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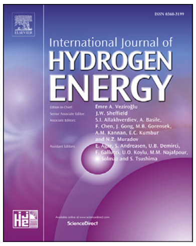

A novel promoting effect of chelating ligand on the dispersion of Ni species over Ni/SBA-15 catalyst for dry reforming of methane

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ABSTRACT

A series of Ni/SBA-15 (AM) catalysts were prepared by chelating ligand assisted impregnation method. The results showed that the chelating ligand played a positive promoting role for CH_4 dry reforming with CO_2 over Ni/SBA-15. The electron-pair donor atoms and the high viscosity of chelating agent could inhibit the aggregation of nickel species and contribute to the well-dispersed Ni particles with size of <6 nm. Compared to the Ni/SBA-15 (CM) prepared by conventional impregnation, all the Ni/SBA-15 (AM) exhibited superior catalytic performance, especially the catalyst assisted by ethylenediamine possessed stable activity and the least amount of carbon deposition.

Introduction

With the rapid industrial development, the excessive use of oil has made the petroleum resources rapidly reduced and raised climate change [1]. Now, more and more attention has been focused on the exploitation of natural gas. CH_4 is a principal component of natural gas and the CO_2 reforming of methane (CRM) has received extensive attention for that the other reactant gas, carbon dioxide, usually acts as the main industrial waste gases. The great advantages of this reaction involve not only the utilization of two major greenhouse gases, but also desirable yield of syngas with H_2/CO ration (<1) for Fischer–Tropsch synthesis [2–4].

Nickel-based catalyst is the most frequently reported catalyst of CRM because of its low-cost and excellent catalytic performance as compared with scarce resources and exorbitant price of noble metal-based catalysts such as Ru, Rh, Pt, Pd and Ir [5–8]. Nevertheless, Ni-based catalysts often suffer from sintering and carbon deposition in CRM reaction [9–12]. The reason is the fact that carbon dioxide reforming reaction merely performs at high temperature, leading to active center accumulation (sintering) or the collapse of the support structure. Furthermore, coke deposition is often inevitable during hydrocarbon reforming reactions, which is much more serious in DRM due to the low H/C ratio in the reactants. The formation of carbon can cover the active center. To address these problems, many researchers have done a lot of work and

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they find that the small size of Ni particles is in favor of the excellent resistance to carbon deposition [13–16]. However, small-sized nanoparticles would easily aggregate and sinter during catalytic processes at high temperature [17]. Therefore, the effective methods for stabilization of Ni nanoparticles have attracted much attention. Gong et al. reported that the Ni particles can be stabilized via promoting metal-support interaction [18–25]. Some researchers found that the ordered mesoporous material can stabilize Ni particles by confine effect [26,27]. Nowadays, the impregnation method is widely used for preparing industry catalysts due to the advantages such as the simple synthetic process, the low cost and the environmental-friendly procedure. However, large particles were usually formed in the traditional impregnation method. In this paper, the mesoporous SBA-15 supported Ni-based catalysts were prepared by impregnation method modified with chelating ligand, and it was found that the Ni/SBA-15 modified by chelating ligand presented small size Ni particle and outstanding catalytic performance for CH_4 reforming with CO_2. The physicochemical properties of Ni/SBA-15 were characterized by multiple techniques. And the resistance to coking and sintering of Ni/SBA-15 catalysts was also investigated.

Experimental

Synthesis of SBA-15

The mesoporous silica SBA-15 was synthesized according to the method proposed by Zhao et al. [28]. The 7.5wt% Ni/SBA-15 catalysts were prepared via modified incipient impregnation method. Firstly, a certain amount of aqueous chelated (ethylenediamine (en), citric acid (cit) and acetic acid (ace)) was added to $Ni(NO_3)_2{\cdot}6H_2O$ solution in order to form metal chelate. Secondly, SBA-15 was added to the mixture, which was followed by ultrasonic treatment at 30 °C for 2 h. Then, the samples were dried. The powders were calcined at 500 °C in air for 4 h (heating rate: 1 °C/min) and the samples were denoted as Ni/SBA-15 (AM). To distinguish the samples prepared by adding different chelating ligand, they (Ni/SBA-15 (AM)) were denoted as Ni/SBA-15 (en), Ni/SBA-15 (cit) and Ni/SBA-15 (ace), respectively. For comparison, the conventional 7.5wt% Ni/SBA-15 sample was also prepared by incipient impregnation method and denoted as Ni/SBA-15 (CM).

