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Catalytic Performance of Monolithic Foam Ni/SiC Catalyst in Carbon dioxide Reforming of Methane to Synthesis Gas

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Abstract Carbon dioxide reforming of methane to synthesis gas has been investigated with Ni catalysts supported on monolithic foam SiC, which were prepared by the initial wetness impregnation method. The catalyst of 7 wt%Ni/SiC was verified to be the best one in different Ni content catalysts. Compared with other catalysts such as 7 wt%Ni/SiO_2 and 7 wt%Ni/Al_2O_3, the 7 wt%Ni/SiC catalyst exhibited not only the highest activity but also remarkable stability and excellent coke resistance during 100 h reaction. Furthermore, the conversion of CO_2 and CH_4 remained at about 96% and 94%, respectively in 100 h reaction time. The structure and properties of the catalysts were characterized by BET, XRD, H_2-TPR, XPS and TEM techniques.

Keywords Monolithic foam catalysts · Ni/SiC · CO_2 methane reforming · Synthesis gas · Stability

1 Introduction

CO_2 reforming of methane to synthesis gas is a topic of considerable interest for CO_2 utilization and natural gas conversion due to its important advantages compared with steam reforming of methane. Firstly, this reaction produces hydrogen and carbon monoxide with a desired ratio of H_2/CO close to unity [1]. Moreover, the greenhouse gases, methane and CO_2 will be converted into a valuable feedstock, which has important environmental implication.

One of the obstacles encountered in the application of this process is rapid deactivation of the catalyst due to carbon deposition and/or sintering of metal [2]. A variety of catalysts have been developed for this reaction. Using of noble metal catalysts, such as iridium and rhodium [3] and platinum [4, 5], seems to be less sensitive to coking than the nickel-based catalysts. However, due to limited availability and high cost of noble metals, it is more practical to develop a stable anti-carbon nickel-based catalyst. In order to get a stable nickel-based catalyst, addition of alkaline and/or rare earth oxides to Ni catalysts was shown to improve the anti-carbon property of nickel catalyst [6], which suggests a possibility of improving the catalyst performance by choosing the proper catalyst support and controlling of the nickel-support interaction. Some researchers have greatly enhanced the catalytic activity and stability of Ni catalysts by using different supports [7–12]. The effects of supports on the coke formation and stability of Ni-based catalysts were also extensively investigated [13–15].

Recently, monolithic foam catalyst support has been researched [16, 17]. The crystallized silicon carbide (SiC) exhibits a high thermal conductivity, a high resistance towards oxidation, and chemical inertness, which are necessary for a good heterogeneous catalyst support. Moreover the SiC in a foam monolith structure provides a low-pressure drop [18] and the open structure can prevent blockage of pores by deposition of carbonaceous species. So far SiC-based monolith catalysts have been employed in several catalytic reactions [19–21]. Hence, it would be expected that the monolith foam SiC show good resistance to coking

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during the reaction of CO_2 reforming of methane to synthesis gas. Considering the above, we first reported the monolith foam Ni/SiC catalyst which showed high catalytic performance in this reaction [22]. Herein, this article is devoted to investigating the reducibility and catalytic activities of the monolithic foam Ni/SiC catalyst in detail.

2 Experimental

2.1 Catalyst Preparation

SiC in a monolithic foams form (diameter 9 mm, length 20 mm), provided by Institute of Metal Research Chinese Academy of Sciences, and was used as support for the catalyst. The Ni/SiC catalysts were prepared by impregnating SiC with an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$, followed by drying at 120 °C for 12 h and calcining at 650 °C for 3 h. For comparison, 7.0 wt%Ni/SiO_2 (30–60 mesh) and 7.0 wt%Ni/Al_2O_3 (30–60 mesh) catalysts were also prepared by the same method.

2.2 Activity Measurement

Catalytic reactions were carried out in a vertical fixed-bed flow reactor made of tubular quartz reactor (ID = 10 mm). Before the reaction, the 1.2 mL catalyst was reduced with H_2 (20 mL/min) at increasing temperature from ambient to 700 °C at a rate of 10 °C/min and the final temperature was held for 1 h and then lowered to the 200 °C. CH_4 and CO_2 controlled by a mass flow controller were introduced into the reactor, with a molar ratio of CH_4:CO_2 = 1:1. The effluents were cooled in an ice–water trap and analyzed online with a gas chromatograph (PE, Autosystem XL) equipped with a packed column (TDX-01) and a thermal conductivity detector (TCD).

