Methane dry reforming over Ni/CNFs-SiC monolithic catalyst

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Abstract: A SiC foam monolith decorated with a carbon nanofibers (CNFs) layer was employed as the catalyst support for Ni-based catalyst preparation, used for the CO_2 dry reforming of methane (DRM) reaction. The CNFs decorated SiC composite support provided more anchorage sites for improving the dispersion of the Ni particles and enhanced the metal-support interaction compared to the pristine SiC support. The Ni/CNFs-SiC catalyst exhibited high activity and remarkable stability during DRM reaction. The XRD analysis verified that almost no sintering of nickel particle was detected over the spent Ni/CNFs-SiC catalyst after 100 h TOS DRM reaction at 750 ℃.

Keywords: Methane dry reforming, Carbon nanofibers, Ni/CNFs-SiC catalyst.

1. Introduction

The reduction and transformation of greenhouse gases such as methane and carbon dioxide to other value-added chemicals have received great interest in recent years [1]. Catalytic dry reforming of methane (DRM, $CO_2+CH_4 \rightarrow 2CO+2H_2$) is an efficient route for the conversion of both greenhouse gases into syngas (H_2 and CO) [2]. Recently, the silicon carbide (SiC) with foam structure has been studied as a catalyst support material for methane reforming reaction [3, 4]. The SiC exhibits high thermal conductivity, high mechanical strength, high mass transfer and extreme chemical inertness to acid and base. In this report, CNFs layer decorated SiC foam was prepared through a catalytic chemical vapor deposition (CVD) method, and the obtained CNFs-SiC composite was employed as Ni-based catalyst support for the DRM reaction catalyst preparation.

2. Experimental

A SiC foam (1 pore per mm, D 20 nm × L 20 mm) with a 3D structure (Fig. 1a inset) was purchased from the Institute of Metal Research, Chinese Academy of Sciences. A CNFs layer was coated on the surface of the pristine SiC foam by a catalytic CVD method. The obtained CNFs-SiC support was impregnated with a solution of $Ni(NO_3)_2 \cdot 6H_2O$ through a conventional impregnation method. The final catalyst, denoted as Ni/CNFs-SiC, had 8 wt. % Ni loading amount. In order to compare the catalytic performance of Ni/CNFs-SiC catalyst, other two reference catalysts, denoted as Ni/SiC (without CNFs on SiC foam) and Ni/CNFs (only with CNFs as support), were also prepared by impregnation method.

The DRM reaction was carried out in a fixed-bed quartz reactor (24 mm i.d.) at 750 ℃ and atmospheric pressure for 100 h. The reactant feed molar ratio of $CH_4/CO_2/Ar$ was 45/45/10 and the space velocity (*W*/*F*) was 6.4 g h/mol.

3. Results and discussion

The surface morphologies of the prepared CNFs-SiC composite support was shown in Figure 1a. One CNFs layer with a thickness of about 4 μm closely covers the SiC surface. After being decorated with CNFs, the specific surface area of SiC increased from 4 m^2/g to 24 m^2/g, and the pore volume was also enhanced more than 10 times (BET method). After the DRM reaction at 750 ℃ for 100 h, the nickel particles over

Ni/SiC-S were closely covered by the deposited graphitic carbon species, however, filamentous carbon were observed over Ni/CNFs-SiC-S catalyst, which is known to be less harmful to the catalytic activity.

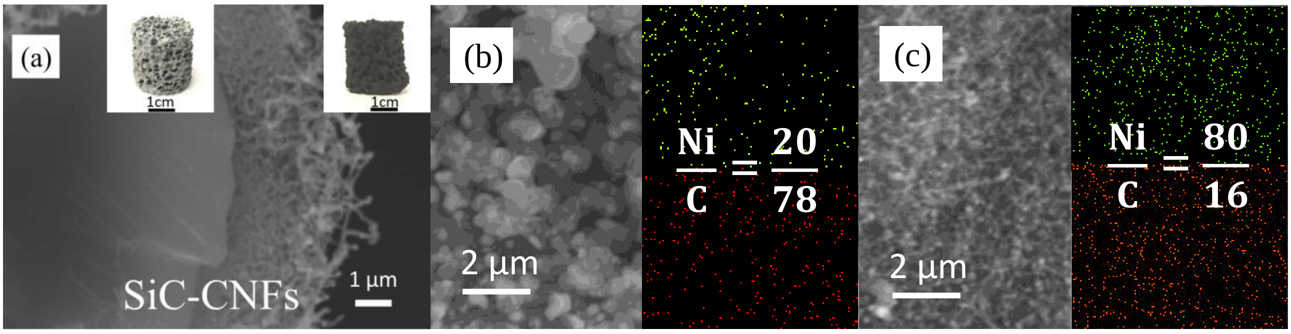

Figure 1. The SEM micrographs of (a) CNFs-SiC support, (b) spent Ni/SiC-S catalyst, (c) spent Ni/CNFs-SiC-S catalyst, and the corresponding elemental mapping of Ni, C elements and the molar ratio of Ni/C.

