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Article

Effects of the oxidation extent of the SiC surface on the performance of Ni/SiC methanation catalysts

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ABSTRACT

Ni/SiC methanation catalysts were prepared by an incipient wetness impregnation method. Effects of the oxidation extent of the SiC surface on low-temperature activity and high-temperature stability of the catalysts were investigated. Samples were characterized by thermogravimetry and differential scanning calorimetry, N₂ adsorption-desorption, Fourier transform infrared spectra, temperature-programmed desorption of NH₃, X-ray diffraction, temperature-programmed reduction of H₂ and H₂ chemisorption. The surface area and nickel dispersion of the catalysts decreased with increasing oxidation temperature of the SiC supports, while both reducibility and stability of the catalysts increased. The Ni/SiC catalyst with the unoxidized SiC support showed the poorest high-temperature stability probably because of the weak anchorage of Ni particles to the support. The Ni/SiC samples prepared on the SiC supports oxidized at 500 and 700 °C had better low-temperature activity and high-temperature stability, which was because Ni particles were well dispersed on and strongly anchored to these properly oxidized supports. The Ni/SiC catalyst with the SiC support oxidized at 900 °C showed the worst low-temperature activity because of the larger Ni particles caused by the less active oxide layer due to the overoxidation of the support.

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1. Introduction

In recent years, production of synthetic natural gas (SNG) from coal has attracted wide attention as a result of the increasing demand for natural gas, the desire to enhance domestic energy security, the opportunity to alleviate environmental pollution, and the higher energetic conversion efficiency [1–3]. The main steps in SNG production are usually: coal gasification, crude gas conditioning, syngas cleaning, and methanation. High-performance methanation catalysts are crucial. Syngas methanation is extremely exothermic, and steam is generally added to the reaction system to lower the temperature rise and to inhibit carbon formation; this added steam means that the

catalyst must be highly active and stable.

Ni-based catalysts are the most widely used for the methanation reaction, in both academic study and industrial applications because of their high activity, relatively low cost, and better selectivity than other metals for methane production [4]. Supports have significant effects on the performance of Ni-based methanation catalysts, and the effects of supports have been studied in depth [5–13]. However, the reported methanation catalysts mostly use poorly thermally conductive oxides as supports; with these supports, a large amount of heat produced by the reaction can rapidly accumulate in some local bed zones, generating hot spots. The hot spots can easily cause catalyst sintering, and in some cases even carbon formation via

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methane cracking. One effective solution to the above problems is to employ highly thermally conductive and thermally stable materials as supports of methanation catalysts, to lower heat accumulation and hot spot temperatures.

SiC has many excellent properties such as high heat conductivity, thermal stability, mechanical strength, and chemical inertness, which make it a very suitable support in demanding conditions, such as high temperatures, highly endothermic or exothermic reactions, and strong acidic or basic solutions [14]. SiC supports have been used for catalysts for many different reactions, e.g., reforming [15–18], automotive exhaust treatment [19,20], catalytic combustion and oxidation [21–25], PEMFC electrooxidation [26,27], methanation [28–30], Fischer-Tropsch synthesis [31,32], oxidative coupling [33], isomerization [34], and dehydrogenation [35,36]. However, metal nanoparticles directly deposited onto SiC are prone to aggregate or sinter because the SiC surface has low reactivity, making the metal-SiC interaction quite weak. Modification of the SiC surface could enhance the interaction between the applied metals and SiC, thereby improving the catalyst stability. Vannice et al. [28] reported that Pt and Ni particles supported on oxidized SiC (air, 700 °C) had better stability than those on the unoxidized SiC. Nguyen et al. [14] pointed out that a $\text{SiO}_2\text{-SiO}_x\text{C}_y$ layer on the SiC surface played the role of a natural washcoat and stabilized the metal particles. Florea et al. [37] also revealed the significant role of SiC surface oxides in anchoring and dispersing the active phase. Nevertheless, the effects of the oxidation extent of the SiC surface on the catalyst performance have not been systematically examined in detail. In this work, Ni-based methanation catalysts were prepared by an incipient wetness impregnation method on SiC supports oxidized at different temperatures, and the correlation between the extent of oxidation of the SiC surface and the catalyst performance was investigated.