2.3 Catalyst Characterization

The porous properties such as surface area, average pore diameter and pore volume were determined using an ASAP 2010 analyzer at liquid nitrogen temperature. Powder X-ray diffraction (XRD) patterns were recorded on a PHILIPS X'Pert PRO powder diffractometer using a Cu Kα radiation (40 kV, 30 mA).

Temperature-programmed reduction (TPR) was carried out by heating the samples (50 mg) from 40 °C to 900 °C at rate of 10 °C min^{-1} in a 10% H_2/Ar gas flow (30 mL min^{-1}). Before the TPR experiment, the catalyst was pretreated at 300 °C for 60 min in Ar atmosphere to remove the absorbed gases.

X-ray photoelectron spectroscopic (XPS) measurements were performed on a Perkin–Elmer PHI-5702 system equipped with a hemispherical analyzer. Mg–Kα radiation was used as the excitation source for the XPS analysis. Binding energies were corrected for charging as reference to the contaminant carbon (C1s binding energy = 284.6 eV).

Transmission electron microscope (TEM) was carried out on a HITACHI H600 with a tension voltage of 100 kV.

3 Results and Discussion

3.1 Catalytic Performance

Table 1 presents the effect of Ni content on catalytic activity at 750 °C. A series of Ni/SiC catalysts with Ni loading 1,3,5,7, and 9 wt% were tested. It is found that the catalytic activity increased with the Ni loading increasing from 1 wt% to 7wt%. For 7 wt%Ni/SiC, the conversion of CO_2 and CH_4 reached at 84.5% and 81.9%, respectively. However, when Ni loading was increased to more than 7wt%, the catalytic activity decreased, which suggested that an excess amount of Ni led to lower Ni dispersion and large Ni ensemble size, making the catalysts lose their active surface area. This conclusion was supported by XRD datum (Fig. 3).

The effect of temperature on the catalytic activity of the 7 wt%Ni/SiC, 7 wt%Ni/SiO_2 and 7 wt%Ni/Al_2O_3 are shown in Fig. 1. It can be seen that the conversion of CO_2 and CH_4 rapidly increased with increasing of temperature in 7 wt%Ni/SiC and 7 wt%Ni/SiO_2 catalysts. Furthermore, the conversion of CO_2 and CH_4 were higher on 7 wt%Ni/SiC catalyst than that on 7 wt%Ni/SiO_2 catalyst. R. Takahashi found that the 9 wt%Ni/SiO_2 catalyst, prepared by the incipient wetness impregnation method, was deactivated very quickly at 700 °C during 12 h [23]. In our experiments some degree of deactivation were also found in 7 wt%Ni/SiO_2 catalyst. The obvious phenomenon was the pressure of system increasing with the reaction time. For the 7 wt%Ni/Al_2O_3 catalyst, which showed a lowest catalytic performance in the same reaction temperature, the

Table 1 Effect of Ni content on the catalytic activity of Ni /SiC (CH_4:CO_2 = 1:1, GHSV = 6,000 mLg (cat)$^{-1}$ h^{-1}, 750 °C)

Catalyst	Conversion, CO_2,%	Conversion, CH_4, %
1 wt%Ni/SiC	80.3	69.0
3 wt%Ni/SiC	81.3	74.7
5 wt%Ni/SiC	83.1	78.1
7 wt%Ni/SiC	84.5	81.9
9 wt%Ni/SiC	79.8	78.0

