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Research article

Design of active and stable bimodal nickel catalysts for methane reforming with CO_2

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ABSTRACT

Dry reforming of methane (DRM) has been investigated in numerous studies as an attractive process to produce synthesis gas. Although nonprecious-metal catalysts are widely employed in this reaction, their large scale application has been hampered due to difficulties in controlling the metal sintering and coking. The main objective of this research was to improve DRM reaction through highly active and effective nickel catalysts with bimodal structure. In this work, the effect of pore structures (nonporous, monomodal and bimodal structures) on the catalytic performance, stability and coke formation were comparatively discussed. Two series of nickel catalysts were developed by one-step and impregnation methods. By using one-step strategy, three kinds of bases ($NH_3{\cdot}H_2O$, Urea and NaOH) were used to prepare monomodal (Ni-SiO_2-$NH_3{\cdot}H_2O$), bimodal (Ni-SiO_2-Urea) and non-porous (Ni-SiO_2-NaOH) catalysts. By using impregnation method, monomodal (Ni/M-SiO_2) and bimodal (Ni/B-SiO_2) catalysts were prepared. The pore structure exerted crucial effect on the catalytic performance in DRM. In comparison to monomodal catalyst, in each series bimodal nickel catalyst exhibited higher activity and more stable performance in DRM. The non-porous Ni-SiO_2-NaOH exhibited inferior activity to the monomodal or bimodal catalyst due to the significant decrease in surface area. The obtained catalysts prepared by one step method contained Ni nanoparticles with diameter of 3 nm, about 1/8 of the catalysts prepared by impregnation method. Ultraviolet-visible diffuse reflectance spectroscopy (UV–Vis DRS) confirmed the well-dispersed Ni particles were incorporated into the silica framework. Temperature programmed reduction and X-ray photoelectron spectroscopy (XPS) also verified the strengthened interaction between Ni species and silica support. Thus, these structural properties led to higher activity over Ni-SiO_2-Urea than the corresponding catalyst with equivalent pore structure. Relative to the initial methane conversion of 74% over Ni/B-SiO_2, Ni-SiO_2-Urea catalyst showed both stable CH_4 and CO_2 conversions and a constant H_2/CO ratio close to 1, without significant decay of the activity during 24 h on stream.

1. Introduction

Fossil fuels have become an important part of daily life, providing us with a multitude of products, energy and electricity. Many important developments are largely owed to the oil, starting with the usage of the illumination fuel to the development of the motor-car, and further to the possibility of air travel. However, in the past decade, the excessive use of oil by the rapid industrial development and population growth have advanced the depletion of the finite oil reserves. The natural gas, whose main component is methane, has been identified as an alternative energy resource being able to substitute the oil. It is available in abundant quantities, but unfortunately often in remote and less hospitable areas, thus bringing natural gas to the reforming process is a main exploration strategy toward rational application of natural gas [1–3].

The process of methane reforming with CO_2, also called as the dry reforming of methane (DRM), is an eco-friendly technology from economic and environmental perspectives [4]. It produces valuable syngas (a mixture of H_2 and CO), which can be utilized as feedstock for producing long-chain hydrocarbons and oxygenated chemicals through Fisher-Tropsch synthesis [5–7].

Catalysts are the essential agent in the reforming process. Considering the balance between the catalytic performance and the cost-effective nature, nickel has been believed to be the most suitable component by reason of affluent source and high initial activity [8–10]. Nevertheless, nickel-based catalysts are often confronted with deactivation due to coke formation or sintering of active component which constraints their application in dry reforming of methane [11–14]. There have been several works on developing different types of

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catalysts which exhibit high catalytic conversion and stability. For example, core/yolk shell structured Ni-yolk@Ni@SiO_2 nanocomposites were able to tackle the carbon deposition while maintaining activity and stability [15–17]. Ni-based perovskite oxides with high oxygen mobility also provided high catalytic stability for hydrocarbon reforming reactions [18–20]. Usually, the active metallic component and appropriate support jointly determine the stability and reactivity of supported nickel catalysts [21,22]. Support is vital to immobilize the active center and maintain the metal dispersion, thus the change in physicochemical property of the support affects the surface properties of the catalyst. Mesoporous materials are intrinsically preferred materials for supporting nickel catalysts owing to their stable structure, regular pore array, high surface area, and large pore volume [23–25]. Additionally, their highly ordered pore structure can effectively confine nickel particles in the channel, thus inhibiting metal agglomeration [26–28]. For example, Massiani et al. reported the stabilization of nickel nanoparticles along the SBA-15 [29] or order mesoporous alumina [30] channels could inhibit nickel sintering and coke formation. On one hand, solely small porous materials usually have high surface area that are beneficial for metal dispersion, yet the diffusion of products or reactants is maybe limited by the small porous channel, and carbon could completely block the pores within a short period [31]. On the other hand, solely large porous materials are efficient for molecular diffusion and transportation in catalyst body, but with low surface area not favorable for the metal dispersion [32–34]. Hence, the unique tailoring of bimodal porosity has attracted increased attention, as the combination of advantageous mass transport properties and large surface area is particularly beneficial in electrochemical applications, adsorption, catalysis and in separation science [35–38].

