

Enhanced activity of Ni/SiO₂ catalyst in dry reforming of CH₄ via a modified impregnation method

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Abstract. A modified impregnation method with the addition of NH₄NO₃ was employed to prepared the supported Ni catalyst (denoted as Ni/SiO₂-N). And the obtained catalyst exhibited an improved catalytic activity and stability in DRM at 800°C with GHSV of 48 L·gcat.⁻¹·h⁻¹ and CH₄/CO₂/N₂=9/9/2. The XRD and H₂-TPR results showed that the Ni/SiO₂-N catalyst was possessed with smaller Ni particles and stronger metal-support interaction than Ni/SiO₂ catalyst prepared by the common impregnation method, leading to the better catalytic performance. It is the decomposition of NH₄NO₃ which can generate extra heat in a short time during the catalyst preparation process that make the change in structure and performance of catalyst.

1. Introduction

Dry reforming of CH₄ with CO₂ (DRM, CH₄ + CO₂ = 2H₂ + 2CO) to syngas can make good use of CH₄ and CO₂ which are both “greenhouse gases”. The obtained syngas consisting of H₂ and CO is an important chemical, which can be further converted to methanol, dimethyl ether, liquid fuels and other chemical products via methanol rout and Fischer-Tropsch synthesis (FTS)[1-4]. So, the DRM reaction not only can contribute to the carbon cycling but also can relieve the environmental and energy crisis.

Various catalysts have been studied for DRM. Compared with the noble metal catalyst (such as Ru, Pt, Rh and so on), Ni-based catalyst has been considered as the best candidate for the industrial application of DRM due to its lower price and better catalytic activity[5-7]. As DRM is a strongly endothermic reaction, it is usually operated at high temperature between 700~900°C. However, for the Ni-based catalyst, it is easy to be deactivated because of sintering and carbon deposits which can wrap the Ni particles and block the reactant molecules from the active site. It is reported that the size of Ni particles has a close relationship to the generation of deposited carbon, for more Ni atoms are needed to promote the side reaction (CH₄ = C + 2H₂) at high temperature. Thus, the catalyst with better Ni dispersion, smaller Ni particle size and stronger Ni-support interaction is benefit for the DRM[8].

It is known that the preparation method plays an important role in the textural, structural and physicochemical characteristics of catalyst, which can ultimately influence the performance of catalyst[9-11]. Sukonket et al prepared a series of ceria-zirconia support by a surfactant-assisted route and a coprecipitation route, and found that the supported Ni catalyst with support prepared by the surfactant-assisted route showed better performance in DRM[12]. Goula et al. reported that the Ni-Al catalyst prepared by the slightly modified Equilibrium Deposition Filtration (EDF) technique exhibited the quite different catalytic behavior, in comparison to the catalyst prepared by the conventional incipient wetness and wet impregnation methods[13].



The wetness impregnation method is the most commonly used catalyst preparation method because of its simplicity and convenience. However, for the supported catalyst prepared by this method, the interaction between metal and support is generally weak, and the metal particles are usually large, which is unfavorable. In this work, the Ni/SiO₂ catalyst was prepared by the modified wetness impregnation method with the addition of NH₄NO₃. And its catalytic activity was evaluated and compared with the reference catalyst prepared by the common impregnation method. XRD and H₂-TPR were used to analyze its microstructure.

2. Experimental

2.1. Preparation of Ni/SiO₂ catalyst

Ni/SiO₂ catalyst was prepared by the modified incipient impregnation method and noted as Ni/SiO₂-N with Ni loading of 10 wt.%. An aqueous solution containing the desired amounts of Ni(NO₃)₂·6H₂O and NH₄NO₃ (the molar ratio of NH₄NO₃/Ni = 1) was added to the support and then dried slowly in a rotary evaporator under vacuum at 80°C for 2 h followed by drying at 120°C in an oven overnight and calcining in air at 550°C for 3 h. Then, the calcined catalyst was crushed and sieved to 40-60 mesh size for catalytic tests. And the common impregnation method without NH₄NO₃ was also used to prepare the reference catalyst noted as Ni/SiO₂.

2.2. Evaluation of catalyst

The DRM reaction was performed in a fixed bed reactor with i.d. of 9 mm at atmospheric pressure. 0.2 g of catalyst (40-60 mesh) was placed at the center of the reactor. Before the reaction, the catalyst was reduced at 750 °C for 2 h by pure H₂ with the flow rate of 60 mL/min. Then the temperature was raised to 800°C and a flow of gas mixture with CH₄/CO₂/N₂ molar ratio of 9/9/2 was fed into the reactor at a flow rate of 160 mL·min⁻¹. Gaseous products were analyzed online by gas chromatography (Agilent GC 7820A with a TCD detector and a Porapak Q column and a 5A molecular sieve column). The conversions of CH₄ and CO₂ were calculated with the following formulas:

$$X_{CH_4} = (F_{CH_4-in} - F_{CH_4-out}) / F_{CH_4-in} \times 100\%$$

$$X_{CO_2} = (F_{CO_2-in} - F_{CO_2-out}) / F_{CO_2-in} \times 100\%$$

where X and F were conversion and gas flow rate of *i* in the feed or the effluent, respectively.