The performance of the catalysts for the DRM reaction was shown in Figure 2. Compared with other catalysts such as Ni/SiC and Ni/CNFs, the Ni/CNFs-SiC catalyst exhibited not only the highest activity but also remarkable stability during DRM reaction. All the H_2/CO ratios were less than 1.0 owing to the combination of reverse water-gas shift reaction and reverse Boudouard reaction.

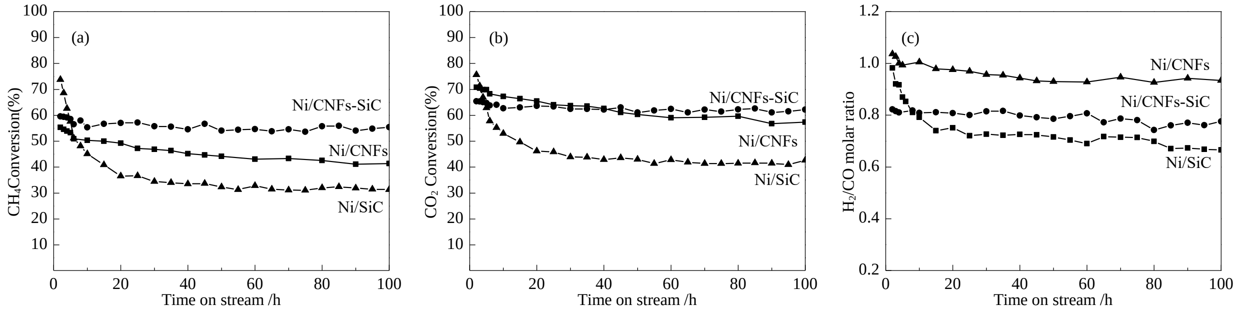

Figure 2. Catalytic performance test of catalysts for DRM reaction: (a) CH_4 conversion, (b) CO_2 conversion and (c) the ratio of H_2/CO in syngas. Reaction conditions: 750 ℃, 0.1MPa, $CH_4/CO_2/Ar$ = 45/45/10, W/F = 6.4 g h/mol.

After 100h of TOS reaction, the average crystallite size of the Ni particles over Ni/SiC sample increased from 43 nm to 54 nm of Ni/SiC-S (see Table 1). However, the Ni particle sizes over Ni/CNFs-SiC and Ni/CNFs fresh samples were much small and almost unchanged after reaction. It demonstrated that the sintering of Ni particles was inhibited to some extent due to the strong metal-support interaction between Ni and the CNFs or CNFs-SiC supports.

Table 1. The Ni particle size of catalyst samples before and after 100 h DRM reaction.

Sample	Ni/SiC(nm)	Ni/CNFs-SiC(nm)	Ni/CNFs(nm)
Fresh	43	37	28
Spent	54	38	30

Estimated by Scherrer formula at 2θ of 44.5 °.

4. Conclusions

In this study, a SiC foam monolith decorated with a layer of CNFs has been successfully designed and used as the support for Ni catalyst preparation. The Ni particles were highly dispersed and attached strongly to the CNFs-SiC support. The concept of CNFs-SiC composite as Ni-based catalyst support was for the first time designed, prepared and employed for DRM reaction, realizing excellent ability on inhibiting the sintering of Ni particles as well as promoting catalyst performance.

References

1. R. Singha, A. Yadav, A. Agrawal, A. Shukla, S. Adak, T. Sasaki, R. Bal, Appl Catal B Environ 191(2016) 165.
2. N. Wang, W. Chu, T. Zhang, X. Zhao. Int J Hydrogen Energy 37 (2012) 19.
3. Q. Ma, J. Sun, X. Gao, J. Zhang, T. Zhao, Y. Yoneyama, N. Tsubaki, Catal Sci Technol 6 (2016) 6542.
4. X. Gao, G. Liu, Q. Wei, G. Yang, M. Masaki, X. Peng, R. Yang, N. Tsubaki, Int J Hydrogen Energy 26 (2017) 16547.