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Catalytic performance and characterization of Neodymium-containing mesoporous silica supported nickel catalysts for methane reforming to syngas

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ABSTRACT

Ordered mesoporous silica materials based on nickel and other elements have been extensively studied because controlling the size of metal nanoparticles is an effective method to tune the superficial physicochemical process. Neodymium (Nd)-promoted mesoporous silica xNdMS (x: molar ratio of Nd/Si = 0.01, 0.02, 0.04, 0.06) were prepared through a sol–gel strategy. Nickel-based catalysts with high dispersion by using xNdMS as supports were investigated for methane reforming with carbon dioxide and/or oxygen to produce syngas. xNdMS supports and nickel catalysts were examined by combining textural, structural, local and surface information. The characterization results showed that Nd was successfully incorporated into the mesoporous framework of MS and Nd was beneficial to improve the metal dispersion. All Nd-promoted Ni/MS catalysts were effective for the methane reforming reaction. Ni/0.04NdMS catalyst exhibited the highest initial catalytic activity during 12 h time on stream, which was attributed to its high metal dispersion, more basic sites and the strengthened nickel-support interaction. The readily deactivation and poorest catalytic activity of Ni/MS catalyst were due to the serious oxidation of metallic nickel under reaction medium.

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Introduction

The dry reforming of methane (DRM) has sparked an increased level of interest from the environmental point of view being that the process involves the conversion of two greenhouse gases into syngas (a mixture of H₂ and CO) with lower H₂/CO, which can be used for the production of long

chain hydrocarbons via Fischer–Tropsch synthesis [1–3]. However, DRM is strongly endothermic and suffers from high energy cost. The addition of oxygen can compensate the energy requirement, enabling to reach a thermoneutral operating condition [4]. This combined process is referred to as oxidative CO₂ reforming of methane (OCRM) [5–7].

It has always been a major challenge to develop a suitable catalyst with superior activity in the reforming process. A

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great number of supported nickel (Ni) catalysts have been widely evaluated in this reaction and have become the most potential candidate for the large scale application due to its high initial catalytic performance and cost-effective price [8,9]. However, the main problem of Ni catalyst is the deactivation caused by the carbon deposition [10], agglomeration of Ni metal particles during high temperature reaction condition [11,12], and oxidation of nickel in the coexistence of oxygen and methane [13,14]. Thus, efforts have been directed at improving catalyst carbon resilience, for example, developing alloy [15,16], spinel [17] and perovskite materials [18], embedding nanoparticles inside controlled cavities [19] or channels of mesoporous materials families [20], and constructing metal@silica core/yolk shell nanostructures [21–23].

In particular, manifold works have shown that the above deficiencies of nickel catalysts can be improved when Ni is paired with suitable lanthanide-group promoters [24–28]. The promotion effect of the lanthanide oxide addition was probably due to great capability for oxygen storage which can oxidize carbon intermediates on the catalyst surface [8,29], and the strong basicity to promote CO₂ adsorption on the catalyst surface which can accelerate the elimination of surface carbonaceous species [30,31].

Among the lanthanide oxides, the use of Neodymium (Nd) has recently been reported because of its great performance in methane conversion. Choudhary [32] concluded that perovskite-type mixed metal oxide (CoNdO₃) with strong metal-support interaction (Co⁰-Nd₂O₃) displayed high resistance to carbon formation at different reaction conditions (temperature = 750–900 °C and gas hourly space velocity = 10,000–50,000 cm³/g h) in the CO₂ reforming process. Xie [33] found Ni–Nd/γ-Al₂O₃ catalyst had high carbon resistance after 48 h reforming reaction, the amount of carbon deposition being only one-tenth compared with Ni/γ-Al₂O₃ due to the formation of mezzanine structure. However, Bhargava [34] gave a contradictory result that the addition of Nd to a Ni/γ-Al₂O₃ catalyst adversely affected its activity. More recently, Yamada [35] predicted the promoting effect of Nd on Ni/α-Al₂O₃ in methane conversion of oxidative reforming reaction by using artificial neural network training and observed the experimental activity of Ni–Nd/α-Al₂O₃ was three times higher than that of un-promoted Ni/α-Al₂O₃ catalyst.

