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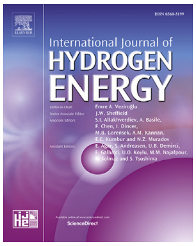

The effect of $NH_3 \cdot H_2O$ addition in Ni/SBA-15 catalyst preparation on its performance for carbon dioxide reforming of methane to produce H_2

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ABSTRACT

Three kinds of Ni catalysts loaded on SBA-15 were prepared by impregnation method, adding $NH_3 \cdot H_2O$ or $C_2H_2O_4$ in the impregnant, and applied to CO_2 reforming (DRM) of methane to generate hydrogen at 750 °C. The results showed that the catalyst prepared with $NH_3 \cdot H_2O$ addition exhibited high activity and stability. TEM, H_2-TPR, XPS, XRD, and TG-MS characterization indicated that with addition of $NH_3 \cdot H_2O$ (0.1 mol L^{-1}) in the preparation process, small nickel oxide particles, with average size of about 7 nm, were obtained on the catalyst, and the strong association between support and Ni species made them uniformly dispersed, enabling the capacity to resist carbon deposition and metal sintering, which contributed to the excellent activity, stability and selectivity for the DRM to H_2 production.

Introduction

Nowadays, hydrogen has gained widely application in various processes: hydrogenation in petroleum industry, ammonia synthesis, fuel cell and energy resource for some mechanical devices, such as turbines and internal-combustion engine, due to the fact that hydrogen energy is eco-friendly with high specific energy density [1–5]. Yet, whether the main market of hydrogen energy industry will flourish in the future will mainly depend on its cost competition with other energy systems, and the key factor is to find low cost raw materials and methods for hydrogen production [6,7]. Methane, generally considered as a greenhouse gas, is an unconventional clean and low-cost resource, widespread in natural gas, biogas, shale gas and other natural resources, and could be cracked into hydrogen. Among the methods of methane conversion to hydrogen investigated: steam reforming, partial oxidation, and DRM [1,6,8], DMR differentiates itself because of at least the following aspects. Firstly, another greenhouse gas CO_2 is put into utilization, which could be helpful for reducing the greenhouse effect [9–11]. Secondly, this conversion makes it possible to increase the commercial value of the natural resources, such as shale gas, the digested marsh gas (the main components are CO_2 and CH_4), and so on [12,13]. Thirdly, the high purity hydrogen and CO produced in DRM could be more preferred for the direct application in fuel cells [14–17].

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Low cost and high activity Ni-based catalysts were studied extensively operating at high temperature [18–20], which is necessary for the activation of the C–H bonds in CH_4 and the C–O in CO_2. Nevertheless, the deactivation of catalysts caused by coke and sintering easily occurred at high temperature, which has greatly stunted the development of DRM to produce H_2 [21–25]. The approaches for overcoming the drawbacks put forward currently are mainly in the three aspects: (1) adding promoters (2) modifying the carriers (3) optimizing the preparation methods [26–28]. Thus, optimization of the support and the preparation method attracted much attention [17,29,30]. In comparison to Al_2O_3, La_2O_3, Y_2O_3, MgO and SiO_2 [9,30–34], ordered mesoporous support, such as SBA-15, ZSM-5, and KIT-6 showed outstanding performance, owing to the features of narrow pore size distribution, large specific surface area and pore volume [35,36]. Particularly, the 5–15 nm [37] pore size would confine the Ni species just in the pore of SBA-15.

Zhang et al., applied chelating ligand assisted impregnation method to make a novel Ni/SBA-15 catalyst [38], and obtained dispersed nickel particles with small size of <6 nm, which showed outstanding performance for DRM, particularly in inhibiting the aggregation of nickel species. Gálvez group found that the Ni species prepared via reduction-precipitation method were successfully confined inside the pore of support, consequently, the deactivation of the catalyst was effectively depressed [31]. Moreover, the impregnation solvent had obvious effect on the reactivity of the catalyst by adjusting the interaction between active metal and the support [39]. Miao developed a kind of Ni/SBA-15 catalyst, using ethanol instead of water as solvent in the preparation. The catalyst exhibited higher CH_4 yield in CO methanation than that obtained by traditional preparation method. It was suggested that the polarity of the solvent could influence the association between the nickel species and SBA-15 as well the dispersion of nickel species [39]. In contrast to the ordinary impregnation method, the Pd-Ni/SBA-15-AT, made by co-impregnation with acid treatment, brought much better catalytic activity, on account that the slight acid treatment could effectively remove the large-size nickel oxide particles blocked in the pores of the support [40]. By NH_3/H_2O vapor-induced internal hydrolysis process, about 60 wt% Mn_2O_3 was successfully loaded on SBA-15 support without pore blockage [41], which provided constructive guidance in modifying the preparation methods of Ni-based catalyst for high catalytic activity, stability and selectivity to produce H_2.