2. Experimental

2.1. Catalyst preparation

SiC supports were synthesized by the reaction of metallic silicon with carbon [14]. Stoichiometric amounts of silicon powder (99.9% purity, Shanghai CNPC Powder Material Co., Ltd) and active carbon powder (CP, Kermel Reagents) were mixed and kneaded together with hydroxypropyl methylcellulose, tung oil, and deionized water in a kneader (HyN1L, Rugao Huayu Machine Factory). The mixture was extruded into small sticks ($\varnothing 3$ mm) in a twin screw extruder machine (F-26III, SCUT Machine Factory), dried overnight at 110 °C, and then calcined in flowing argon at 1400 °C for 2 h to form self-bonded SiC sticks. The SiC sticks obtained were crushed, and the 40–60 mesh sized granules were screened to be used as the support, denoted S. S was then oxidized in air at 500, 700, or 900 °C for 4 h, to give supports denoted S-500, S-700, and S-900, respectively. The four SiC supports were impregnated with 1 mol/L $\text{Ni}(\text{NO}_3)_2$ aqueous solution, dried at 110 °C for 4 h, and calcined at 500 °C for 2 h. The obtained catalysts were denoted NS, NS-500, NS-700, and NS-900; all the catalysts had a 9 wt% NiO

nominal loading.

2.2. Catalyst characterization

Thermogravimetry and differential scanning calorimetry (TG-DSC) analysis was conducted under air flow from room temperature to 1000 °C at a heating rate of 10 °C/min on a NETZSCH STA 449 F3 thermoanalyzer.

The specific surface areas and pore structures were measured by N_2 adsorption-desorption at liquid nitrogen temperature on a Quantachrome NOVA2200e analyzer. Prior to analysis, the samples were degassed under dynamic vacuum at 300 °C for 2 h. The specific surface area (A_{BET}) was calculated using the multi-point BET method. The accumulated volume of adsorbed N_2 at $p/p_0 = 0.97$ was designated as the total pore volume (V_p). The average pore size (D_p) was calculated from the equation: $D_p = 4V_p/A_{\text{BET}}$.

Fourier transform infrared (FT-IR) spectra were recorded using a Thermo Scientific Nicolet 6700 spectrometer. Typically, 32 scans were collected at 4 cm^{-1} spectral resolution in the range of 4000–650 cm^{-1} . The sample powder was mixed with KBr powder at a fixed mass ratio, pressed, and placed in the center of the IR cell. The spectra were recorded in air.

Temperature-programmed desorption of NH_3 (NH_3 -TPD) profiles were obtained on a Quantachrome ChemBET Pulsar automated chemisorption analyzer. The sample was first flushed with He at 300 °C for 0.5 h to desorb surface impurities. After cooling to room temperature, 0.5% NH_3/N_2 was passed over the sample for 1 h. Then the gaseous and physisorbed NH_3 was removed by flowing He for another 1 h at 120 °C. Finally, the sample was heated to 900 °C at a ramping rate of 10 °C/min. The effluent gas was continuously monitored with a thermal conductivity detector (TCD).

X-ray diffraction (XRD) measurements were carried out on a Rigaku RINTD/MAX-2500PC diffractometer with a monochromatic $\text{Cu K}\alpha$ radiation source ($\lambda = 0.15406$ nm, 40 kV, 200 mA). The sample was scanned at a rate of 5°/min over a 2θ range of 20°–80° with a step size of 0.02°. The crystalline phases were identified using JCPDS data files.

Temperature-programmed reduction of H_2 (H_2 -TPR) tests were performed in flowing 10% H_2/Ar using the Quantachrome ChemBET Pulsar automated chemisorption analyzer. The sample was first flushed with Ar at 300 °C for 0.5 h to desorb impurities, and then cooled to room temperature, and finally heated to 900 °C at a ramping rate of 10 °C/min. After passing through a cold trap to remove steam formed in the reduction process, the effluent gas was continuously monitored with a TCD.

Hydrogen chemisorption experiments were also conducted using the Quantachrome ChemBET Pulsar automated chemisorption analyzer. The sample was reduced at 500 °C under flowing H_2 for 2 h and then flushed with Ar at the same temperature for 1 h. After cooling to room temperature under Ar flow, hydrogen pulses (loop volume 50 μL) were automatically injected into the system until saturation of the sample was attained. The specific surface area of Ni metal particles was calculated assuming a 1:2 H_2 to Ni molar ratio and complete re-

duction. The average Ni particle size was thus calculated based on a surface-averaged model, assuming spherical Ni particles.