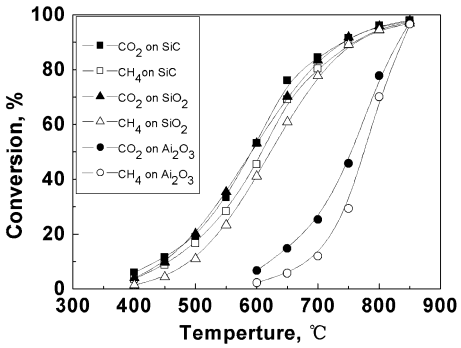

Fig. 1 Compare of 7 wt%Ni/SiC with other catalyst in the effect of temperature on the catalytic activity (CH_4:CO_2 = 1:1, GHSV = 6,000 mLg (cat)$^{-1}$ h^{-1})

reaction started at a higher temperature. Therefore, the monolithic foam 7wt%Ni/SiC catalyst was the highest active catalyst in all tested samples. It should be noted that the conversion of carbon dioxide was always higher than that of methane, especially for 7 wt%Ni/Al_2O_3 catalyst, which strongly suggested that the reverse water gas shift (RWGS) reaction occurred simultaneously [13]. But in the case of 7 wt%Ni/SiC catalyst the conversion of carbon dioxide and methane were very closer, which indicated that RWGS was the smallest in this sample.

3.2 Stability Test

The stability of the monolithic foam 7 wt%Ni/SiC catalyst was tested at 800 °C. As shown in Fig. 2, the catalyst exhibited excellent catalytic activity and stability, and provided over 96.0% and 94.0% conversion of carbon dioxide and methane, respectively. The ratio of H_2/CO closing to one remained almost unchanged for 100 h of time on stream. Meanwhile, the catalyst did keep its original shape without any shattering after 100 h of continuous reaction.

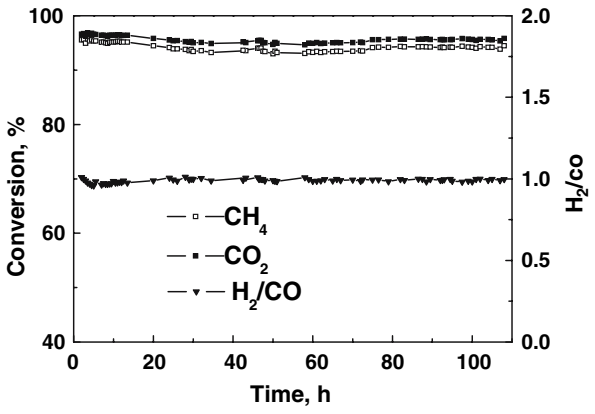

Fig. 2 Change of the catalytic activity of 7 wt%Ni/SiC for CO_2 reforming of methane with reaction time. (CH_4:CO_2 = 1:1, GHSV = 6,000 mLg(cat)$^{-1}$ h^{-1} and T = 800 °C)

3.3 Catalysts Characterization

The BET surface area, the average pore size and pore volume were given in Table 2. It was found that the surface of monolithic foam SiC support was 8.1 m^2 g^{-1}, and it decreased to 4.4 m^2 g^{-1} when 7% Ni was loaded, while the pore size changed from 14.1 nm to 13.5 nm.

XRD patterns of fresh, reduced and used Ni/SiC samples with different Ni content were presented in Fig. 3. The result showed that for monolithic foam support, the strong diffraction peaks at 2θ = 35.6°, 60.0°, and 71.7°, were attributed to a typical cubic and hexagonal structure of SiC. A few of diffraction lines assigned to Si (2θ = 28.4°, 47.3°, and 76.4°) and SiO_2 (2θ = 20.8°, 26.6°, 65.6°, and 73.3°) were also detected. For fresh Ni/SiC catalysts the existence of the diffraction lines of NiO at 2θ = 37.3° and 43.3° were observed. The peaks of NiO became sharper with increasing the Ni content; meaning the bigger NiO particles were formed in higher Ni content simple. When 7 wt%Ni/SiC catalyst was reduced by hydrogen, NiO was decomposed into microcrystalline of nickel particles. Hence, the diffraction lines of NiO disappeared. The peak broadness of nickel (2θ = 44.5° and 51.8°) indicated that the nickel particles were small on the surface of support. Noticeably, no new phase about Ni was detected due to the chemical

Table 2 Surface areas, average pore size and pore volume from N_2 adsorption/desorption

Catalyst	Surface area, m^2/g(BET)	Volume, cm^3/g(BJH)	Pore size, nm (BJH)
SiC	8.1	0.024	14.1
7 wt%Ni/SiC	4.4	0.017	13.5