2.3. Characterization of catalyst

The powder X-ray diffraction (XRD) patterns of reduced and spent catalysts were recorded on a Bruker AXS D8 Advance diffractometer using Cu Kα radiation (λ=1.5406 Å) over a 2θ range of 5-90° at a scanning rate of 6 °/min. H₂ temperature programmed reduction (H₂-TPR) experiments of catalysts were conducted in an auto-controlled flow reactor system (TP-5076, Tianjin Xianquan Instrument, Co., Ltd., China) equipped with a thermal conductivity detector (TCD). 50 mg of catalyst sample was charged in a quartz-tube reactor and pretreated in a N₂ stream at 473 K for 1 h and then cooled down to 303 K. After that, the sample was heated to 950 °C in a 30 mL/min flow of 5%H₂/N₂ at a rate of 10 °C/min to obtain the H₂-TPR pattern.

3. Results and discussion

3.1. Evaluation results

Figure 1 shows the catalytic performances of Ni/SiO₂-N and Ni/SiO₂ catalysts in DRM reaction at 800 °C with GHSV of 48 L·gcat.⁻¹·h⁻¹ and CH₄/CO₂/N₂=9/9/2. It can be seen clearly that, the CH₄ and CO₂ conversions over Ni/SiO₂ catalyst drop from 78% and 85% to 53% and 67% during 10 hours. In contrast, Ni/SiO₂-N catalyst displays a relatively stable catalytic performance over the whole reaction period. The CH₄ and CO₂ conversions are 80% and 86% at the first hour, and slightly decrease to 70 and 81% after 10 hours. Moreover, CO₂ conversion is higher than CH₄ conversion for

both catalysts, which is caused by the reverse water gas shift (RWGS) reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$) [14-16]. It is worth noting that the gap between CH_4 conversion and CO_2 conversion over Ni/SiO_2 catalyst increases from 7% to 14%, and it increases from 6% to 11% over $\text{Ni}/\text{SiO}_2\text{-N}$ catalyst. The increase in gap indicates the increase in RWGS reaction.

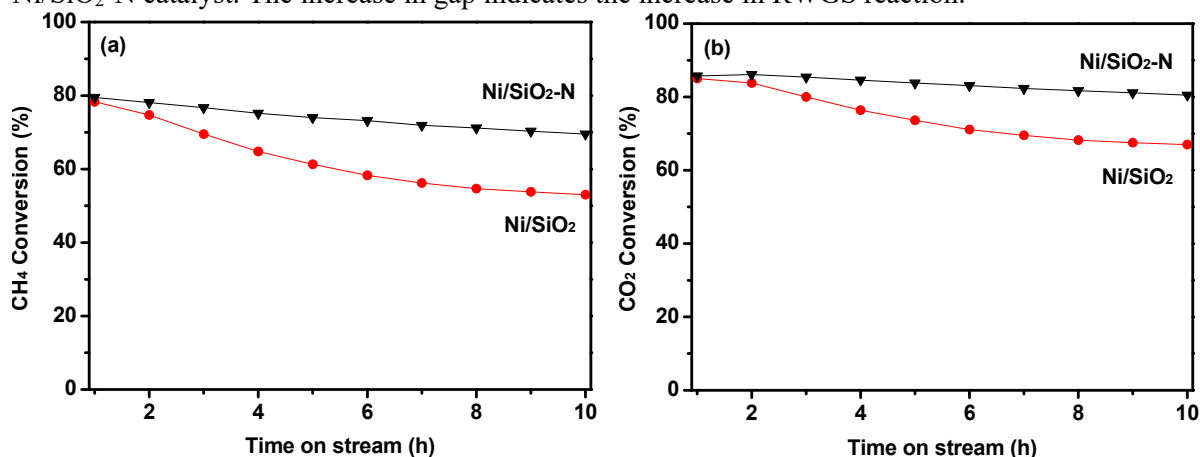


Figure 1. Catalytic performance of different catalysts: (a) CH_4 Conversion; (b) CO_2 Conversion.

3.2. Characterization of catalyst

Figure 2 shows the XRD patterns of different samples. It can be seen clearly from Figure 2(a) that there are five visible peaks at 2θ values of 37.3° , 43.3° , 62.9° , 75.4° and 79.4° , corresponding to the metal oxide of NiO (JCPDS 22-1189). And after reduction, there are three peaks at 44.6° , 51.9° and 76.8° , corresponding to metallic Ni (JCPDS 1-1260). It can be seen clearly that the Ni and NiO peaks of Ni/SiO_2 catalyst are more sharper than that of $\text{Ni}/\text{SiO}_2\text{-N}$ catalyst, indicating the better crystallinity and the larger particles. It is generally believed that small Ni particles and stronger metal-support interaction are benefit to the catalytic activity and stability [17-19], which agree well with our experimental results.