2.3. Catalyst test

Methanation reactions were performed in a continuous-flow fixed-bed tubular reactor (inner lined corundum tube, ID 8 mm). The catalyst was packed in the isothermal region of the reactor and reduced in situ in pure H₂ at 500 °C for 4 h before the reaction. The reactant gases consisted of 6.2% H₂, 2.0% CO, 3.8% H₂O, and 88.0% Ar. The reaction was performed at 300–500 °C under a pressure of 3.0 MPa with a GHSV of 40000 h⁻¹. The gas flow rates were controlled by Brooks 5850E mass flow controllers. Steam was generated in a vaporizer by quantitatively pumping in deionized water using an SSILabAlliance Series II high pressure pump. The product gases were analyzed online using an Agilent 7890A gas chromatograph equipped with a TDX-01 packed column, a TCD, and a flame ionization detector.

3. Results and discussion

3.1. Effects of surface oxidation on the properties of the support

3.1.1. TG-DSC

TG-DSC curves of the S support under air atmosphere are shown in Fig. 1. From the curves, the weight loss of the S support before 500 °C was only 0.35%, which can be attributed to the desorption of surface moisture. From 500 °C, the S support started to gain weight slowly; up to 700 °C, the cumulative weight gain was ca. 0.4%; above 700 °C, the mass of the support clearly increased; up to 1000 °C, the total mass increase reached 3%. The weight gain was caused by the formation of SiO_xC_y or SiO₂ via oxidation of the SiC surface, which indicated that the S support began to oxidize slowly from 500 °C and quickly oxidized above 700 °C.

3.1.2. Surface area and pore structure

Table 1 summarizes the surface area, pore volume, and average pore size of the SiC supports oxidized at different temperatures. Both surface area and pore volume of the supports

Table 1

Surface area, pore volume, and average pore size of the SiC supports oxidized at different temperatures.

Support	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_{\text{p}}^{\text{a}}/(\text{cm}^3/\text{g})$	$D_{\text{p}}^{\text{b}}/\text{nm}$
S	23.1	0.054	9.4
S-500	20.9	0.048	9.3
S-700	17.8	0.046	10.4
S-900	11.3	0.026	9.3

^a Total pore volume at 0.97 p/p_0 . ^b Average pore diameter calculated according to equation $D_{\text{p}} = 4V_{\text{p}}/A_{\text{BET}}$.

declined with increasing oxidation temperature, while the average pore size changed only slightly. The surface area and pore volume of S-500 slightly reduced compared to those of S, indicating a small amount of oxidation. For S-700, the surface area and pore volume decreased by ca. 23% and 15%, respectively, suggesting a moderate extent of oxidation. For S-900, these parameters decreased by more than half, indicating the occurrence of severe oxidation. The decrease in surface area and pore volume after oxidation could result from either the blockage of small pores by silicon oxides or the agglomeration of very fine particles.

3.1.3. FT-IR

FT-IR spectra of the SiC supports oxidized at different temperature are presented in Fig. 2. All the supports have similar transmission bands. The strong and broad band centered at ca. 816 cm⁻¹ is assigned to the stretching vibration of Si–C bonds, and is a characteristic peak of SiC. Bands at 1238 and 1100 cm⁻¹ are attributed to the asymmetric stretching vibrations of Si–O bonds [38]. For the S support, the intensity of the Si–O vibration peak is very weak, which suggests a very small amount of silicon oxides in support S. As the oxidation temperature increases, the Si–O vibration peaks clearly become stronger for S-500, S-700, and S-900, indicating an increased content of silicon oxides in the support, which is in agreement with the results of TG-DSC and physisorption tests.

3.1.4. NH₃-TPD

NH₃-TPD profiles of different SiC supports are collected in Fig. 3. The profile of the S support shows two desorption peaks

Fig. 1. TG-DSC curves of the S support under air.

Fig. 2. FT-IR spectra of the SiC supports oxidized at different temperatures.