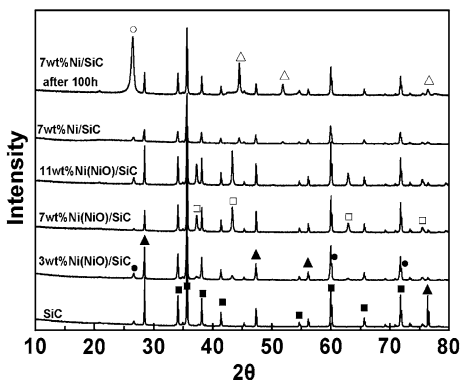

Fig. 3 XRD patterns of support SiC and the Ni/SiC catalysts (■SiC; ▲Si; ●SiO_2; △Ni; □NiO; ○C)

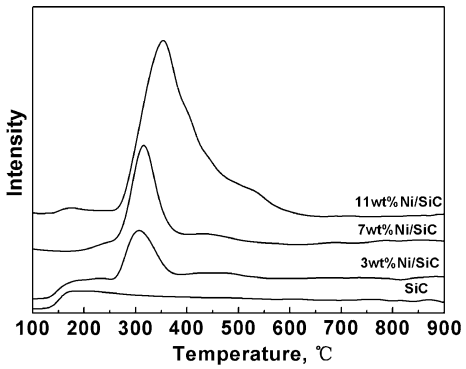

Fig. 4 TPR profiles of catalysts

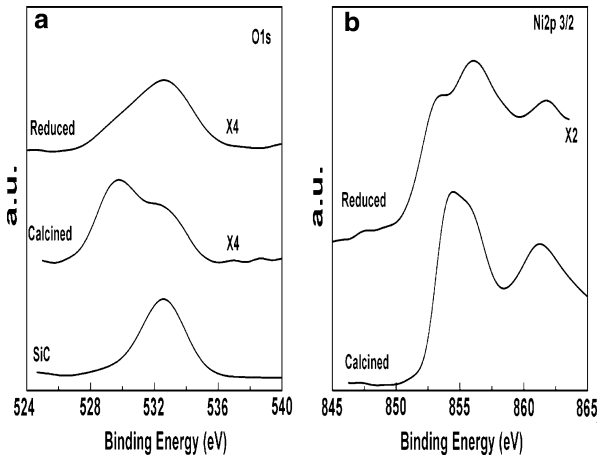

Fig. 5 XPS spectra of the catalysts

inertness of SiC. These results suggested that the nickel was dispersed on the surface of catalyst in the form of elemental state, so nickel oxide could be reduced at low temperature, which was proved by TPR measurements (Fig. 4). For used 7 wt%Ni/SiC catalyst (for 100 h) the diffraction line of coked C was observed at $2\theta = 26.5°$ and the diffraction lines of Ni became stronger than those of the reduced catalyst, indicating that the nickel sintering was happened during the long reaction time. However, its catalytic performance did not show an obvious deactivation (Fig. 2).

The H_2-TPR profiles of all samples are illustrated in Fig. 4. The results showed that all catalysts displayed almost the same reduction profiles in shape. A starting reduction temperature at about 270 °C was found for all samples. The peak became larger with increasing Ni content, and a proportional relation was observed between the absolute peak area and nickel content within the experimental error. In all samples most of nickel oxide was reduced below 500 °C. It has been reported [24] that the nickel oxide powders showed a single reduction peak at 300–400 °C. In [25] Brynmor Mile reported that there were two kinds of the reducible nickel oxide on SiO_2 support. One resembling bulk NiO located mainly in the small pores (<9 nm) has negligible interaction with the silica and easily to be reduced at low temperature. The other located in larger pores (15–30 nm) need higher temperature to be reduced (above 500 °C). For the SiC support, even with a larger pores (13.5 nm from Table 1), the NiO could be reduced at a low temperature. So the peaks could be assigned to the relatively free NiO weakly interacted with the SiC support.

The XPS technique was adopted to analyze the chemical state of the elements. The spectrums of the fresh and reduced 7 wt%Ni/SiC catalysts were displayed in Fig. 5. For SiC support (Fig. 5a), it is only found O^{-2} of SiO_2 at 532.6 eV. For calcined catalyst there were two components centered at 532.6 and 529.8 eV. The former could be ascribed to elemental O_{1s} in SiO_2, and the latter to NiO. The signal of O_{1s} in NiO became attenuated obviously after being reduced.

