqueous solution containing $Mg(NO_3)_2$ and NH_4Cl followed by a calcination process. Corresponding to the $Mg(NO_3)_2$ concentrations of 0.05 mol L^{-1}, 0.15 mol L^{-1}, 0.25 mol L^{-1} and 0.35 mol L^{-1}, the resulting catalysts are denoted as Cat-1, Cat-2, Cat-3 and Cat-4, respectively. Details of catalyst preparation, characterization, and evaluation are available in the Supporting material.

3. Results and discussion

3.1. Geometry, morphology and structural features

Fig. 1 shows the geometry, morphology and structural features of our representative foam-structured catalysts, while their textual properties, NiO crystallite size as well as NiO and MgO contents and the specific surface area (SSA) are collected in Table S1. Fig. 1A and Fig. S1 shows the untreated circular Ni-foam wafers with a diameter of 6 mm and its interconnected porous framework and zigzag structure. After hydrothermal treatment of Ni-foam using aqueous solution containing $Mg(NO_3)_2$ and NH_4Cl with varied $Mg(NO_3)_2$ concentration from 0.05 to 0.35 mol L^{-1} followed by calcination, as shown in Fig. 1B, the obtained foam-structured catalysts of Cat-1 to Cat-4 all showed formation of NiO phase (JCPDS no. 78-0429) but not MgO phase clearly evidenced by XRD patterns at 2θ of 37.3°, 43.3°, 62.9°, 75.4° and 79.4°. For comparison, a pristine Ni-foam circular chip was calcined merely in air for

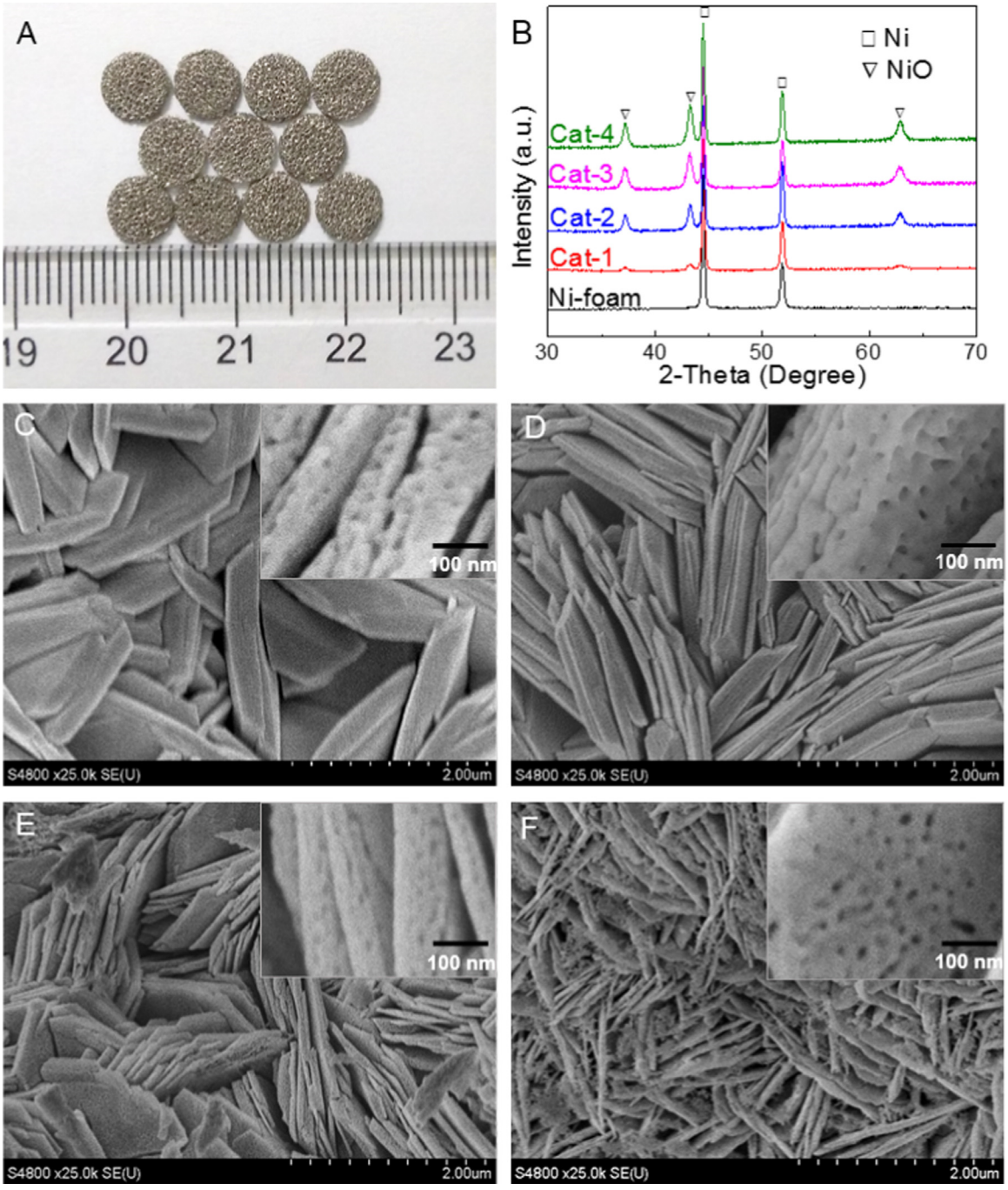

Fig. 1. The photograph (A) of the untreated monolithic Ni-foam wafers. (B) XRD patterns of the as-prepared NiO–MgO/Ni-foam catalysts and Ni-foam substrate calcined at 450 °C in air for 2 h. SEM images of the fresh catalysts: Cat-1 (C), Cat-2 (D), Cat-3 (E) and Cat-4 (F).