Fig. 3. NH_3 -TPD curves of the SiC supports oxidized at different temperatures.

at ca. 300 and 676 °C, correlating with the weak acidic sites and strong acidic sites of the surface oxides. The curves of S-500 and S-700 exhibit broad peaks at ca. 660 and 612 °C, respectively, with larger peak areas than that of S, indicating that the acid strength of the support decreased with increasing oxidation temperature, while the acid content increased. Only a weak and narrow peak appears at ca. 600 °C in the curve of S-900, with both acid strength and acid content clearly diminished. The acidic sites of SiC originate from hydroxyl species in surface SiO_xC_y or SiO_2 [39]. As the oxidation temperature increased within a certain range, surface silicon oxides, hydroxyl species, and total acidic content all increased; however, overoxidation (900 °C) of the support caused loss of both capacity to adsorb NH_3 and acidic content resulting from the formation of less reactive oxides and fewer hydroxyl species.

3.2. Characterization of Ni/SiC catalysts

3.2.1. Surface area and pore structure

Table 2 presents the surface area, pore volume, and average pore size of the as-prepared Ni/SiC catalysts. Compared to each individual parent support, the surface areas of NS and NS-500 declined, while those of NS-700 and NS-900 increased slightly; the pore volumes and average pore sizes of all the catalysts increased. The micropores and mesopores contribute considerably to surface area, while macropores (> 50 nm) make small contributions. Pore volume is mainly determined by the pore number and pore size distribution. In the process of catalyst preparation, the surface area and pore volume would diminish because of the blockage of some small pores by Ni particles; however, new mesopores would be formed by the deposition of Ni particles into some macropores, which would in turn cause

Table 2

Surface area, pore volume, and average pore size of the as-prepared Ni/SiC catalysts.

Catalyst	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_p/(\text{cm}^3/\text{g})$	$D_p/(\text{nm})$
NS	22.2	0.058	10.5
NS-500	18.2	0.053	11.7
NS-700	18.5	0.056	12.1
NS-900	11.5	0.034	11.9

Fig. 4. XRD patterns of freshly reduced Ni/SiC catalysts.

increases in surface area and pore volume. The above two factors together determine the surface area and pore volume of the catalysts.

3.2.2. XRD

XRD patterns of freshly reduced Ni/SiC catalysts are shown in Fig. 4. The diffraction peaks at 35.6°, 41.3°, 51.9°, 71.7°, and 75.4° are indexed to β -SiC (JCPDS 29-1129), and the peaks at 44.4°, 51.8°, and 76.4° are assigned to distinct peaks of face centered cubic Ni (JCPDS 87-0712). The broad peak at 21.7° in the pattern of NS-900 is attributed to cristobalite phase (JCPDS 71-0785), which indicates the generation of some inert SiO_2 on the SiC surface after oxidation at 900 °C and substantiates the deduction about less reactive silicon oxides in this sample, proposed in Section 3.1.4. From NS to NS-900, the diffraction peaks of Ni gradually become narrower and stronger. The mean sizes of the nickel crystallites are 13, 15, 16, and 19 nm respectively, as estimated from Ni(111) plane reflection using the Scherrer equation. In other words, Ni particle size increases with rise in oxidation temperature of the support.

3.2.3. H_2 -TPR

H_2 -TPR profiles of the as-prepared Ni/SiC catalysts are presented in Fig. 5. TPR profiles of NS and NS-500 are similar, with

Fig. 5. H_2 -TPR profiles of the as-prepared Ni/SiC catalysts.

Table 3

Dispersion degree, active surface area, and Ni crystallite size of fresh and used Ni/SiC catalysts.

Catalyst	D (%)	S_{Ni} (m ² /g)	d_{Ni} (nm)
NS fresh	4.6	30.5	22.1
NS-500 fresh	2.2	14.6	46.2
NS-700 fresh	2.3	15.4	43.9
NS-900 fresh	1.8	11.7	57.4
NS used	1.9	12.5	54.0
NS-500 used	2.1	13.9	48.4
NS-700 used	2.1	14.2	47.3
NS-900 used	1.6	10.7	63.0

a strong peak centered at 430 °C and a shoulder peak at 520 °C, the former related to surface NiO species weakly interacting with SiC, and the latter to Ni-Si mixed oxides, which are less reducible, and interact moderately strongly with the support. In addition, the weak peak at 726 °C can be attributed to the reduction of surface nickel silicate strongly interacting with SiC [40]. In contrast, the peak at 410 °C in the profile of NS-700 becomes stronger, while the shoulder peak at 520 °C almost disappears and the peak at 730 °C is weakened. For NS-900, only a stronger low-temperature reduction peak appears, and the high-temperature reduction peak completely vanishes. The TPR tests imply that SiC-supported catalysts are easier to reduce when the SiC support oxidizes at higher temperature, because high temperature oxidation reduces the adsorptive reactivity of surface oxides and weakens the interaction between NiO and the SiC support.