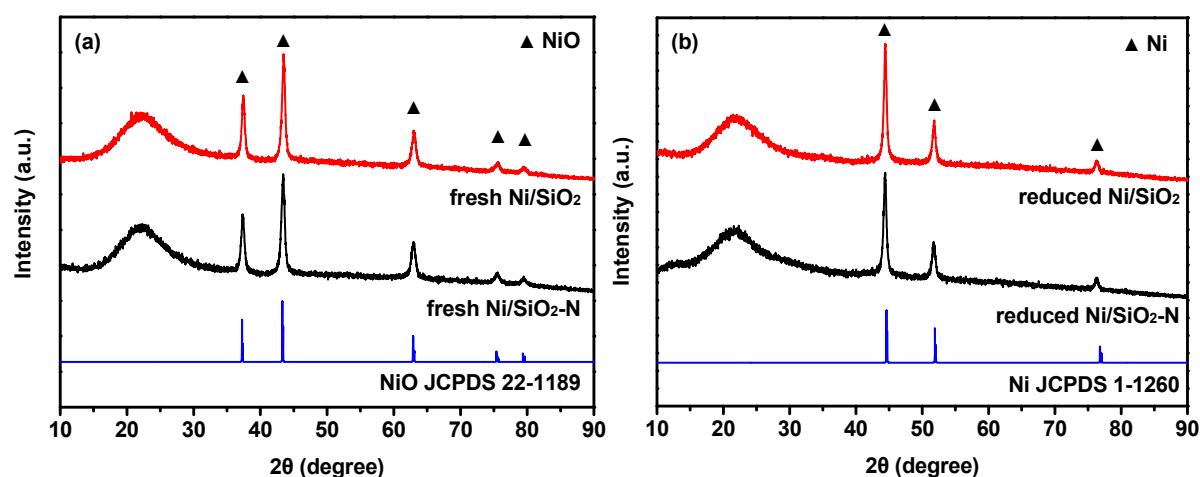


Figure 2. XRD patterns of different samples: (a) fresh catalysts; (b) reduced catalysts.

Figure 3 exhibits the reduction behavior of the fresh catalysts to clarify the interaction between Ni and support. The Ni/SiO_2 catalyst shows a sharp reduction peak at 390°C , and two shoulder peaks at 350°C and 480°C , respectively. Generally, the peaks at the low temperature zone ($400 \sim 500^\circ\text{C}$) are assigned to the reduction of NiO species which have weak interaction with support, while the peaks in the intermediate temperature zone ($500 \sim 600^\circ\text{C}$) are assigned to the reduction of NiO species having medium strength interaction with support. The peaks in the high temperature zone ($> 600^\circ\text{C}$) are

attributed to the reduction of NiO species with strong chemical interaction with support[20, 21]. Obviously, the interaction between Ni and SiO₂ support is weak, there is no chemical interaction between Ni and SiO₂. However, the peak at 350°C over Ni/SiO₂-N catalyst is smaller than that of Ni/SiO₂ catalyst, indicating the stronger metal-support interaction of Ni/SiO₂-N catalyst. The increased metal-support interaction can effectively inhibit the sintering and agglomeration of Ni particles, bring in the better catalytic stability.

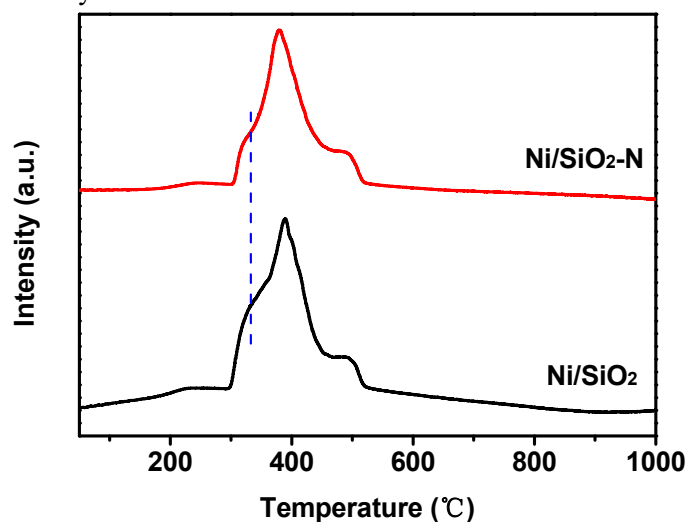


Figure 3. H₂-TPR patterns of different catalysts.

4. Conclusions

The Ni/SiO₂-N catalyst was prepared by a modified impregnation method with the addition of NH₄NO₃, and the prepared catalyst was possessed with smaller Ni particles and stronger metal-support interaction, leading to the better catalytic performance in DRM. According to the XRD and H₂-TPR results, it can be deduced that the decomposition of NH₄NO₃ during the catalyst preparation process (calcination process) may release some heat in a very short time, leading to the formation of smaller Ni particles and stronger metal-support interaction.

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