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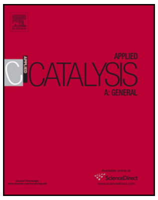

Effect of Ni-CNTs/mesocellular silica composite catalysts on carbon dioxide reforming of methane

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ABSTRACT

In this research, the novel composite catalysts between nickel and carbon nanotubes (CNTs) over mesocellular silica (MS) support were synthesized with an attempt to improve their stability to deactivation due to coke deposition in dry reforming reaction. Accordingly, the MS support was primarily prepared based on the synthesis of SBA-15 mesoporous silica with 1,3,5-trimethylbenzene (TMB) as a pore expanding agent. After that, nickel metal was loaded onto the MS support by using an incipient-wetness impregnation method, followed by CNTs synthesis via catalytic chemical vapor deposition (CCVD) technique through tip-growth mechanism. It was found that the existence of CNTs composite catalysts with nickel metal clusters on the tips of CNTs (Ni-CNTs/MS catalysts) could significantly improve the catalyst stability in dry reforming reaction (at 650 °C for 24 h) and simultaneously inhibit reverse water–gas shift reaction compared to that of Ni/MS catalyst. After 24 h time on stream, CO_2 and CH_4 conversions of Ni/MS catalyst were approximately decreased by 10%, while those of Ni-CNTs/MS catalyst were increased by 3%. This outstanding performance could be attributed to selective formation of carbon by-products as the tube-length extension of the existing CNTs. Accordingly, the active surface of Ni-CNTs/MS catalysts were remained constant throughout the period of dry reforming reaction.

1. Introduction

Carbon dioxide (CO_2) and methane (CH_4) are continuously released in the atmosphere by the result of industrial processes, and man-made activities play a major role in global warming [1–5]. Many attempts have been made to eliminate these greenhouse gases, for example, using as raw materials in various reactions such as dry reforming [1–6], methane cracking [7–9], steam reforming of methane [10–13], and carbon dioxide dehydrogenation [14–16]. In dry reforming reaction, CO_2 and CH_4 are primarily converted to carbon monoxide and hydrogen (synthesis gas),which are further converted to alcohols (methanol and ethanol) and hydrocarbon feedstock for petrochemical industries through Fischer–Tropsch synthesis reaction [17,18]. However, several problems such as highly endothermic nature of dry reforming reaction, competitiveness among many side reactions, sintering of catalysts, and carbon deposition are significantly observed [3–6,19,20]. Among these, carbon deposition is concerned as a major problem because of its direct and immediate effect on the activity and selectivity of catalysts [3–6,12].

Many researchers have attempted to diminish carbon formation and enhance catalyst activity in dry reforming reaction by means of oxide supports and promoters. Consequently, the use of oxide catalyst support (MgO, ZrO_2, and CeO_2) is also one alternative for carbon mitigation [21–26]. The oxide catalyst support can improve CO_2 adsorption on oxygen-containing surfaces and reduce the amount of carbon formation through reversed Boudouard reaction to form carbon monoxide. Moreover, the lanthanide-group metals (La, Ce, Pr and Sm) have been widely used as the catalyst promoter to increase the resistance to carbon deposition because of their highly stable oxidation states. However, the availability and cost are the main limitation of the lanthanide-group metals [3,27–29].

Due to the fact that silica support provides large surface area and high metal dispersion [30–32], while Ni metal is a promising

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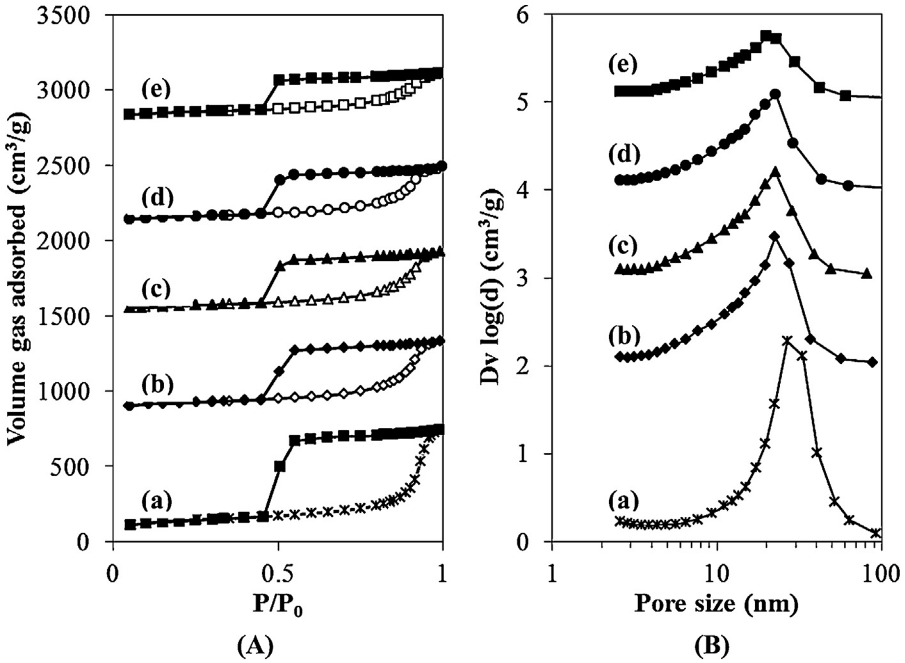