3.2.4. Hydrogen chemisorption

Table 3 shows the chemisorption results of the Ni/SiC catalysts before and after reaction at 500 °C for 50 h. For the fresh catalysts, the dispersion degree and active Ni surface area declined with increasing oxidation temperature of the support, and Ni particle size increased. Of the used catalysts, an obvious decrease in dispersion degree and active Ni surface area and concomitant rise in Ni particle size occurred for the NS catalyst, but the other three catalysts had smaller variations. For the NS catalyst, the smaller Ni particles could migrate and coalesce

easily because of both their higher surface energy and the weaker anchoring between Ni particles and the unoxidized SiC support (with fewer surface silicon oxides). In contrast, more surface SiO_xC_y and SiO₂ on the oxidized supports meant that the Ni particles were strongly anchored [14,37], effectively suppressing the aggregation of Ni particles. However, overoxidation of SiC would weaken the anchoring effect, so the Ni particle size of used NS-900 increased more than that of used NS-500 and NS-700.

3.3. Low-temperature activity of the catalysts

The performance of different Ni/SiC catalysts in methanation reactions at 300 °C is shown in Fig. 6. From the traces of CO conversion, all the catalysts deactivated to different extents. The deactivation order was NS-900 > NS > NS-700 > NS-500, while the order of overall activity was the opposite. The CH₄ selectivity dropped rapidly during the initial stages, and then remained almost constant after a stabilization period of about 3 h. Compared to NS-500 and NS-700, NS-900 and NS were somewhat better in CH₄ selectivity but much worse in CO conversion, so their overall CH₄ yields would still be lower. Considering both CO conversion and CH₄ yield, catalyst performance in low-temperature methanation decreased as follows: NS-500 > NS-700 > NS > NS-900.

Each catalyst deactivated at low temperature, but this deactivation disappeared when the reaction temperature increased. Pedersen et al. [41] also reported a similar deactivation phenomenon for a Ni/Al₂O₃ catalyst and called it “β-deactivation”. It is probable that, CO dissociated to less reactive surface carbon species (β-Cs) at low temperature, and the rate of hydrogenation of these species may be lower than that of formation of β-Cs. This would lead to active sites being covered by unreacted surface carbon, and thus cause catalyst deactivation. As well as this, Ni has a higher affinity towards CO at low temperature, resulting in binding of the active sites with CO, which is another mechanism for deactivation [42]. With increasing reaction temperature, the rate of Cs hydrogenation increased and the binding of CO became weak, so the covered sites were re-exposed and the activity was restored. In contrast to the

Fig. 6. Low-temperature methanation performance over different Ni/SiC catalysts. (a) CO conversion; (b) CH₄ selectivity. Reaction conditions: 300 °C, 3.0 MPa, 40000 h⁻¹.

Fig. 7. High-temperature stability of different Ni/SiC catalysts. (a) CO conversion; (b) CH₄ selectivity. Reaction conditions: 500 °C, 3.0 MPa, 40000 h⁻¹.

other three catalysts, NS-900 deactivated much more at low temperature because of the poorer dispersion and larger Ni particles caused by overoxidation of the support. Generally, methanation activity increases with decreasing Ni particle size [43,44], so the rate of Cs hydrogenation over NS-900 was much lower, and active sites became covered more quickly by surface carbon species, leading to much faster deactivation. Although it had the smallest Ni particles, NS showed the second highest deactivation; this may be ascribed to coverage of the active sites as a result of the stronger bonding of CO to smaller Ni particles.

3.4. High-temperature stability of the catalysts

The performance of different Ni/SiC catalysts in methanation reactions at 500 °C is shown in Fig. 7. Over the NS catalyst, CO conversion first diminished continuously to a certain minimum value and then increased slowly with time on stream, while CH₄ selectivity dropped continuously. For NS-500, NS-700, and NS-900, both CO conversion and CH₄ selectivity remained almost unchanged during the reaction, but the conversion and selectivity on NS-700 and NS-900 were clearly higher than those on NS-500. Thus the high-temperature methanation performance of the catalysts was: NS-700 ≈ NS-900 > NS-500 > NS.