On the other hand, the structure and nature of the support play an important role in the novel properties of the catalyst. The successful synthesis of mesoporous silica (MS) opened a new era in the investigation of inorganic molecular sieves and has revealed exciting possibilities in applications not only in catalysis but also in other areas of chemistry. Currently, hydrothermal method is the most popular approach for the introduction of the active metal into the ordered mesoporous silica [36,37]. However, this method has difficulty in obtaining the desired stoichiometric composition [38], because the metal ion precursor usually is added to the synthesis system before the hydrothermal treatment so that the succedent filtration inevitably leads to the loss of the metal content. Recently, sol–gel has been found as a promising alternative to the hydrothermal treatment, since it has the advantages of facile controlling stoichiometric composition and shape of target product [39,40]. The combination of the advantages of Neodymium dopant and mesoporous silica material is

potential to improve the performance of a nickel-based catalyst. However, there has been no study of the Neodymium containing mesoporous silica (NdMS) materials, and the understanding of the effect of Neodymium on the performance of supported nickel catalysts still lacks.

In order to evaluate the effect of Neodymium dopant on MS supported nickel catalysts, a series of nickel supported on NdMS catalysts (Ni/NdMS) were prepared by sol–gel method and the catalytic performance were evaluated in the oxidative CO₂ reforming of methane in this work. One aspect that awaits clarification is how Neodymium contributes to nickel catalyst during the methane reforming. The superiority of the optimized Ni/NdMS catalyst was demonstrated by performing X-ray power diffraction (XRD), temperature programmed reduction (TPR), temperature programmed desorption (TPD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS).

Experiments

Preparation of Nd-containing mesoporous silica (NdMS) support and Ni/NdMS catalysts

The Nd-containing mesoporous silica (NdMS) materials were synthesized by sol–gel method. 1.0 g Pluronic P123 (EO₂₀PO₇₀EO₂₀, molecular weight 5800, Aldrich) and a stoichiometric amount of Nd(NO₃)₃·6H₂O were dissolved in 5.0 g ethanol and stirred for 30 min to obtain a homogeneous solution. 2.08 g tetraethylorthosilicate (TEOS) and 0.20 g hydrochloric acid (HCl, 1 mol/l) was added dropwise into the above solution. After continuous stirring for 30 min, the mixture was transferred into a crucible and kept at room temperature under static condition for 18 h to form a rigid gel. Then the gel was dried at 60 °C for 18 h and calcined at 550 °C (heating ramp rate 2 °C/min) in air for 6 h enabling the complete removal of the template. The calcined supports were designated as xNdMS, where x indicates the Nd/Si molar ratio equal to 0.01, 0.02, 0.04, and 0.06.

Ni/xNdMS catalysts were prepared by impregnating the xNdMS support with aqueous solution of Ni(NO₃)₂·6H₂O. The obtained solution was sonicated at 60 °C in an ultrasonic bath for 2 h to gradually evaporate the excess water. After that, the resulting solid was dried at 110 °C overnight and calcined in air at 550 °C for 6 h with a heating rate of 2 °C/min. The nickel loading was fixed at 5 wt.% with respect to the support.

Catalytic activity test

Methane reforming reaction was conducted under atmospheric pressure in a continuous down flow quartz reactor (OD 8 mm, ID 6 mm, length 450 mm). 0.1 g catalyst with particle size of 180–250 μm was loaded in the center of the reactor and supported by quartz wool. A nickel–chromium/nickel–silicon thermocouple sheathed by a quartz thermocouple-well (ID 1.5 mm) was located at the outlet of the catalysts bed for monitoring the reaction temperature. OCRM reaction was carried out at 700 °C with a feeding gas of CH₄/CO₂/O₂ (molar ratio: 40/20/10) at a total flow rate of 70 ml/min and DRM was performed at the same temperature with a feeding

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