In this paper, the effect of $NH_3 \cdot H_2O$ addition in Ni/SBA-15 catalyst on the performance for CO_2 reforming of methane to produce H_2 and CO was researched. The results were also compared to those obtained on the samples prepared with $C_2H_2O_4$ addition and only H_2O solvent. The relationship between the structure of the catalysts prepared with different treatments and the performance for DRM was also studied specifically.

Experimental

Catalyst preparation

The three kinds of 10% Ni-based catalysts were prepared by impregnation method. The designed amount of $Ni(NO_3)_2 \cdot 6H_2O$ was added into the H_2O, $C_2H_2O_4$ aqueous solution or $NH_3 \cdot H_2O$ aqueous solution, respectively. Then 2 g SBA-15 was separately put into the three kinds of solutions before ultrasonicated for 30 min. The next steps were the same as those reported in Ref. [42]. According to the solution used in the impregnation process, the three kinds of catalysts obtained were labeled as Ni/SC (Ni/SBA-15-$C_2H_2O_4$), Ni/SN (Ni/SBA-15-$NH_3 \cdot H_2O$) and Ni/SH (Ni/SBA-H_2O).

Catalytic performance test

The DRM runs with Ni/SC, Ni/SN, Ni/SH catalysts were performed on a micro-quartz-tube reactor (10 mm in diameter), respectively. The three kinds of catalysts were measured at 750 °C under atmospheric pressure. Before the activity test, 0.25 g calcined catalyst (20–40 mesh) was heated to 750 °C (rate: 10 $^{\circ}C \cdot min^{-1}$) in argon flow, and then reduced at a constant temperature of 750 °C in diluted hydrogen (hydrogen/argon = 1/1, F = 60 ml min^{-1}) for 1 h. Next, a mixture of reactants (methane/carbon dioxide = 1, F = 60 ml min^{-1}) was introduced into the system. A gas chromatograph with Plot-C2000 capillary column was used for the on-lone analysis of the products.

The conversion of the reactants, the yield of products and selectivity to both H_2 and CO were determined by the following formulas:

$$X_{CH_4} = \frac{n_{CH_4,in} - n_{CH_4,out}}{n_{CH_4,in}} \times 100\%$$

$$X_{CO_2} = \frac{n_{CO_2,in} - n_{CO_2,out}}{n_{CO_2,in}} \times 100\%$$

$$Y_{H_2} = \frac{n_{H_2}}{2n_{CH_4,in} - 2n_{CH_4,out}} \times 100\%$$

$$Y_{co} = \frac{n_{CO}}{(n_{CH_4,in} + n_{CO_2,in}) - (n_{CH_4,out} + n_{CO_2,out})} \times 100\%$$

$$H_2/CO\ ratio = \frac{n_{H_2 \cdot out}}{n_{CO \cdot out}}$$

where X_{CH_4}, X_{CO_2} were the conversion of CH_4 and CO_2, Y_{H_2} and Y_{CO} were the yield of H_2 and CO. $n_{CH_4,in}$ and $n_{CO_2,in}$ were the number of moles of CH_4 and CO_2 introduced into the reactor, while $n_{CH_4,out}$, $n_{CO_2,out}$, $n_{H_2 \cdot out}$ and $n_{CO \cdot out}$ represented the mole number of methane, carbon dioxide, hydrogen and carbon monoxide flowed out from the reactor.

Catalyst characterization

BET

Micromeritics Tristar II instrument was applied to determine the specific surface area of the three kinds of catalysts by N_2 adsorption. Before measurements, the samples, each about 100 mg, were outgassed at 150 °C for 2 h, and at 300 °C for 2 h under vacuum.

ICP

The actual content of the nickel in the calcined samples were obtained by ICP-EDS (inductively coupled plasma atomic

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