Three independent reactions exist in this reaction system: CO methanation, water gas shift, and CO disproportionation. The disproportionation reaction will barely happen when steam is introduced into the feed gas with a H₂/CO ratio more than 3, so CO conversion must be mainly determined by the first two reactions. The results from hydrogen chemisorption imply that sintering of the NS catalyst occurred, which probably contributed to its poor stability at high temperature. In the first 20 h, the CO methanation reaction predominated, and CO conversion and CH₄ selectivity declined with increasing Ni particle size. Subsequent increase in Ni particle size had less of an effect on the rate of CO methanation, and thus the water gas shift reaction predominated, so CO conversion instead increased with increasing Ni particle size, and CH₄ selectivity continued to

diminish. For the other three catalysts, Ni particle size changed only slightly after reaction, because of the strong anchoring effect of surface silicon oxides, so these catalysts had better stability at high temperature.

4. Conclusions

Effects of the oxidation extent of the SiC surface on the performance of Ni/SiC methanation catalysts were studied. The surface area and nickel dispersion of the catalysts decreased with increasing oxidation temperature of the supports, while reducibility and stability of the catalysts increased. The order of performance of the catalysts at low temperature was NS-500 > NS-700 > NS > NS-900, while the order was NS-700 ≈ NS-900 > NS-500 > NS at high temperature, meaning that NS-700 showed the best performance overall. Proper oxidation of the SiC support could enhance low-temperature activity and high-temperature stability of the catalyst; the catalyst supported on unoxidized SiC had poor stability at high temperature and overoxidation of SiC caused severe low-temperature deactivation of the catalyst. This is because the active silicon oxides formed by proper oxidation can disperse and strongly anchor Ni particles.

References

- [1] Kopyscinski J, Schildhauer T J, Biollaz S M A. *Fuel*, 2010, 89: 1763
- [2] Liu Z G, Gong H J, Yu L M. *Coal Chem Ind* (刘志光, 龚华俊, 余黎明. 煤化工), 2009, 37(2): 1
- [3] Li D S. *Coal Chem Ind* (李大尚. 煤化工), 2007, 35(6): 1
- [4] Mills G A, Steffgen F W. *Catal Rev*, 1973, 8: 159
- [5] Zhang H, Dong Y Y, Fang W P, Lian Y X. *Chin J Catal* (张罕, 董芸芸, 方维平, 连奕新. 催化学报), 2013, 34: 330
- [6] Tian D Y, Yang X, Qin S D, Sun S L, Sun Q. *Chem Ind Eng Prog* (田大勇, 杨霞, 秦绍东, 孙守理, 孙琦. 化工进展), 2012, 31(suppl): 229
- [7] Li X, Yang X Z, Tang H D, Liu H Z. *Chin J Catal* (李霞, 杨霞珍, 唐浩东, 刘化章. 催化学报), 2011, 32: 1400
- [8] Zhu R C. *Mod Chem Ind* (朱瑞春. 现代化工), 2012, 32(8): 33

Graphical Abstract

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Proper oxidation of SiC can improve low-temperature activity and high-temperature stability of Ni/SiC catalysts by enhanced dispersal of Ni and better anchoring of Ni to the surface oxides.