Several preparation methods were reported to obtain bimodal support [39–42]. A simple method was developed by Tsubaki et al., via direct introduction of colloidal zirconia sol solutions into macroporous silica gel [43]. Due to the increased surface area and decreased pore volume, the bimodal ZrO_2-SiO_2 material supported cobalt catalyst was very effective in the liquid phase for Fischer-Tropsch synthesis [44]. This novel bimodal support loaded nickel catalyst also exhibited higher oil conversion and H_2 formation rate in the steam reforming of vegetable oil [45]. Later, a bimodal SiO_2 support via incipient-wetness impregnation of silica gel with silica sol was synthesized and used for preparation of highly loaded platinum catalyst [46]. Because of high surface area and fast intra-pellet diffusion of reactants and products, this bimodal material presented much better catalytic performance in carbon dioxide reforming of methane than the mono-modal analogs [47]. Then, not limited to the silica, a bimodal alumina material by impregnating γ-Al_2O_3 inside α-Al_2O_3 was synthesized and used as support for nickel catalyst. The prepared catalyst exhibited a higher conversion of methane at a high space velocity (6×10^{-6} mol/s) in the stream reforming of methane [48]. However, in the above "tailor-made" methodology, the regulating of the pore size was limited by porosity of the raw materials. In fact, the template is commonly used in the preparation of the mesoporous materials. With chitosan as template, Chareonpanich et al. [49] reported bimodal porous silica supports with smaller and larger pore size at respectively, 6–100 nm and 195 nm. Alternatively, with cetyltrimethyl ammonium bromide as template, Hou et al. [50] synthesized several bimodal silica supports with the first pore size at 2.5 nm and the second at 8–22 nm. The bimodal catalysts with second larger pore exhibited higher CO conversion (79%) and C_{5-18} selectivity (65.5%) in Fischer-Tropsch synthesis, which was connected with the larger cobalt particle size and higher reducibility.

Apart from the promotional effect of bimodal nature, the particle size of nickel species is another crucial factor for the catalytic reforming reaction [51,52]. Many experimental and theoretical studies have confirmed that the size of Ni particle has a significant effect on the carbon formation [53–56]. In general, the smaller size of nickel particle, the higher suppression ability for metal sintering or carbon deposition [57–59]. Over nickel-alumina aerogel catalysts, large nickel particles were prone to grow carbon whiskers and a minimum diameter of about 7 nm was required for Ni particles to generate filamentous carbon [60]. This result was in agreement with the study of Bilbao et al. on the particle size limit for carbon filament formation [61]. Preparation methods usually played vital role in controlling Ni particle size [8,57]. Impregnation method has widely been applied for catalyst preparation, because this process is convenient to operate and tends to easily control stoichiometric composition of product. However, this method easily induced the weak interaction between metal and support, leading to severe nickel aggregation and coke formation during the dry reforming of methane in high temperature [62–64]. Roh et al. [65] compared the influence of preparation method on the performance for MgO modified Ni-$Ce_{0.8}Zr_{0.8}O_2$ catalysts. Ni-MgO-$Ce_{0.8}Zr_{0.2}O_2$ prepared by co-precipitation method exhibited improved CH_4 conversion and stability compared to that prepared by impregnation method, which could be attributed to the small nickel particle size and facile reducibility. The former gave over 95% conversion at 800 °C and maintained its high performance over 200 h without deactivation by coking. In a recent work Sun found mesoporous catalyst NiO-Y_2O_3-Al_2O_3 prepared with a one-pot evaporation-induced self-assembly method was more stable than the impregnated sample [66], which was due to the small Ni particles embedded in the ordered mesoporous framework. Further, Centeno reported a co-impregnation procedure to load nickel and ruthenium simultaneously with Al_2O_3 support [67]. The catalyst prepared this way showed better activity performance and coke resistance, compared to the one obtained by sequential impregnation. However, in our previous work [68], the best performance was obtained over Ni-Y_2O_3-γ-Al_2O_3 catalyst prepared by sequential impregnation method, which was related to smaller metallic nickel particle and more basic sites. Besides, Bordoloi et al. [69] adopted solvothermal treatment combined with urea deposition approach to prepare MgO modified CeO_2-ZrO_2 nanoporous composite and dispersed Ni species on it. Owing to the basic property of MgO, the final Ni-MgCeZr catalyst showed superior coke resistance ability, and maintained 95% methane conversion for 100 h in the reforming reaction. The author considered that, the superb activity and stability of prepared catalyst were attributed to the bimodal structure of support, and the small size of Ni particles produced by urea deposition method.

Motivated by the successful synthesis of surfactant-templated mesoporous materials, the control synthesis of bimodal porous silica was attempted in this paper. The main objective of this research was to improve DRM reaction through highly active and effective bimodal nickel catalysts. In this work, bimodal nickel catalysts were developed by two different processes: one-step and impregnation methods. In the light of detailed characterization techniques, the effect of structural and compositional properties of nickel catalysts with different structures (nonporous, monomodal and bimodal structures) on the catalyst activity, stability and coke formation were discussed.

2. Experimental

2.1. Synthesis of M-SiO_2, B-SiO_2 supports and nickel-based catalysts

Bimodal porous silica support (B-SiO_2) was synthesized by the chemical templating-scaffolding strategy [70]. Tetraethylorthosilicate (TEOS) was used as the silica source and cetyltrimethyl ammonium bromide (CTAB, Alfa Aesar) as the template. Typically, TEOS, CTAB, ammonia solution (25 wt%) and distilled water were mixed in a molar ratio of 1:0.2:0.18:160 under the ambient temperature (25–30 °C). Under vigorous agitation, the mixture became at first a homogeneous sol, gradually more viscous as time went on, and eventually changing into a white gel. Afterwards, it was aged at 100 °C for 48 h in the polypropylene bottle. The product was filtered, washed several times with distilled water and dried at 120 °C for 3 h. Subsequently, the white solid was heated to 550 °C in the static air with a slow heating rate