The signal of $Ni_{2p3/2}$ was shown in Fig. 5b. It was found that the electronic state was different between the reduced and the calcined catalysts. The change of the position of the $Ni_{2p3/2}$ peak indicated most of the nickel had been reduced to metallic form. In the calcined sample the $Ni_{2p3/2}$ peak was centered at 854.6 eV, which could be identified as Ni^{2+}. After being reduced by H_2, Ni^0 was detected at 852.8 eV. The Ni^{2+} peak at 854.6 eV was still predominant for reduced sample, but the intense of the peaks became weak due to the decrease of Ni^{2+} by reduction.

In most case an important reason for catalytic activity decreasing was the formation of carbonaceous deposits on the surface of catalysts. The carbon deposition during the reforming of methane was suggested to be due to either methane decomposition (1) or carbon monoxide disproportionation (2) [14, 23, 26]:

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H = 75\text{KJ/mol} \tag{1}$$

$$2CO \rightarrow C + CO_2 \quad \Delta H = -171\text{KJ/mol} \tag{2}$$

The deposition of carbon could occur on Ni particles in the various forms such as adsorbed atomic carbon, amorphous carbon and whiskers. For our Ni/SiC catalyst two kinds of carbon: tubular whisker and graphite carbon were found (Fig. 6), and the latter was the main type of coke. The difference in the structure of carbon growing on the surface of the catalyst would be attributed to the difference in particle size of Ni metal. On the small Ni particles deposited carbon forms a layered structure. In contrast, carbon can grow on the large Ni particles to be long fiber. J.H. Kim [26] found that the average particle size of no less than 7 nm would be required in order to form tubular whisker carbon. In our catalyst the nickel sintering existed after long reaction time (proved by XRD).

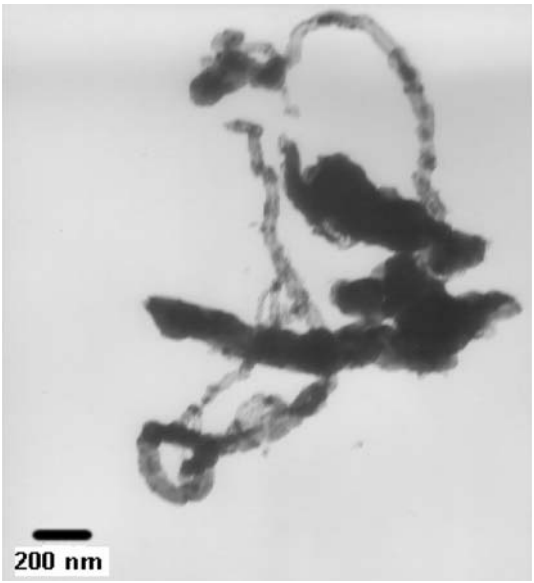

Fig. 6 TEM photograph of coked carbon

The Ni particles should become big enough to form tubular whisker carbon. According to literatures [27–29], the Ni particles at the tip of carbon filaments are still accessible to reactants, so whisker carbon has been found not to affect the catalytic activity of the catalyst. But it is necessary to avoid the formation of whisker carbon because Ni-based catalysts tend to form unreactive carbon residues which block active sites and catalyst pores, and ultimately lead to the formation of carbon filaments and to the elution of Ni crystallites from catalyst pellets and reactors [30, 31].

4 Conclusion

In this work, carbon dioxide reforming of methane to synthesis gas has been investigated with Ni-supported monolithic foam SiC catalyst. It was found that 7 wt%Ni/SiC catalyst provided the highest catalytic activity and stability in all tested catalysts for this reaction. During 100 h time on stream, the conversion of CO_2 and CH_4 remained at about 96% and 94%, respectively, while no obvious deactivation was observed. XRD results indicated that active metal Ni and SiC monolithic foam support did not form new compound and phase in Ni/SiC catalysts. The TPR and XPS results showed that Ni was dispersed on SiC support in small particles, and there was a weakly interaction between active metal and support. The coked carbon was detected in the form of tubular whisker and graphite by TEM images. In conclusion, 7 wt%Ni/SiC is a very promising catalyst to be further investigated in carbon dioxide reforming of methane to synthesis gas in the future work.

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