Characterization of catalysts

The specific surface areas, total pore volume and average pore diameter were measured derived from N_2 adsorption–desorption isotherms using Micromeritics TriStar II 3020 static volumetric instrument. Before the measurements, the samples were degassed in vacuum at 300 °C for 4 h to remove the surface impurities.

The crystalline phases of the NiO species in the catalysts were measured by X-ray diffraction (XRD) measurements using Ni-filtered Cu Kα radiation ($\lambda = 0.15406$ nm) radiation source Bruker D8 Advance, operated at 40 kV and 40 mA.

Transmission electron microscopy (TEM) was performed for the observation of catalyst morphology. Previously, the catalyst was dispersed ultrasonically in alcohol and a drop of dispersion was deposited and dried on holey carbon film grid. Then the samples were characterized by FEI Tecnai G20 transmission electron microscopy, which used an accelerating voltage of 300 kV.

Thermogravimetric differential scanning calorimetry (TG-DSC) measurements were carried out on a SDT Q600 thermogravimetric analyzer from room temperature to 900 °C at a rate of 10 °C min^{-1} under air atmosphere.

Hydrogen temperature-programmed reduction (TPR) was carried out on gas chromatography equipped with a TCD detector. Before the test, 50 mg samples were activated at 400 °C for 40 min in N_2 (40 mL min^{-1}). TPR was performed from 150 °C to 850 °C under 5% H_2/Ar (30 mL min^{-1}) with a heating rate of 10 °C min^{-1}.

Catalytic reaction experiments

The catalytic reaction was carried out under atmospheric pressure using a continuous fixed-bed flow reactor (OD: 8 mm, ID: 6 mm). Typically, 80 mg (180–250 μm) of catalyst was placed in the center of the reactor. Prior to each test, the catalyst was reduced at 700 °C for 1 h under pure hydrogen (20 mL min^{-1}). A reaction mixture of CH_4 and CO_2 (molar ratio = 1: 1) was introduced into the reactor at a gas hourly space velocity (GHSV) of 22,500 mL·($g^{-1}h^{-1}$). The activity tests were carried out in the temperature range of 600–800 °C with an increment of 50 °C and the reaction temperature at 800 °C was kept constant for 3 h before the temperature cooled down. The long-term stability test experiment was conducted at 700 °C for 50 h. The product from the reactor was analyzed online by a gas chromatograph (Fuli 9790) equipped with a TDX-01 column and a thermal conductivity detector (TCD).

Results and discussion

XRD patterns of fresh catalysts

The small-angle XRD patterns were presented in Fig. 1. All samples presented the similar patterns with a strong diffraction peak centering at about 1°, indicating that ordered hexagonal mesostructures of all the samples were well maintained [28,29]. It demonstrated that the structure of SBA-15 was not destroyed after introduction of Ni by the impregnation method. Obviously, the diffraction peaks of the Ni/SBA-15 (AM) samples moved to lower angles, which could be explained by the dilation of the crystal unit structure. Considering the larger radius of Ni^{2+} (Paulling radius = 72 pm) than Si^{4+} (Paulling radius = 42 pm), the Ni–O bond length was longer than that of Si–O, and it could be inferred that Ni species were incorporated into the mesoporous framework of SBA-15 [29,30].

Fig. 2A displayed the wide-angle XRD of all fresh samples. There was a broad peak originated from $2\theta = 15°–35°$ on all catalysts, which should be attributed to the SiO_2 frameworks of SBA-15 support. As shown in Fig. 2A, the sharp and strong diffraction peaks at $2\theta = 37.3°$, 43.3°, 62.9° and 75.3° were indexed to (111), (200), and (220) diffraction of cubic NiO phase (JCPDS 71-1179) on the Ni/SBA-15 (CM) catalyst, suggesting the

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