Fig. 1. (A) Nitrogen adsorption–desorption isotherm and (B) pore size distribution of MS support and catalysts.
(a) MS, (b) 5Ni/MS, (c) 10Ni/MS, (d) 5Ni-CNTs/MS, (e) 10Ni-CNTs/MS.

catalyst in dry reforming reaction because of its low cost, availability and good performance in this reaction [4,9,11], nickel on silica support is therefore potentially used. In addition, carbon nanotubes (CNTs) are attractive for the use as catalyst supports regarding their unique structural properties and interaction between support and metal particle [33–36]. It should be noted that the CNTs synthesized by using catalytic chemical vapor deposition (CCVD) technique have a unique structure that contained metal on the tip of nanotubes [37,38]. Therefore, the combination of these materials as the composites is of interest.

In this research, the composite catalysts with nickel metal on the tips of carbon nanotubes over mesocellular porous silica (MS) support were proposed with an attempt to improve the catalyst stability in dry reforming reaction. The textural properties, structure of composite catalyst, carbon types on the composite of Ni-CNTs/MS catalyst were characterized using nitrogen-sorption analysis, field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), thermal gravimetric analysis (TGA) and Raman spectroscopy, respectively. The effect of Ni-CNTs/MS composite catalysts on the activity of dry reforming reaction and their deactivation phenomena were investigated and compared to that of the conventional Ni/MS catalyst. The carbon formation mechanisms of the catalysts without and with CNTs were proposed.

2. Experimental

2.1. Composite catalyst preparation

Nickel metal on tips of carbon nanotubes were prepared over mesocellular porous silica support by catalytic chemical vapor deposition technique. The synthesis procedure is as follows:

2.1.1. Mesocellular silica preparation

Mesocellular silica support was prepared from sodium silicate solution (SS: 32 wt.% SiO_2) using Pluronic P123 (P123: $EO_{20}PO_{70}EO_{20}$, Aldrich) as a pore structure-directing agent and 1,3,5-trimethylbenzene (TMB) as a swelling agent. The synthesis process was based on SBA-15 mesoporous silica synthesis with the gel composition (in molar unit) of 1 SiO_2: 0.088 Pluronic P123: 4 HCl: 200 H_2O [39]. In this research, the ratio of Pluronic P123 to TMB was fixed at 2 (g/g). Pluronic P123 was firstly dissolved in distilled water under stirring at room temperature until the solution was completely clear, and sodium silicate solution was slowly dropped into Pluronic P123 solution. Then, hydrochloric acid and TMB solutions were consecutively added into the obtained mixture under vigorous stirring. The mixture was kept stirring at 40 °C for 24 h with the stirring speed of 300 rpm and then hydrothermally treated in autoclave at 100 °C for 24 h. After that, the solid product was filtrated, washed with distilled water, dried at 100 °C overnight, and calcined in air at 550 °C for 6 h. The final product was denoted as mesocellular silica (MS).

2.1.2. Nickel catalyst loading

Nickel/MS catalysts with different amounts of Ni loading were prepared by incipient wetness impregnation method using nickel(II) acetate as a Ni precursor. Nickel(II) acetate was completely dissolved in distilled water and dropped onto MS support under stirring at room temperature. The obtained mixture was air-dried in an oven at 100 °C overnight and calcined in air at 550 °C

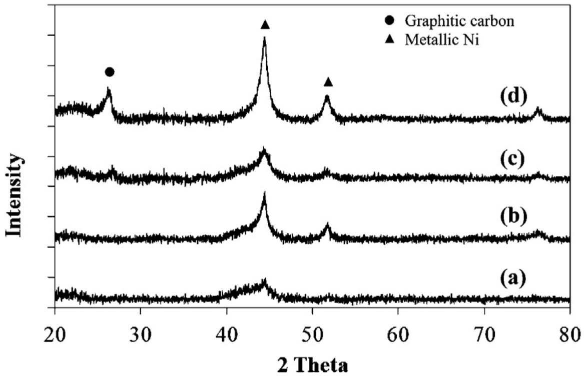

Fig. 2. XRD patterns of fresh catalysts.
(a) 5Ni/MS, (b) 10Ni/MS, (c) 5Ni-CNTs/MS, (d) 10Ni-CNTs/MS.