- [9] Hu D C, Gao J J, Jia C M, Ping Y, Jia L H, Wang Y L, Xu G W, Gu F N, Su F B. *Chin J Process Eng* (胡大成, 高加俭, 贾春苗, 平原, 贾丽华, 王莹利, 许光文, 古芳娜, 苏发兵. 过程工程学报), 2011, 11: 880
- [10] Shi J G, Tian Y Y, Liu X, Xin S J. *Mod Chem Ind* (史俊高, 田原宇, 刘霞, 邢仕杰. 现代化工), 2012, 32(7): 43
- [11] Tan J, Wang N J, Xiao C W, Zhou J M, Li T, Song C Y. *Clean Coal Technol* (谭静, 王乃继, 肖翠微, 周建明, 李婷, 宋春燕. 洁净煤技术), 2011, 17(2): 43
- [12] He Z, Cui X X, Fan H, Chang Y, Li Z. *Chem Ind Eng Prog* (何忠, 崔晓曦, 范辉, 常瑜, 李忠. 化工进展), 2011, 30(suppl): 388
- [13] Lu X, Chen S H, Wang W L, Ma Z F. *Petrochem Technol* (路霞, 陈世恒, 王万丽, 马紫峰. 石油化工), 2010, 39: 340
- [14] Nguyen P, Pham C. *Appl Catal A*, 2011, 391: 443
- [15] Li X Y, Wang F G, Pan X L, Bao X H. *Chin J Catal* (李星运, 王发根, 潘秀莲, 包信和. 催化学报), 2013, 34: 257
- [16] Kim S M, Woo S I. *ChemSusChem*, 2012, 5: 1513
- [17] Wang Q, Sun W Z, Jin G Q, Wang Y Y, Guo X Y. *Appl Catal B*, 2008, 79: 307
- [18] Leroi P, Madani B, Pham-Huu C, Ledoux M-J, Savin-Poncet S, Bousquet J L. *Catal Today*, 2004, 91-92: 53
- [19] Pesant L, Matta J, Garin F, Ledoux M-J, Bernhardt P, Pham C, Pham-Huu C. *Appl Catal A*, 2004, 266: 21
- [20] Kizling M B, Stenius P, Andersson S, Frestad A. *Appl Catal B*, 1992, 1: 149
- [21] Frind R, Borchardt L, Kockrick E, Mammitzsch L, Petasch U, Herrmann M, Kaskel S. *Catal Sci Technol*, 2012, 2: 139
- [22] Guo X N, Zhi G J, Yan X Y, Jin G Q, Guo X Y, Braut P. *Catal Commun*, 2011, 12: 870
- [23] Nguyen P, Edouard D, Nhut J M, Ledoux M J, Pham C, Pham-Huu C. *Appl Catal B*, 2007, 76: 300
- [24] Ledoux M J, Crouzet C, Pham-Huu C, Turines V, Kourtakis K, Mills P L, Lerou J J. *J Catal*, 2001, 203: 495
- [25] Methivier C, Beguin B, Brun M, Massardier J, Bertolini J C. *J Catal*, 1998, 173: 374
- [26] Xie S, Tong X L, Jin G Q, Qin Y, Guo X Y. *J Mater Chem A*, 2013, 1: 2104
- [27] Lü H F, Mu S C, Cheng N C, Pan M. *Appl Catal B*, 2010, 100: 190
- [28] Vannice M A, Chao Y L, Friedman R M. *Appl Catal*, 1986, 20: 91
- [29] Yu Y, Jin G Q, Wang Y Y, Guo X Y. *Fuel Process Technol*, 2011, 92: 2293
- [30] Zhang G Q, Sun T J, Peng J X, Wang S, Wang S D. *Appl Catal A*, 2013, 462-463: 75
- [31] de la Osa A R, De Lucas A, Diaz-Maroto J, Romero A, Valverde J L, Sanchez P. *Catal Today*, 2012, 187: 173
- [32] Lacroix M, Dreibine L, de Tymowski B, Vigneron F, Edouard D, Bégin D, Nguyen P, Pham C, Savin-Poncet S, Luck F, Ledoux M J, Pham-Huu C. *Appl Catal A*, 2011, 397: 62
- [33] Liu H T, Yang D X, Gao R X, Chen L, Zhang S B, Wang X L. *Catal Commun*, 2008, 9: 1302
- [34] Pham-Huu C, Bouchy C, Dintzer T, Ehret G, Estournes C, Ledoux M J. *Appl Catal A*, 1999, 180: 385
- [35] Xu J, Liu Y M, Xue B, Li Y X, Cao Y, Fan K N. *Phys Chem Chem Phys*, 2011, 13: 10111
- [36] Harlin M E, Krause A O I, Heinrich B, Pham-Huu C, Ledoux M J. *Appl Catal A*, 1999, 185: 311
- [37] Florea I, Ersen O, Hirlimann C, Roiban L, Deneuve A, Houille M, Janowska I, Nguyen P, Pham C, Pham-Huu C. *Nanoscale*, 2010, 2: 2668
- [38] Moene R, Makkee M, Moulijn J A. *Appl Catal A*, 1998, 167: 321
- [39] Guerfi K, Lagerge S, Meziani M J, Nedellec Y, Chauveteau G. *Thermochim Acta*, 2005, 434: 140
- [40] García-Vargas J M, Valverde J L, de Lucas-Consuegra A, Gómez-Monedero B, Sánchez P, Dorado F. *Appl Catal A*, 2012, 431: 49
- [41] Pedersen K, Skov A, Rostrup-Nielsen J R. *Am Chem Soc, Div Fuel Chem, Prepr*, 1979, 25: 89
- [42] Haryanto A, Fernando S D, To S D F, Steele P H, Pordesimo L, Adhikari S. *Energ Fuel*, 2009, 23: 3097
- [43] Andersson M P, Abild-Pedersen F, Remediakis I N, Bligaard T, Jones G, Engbæk J, Lytken O, Horch S, Nielsen J H, Sehested J, Rostrup-Nielsen J R, Nørskov J K, Chorkendorff I. *J Catal*, 2008, 255: 6
- [44] Rostrup-Nielsen J R, Pedersen K, Sehested J. *Appl Catal A*, 2007, 330: 134

载体表面氧化程度对Ni/SiC甲烷化催化剂性能的影响

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摘要: 采用等体积浸渍法制备了Ni/SiC甲烷化催化剂, 研究了SiC载体表面氧化程度对催化剂低温活性和高温稳定性的影响, 并采用热重-差示扫描量热、N₂物理吸附、傅立叶变换红外光谱、氢程序升温脱附、X射线衍射、氢程序升温还原和氢化学吸附技术对样品进行了表征。结果表明, 随着载体氧化温度的提高, 催化剂的比表面积和镍分散度降低, 但还原性和反应稳定性提高。未氧化载体所负载催化剂的高温稳定性最差, 其原因在于载体对镍粒子的固定作用最弱。负载于500和700 °C处理的SiC载体上的催化剂具有较好的低温活性和高温稳定性, 这是因为适度氧化后的载体能较好地分散并固定镍粒子。900 °C处理的载体因过度氧化形成了低活性的氧化层, 使负载的镍粒子变大, 因而催化剂的低温活性最差。

关键词: 甲烷化; 碳化硅; 表面氧化; 镍; 高温稳定性

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1. 前言

近年来, 为了满足日益增加的天然气需求, 保证国内能源安全, 减轻环境污染和提高煤炭的能量利用率, 煤制合成天然气技术受到了极大的关注^[1-3]. 煤制天然气主要包括煤气化、粗煤气变换、合成气净化和甲烷化等步骤, 其中高性能甲烷化催化剂的研发最为关键. 合成气甲烷化是强放热过程, 在工艺上通常加入水蒸气来降低温升和抑制积碳, 这要求催化剂具有高的活性和稳定性.

镍基催化剂活性较高, 成本相对较低, 与其它金属相比具有更好的甲烷选择性, 是研究和应用最广泛的甲烷化催化剂^[4]. 载体对镍基甲烷化催化剂的性能有显著影响, 许多研究者对此进行了深入研究^[5-13]. 但是, 目前报道的甲烷化催化剂大都以氧化物为载体, 其导热性较差, 大量的反应热容易积累在床层局部区域从而形成热点, 极易引发催化剂烧结, 严重情况下甚至会促使甲烷裂解积碳. 采用导热性好的耐高温载体材料来制备催化剂, 可以减少床层的局部热积累, 降低局部温升, 是解决上述问题的有效方法之一.

SiC具有导热性高、热稳定性好、机械强度高和耐化学腐蚀等优良特性, 特别适用于高温、强放热/吸热和有腐蚀性介质存在的反应体系^[14]. 文献报道了SiC作为载体在不同反应中的应用, 如重整^[15-18]、尾气净化^[19,20]、催化燃烧和氧化^[21-25]、燃料电池电催化氧化^[26,27]、甲烷化^[28-30]、费托合成^[31,32]、氧化偶联^[33]、异构化^[34]和脱氢

反应^[35,36]等. 但是, 由于SiC的化学惰性, 金属活性组分和SiC间的相互作用较弱, 导致直接负载在SiC上的金属粒子容易聚集或烧结. 对SiC载体进行表面改性可以增强其与金属活性组分间的相互作用, 从而提高其负载催化剂的稳定性. Vannice等^[28]以在空气中700 °C氧化处理后的SiC为载体, 负载活性组分Pt和Ni, 提高了催化剂的稳定性. Nguyen等^[14]指出SiC表面的SiO₂-SiO_xC_y层起着固定活性组分的涂层作用. Florea等^[37]也发现SiC表面的氧化层对活性组分的锚定和分散起到重要作用. 然而, 有关SiC载体表面氧化程度与其负载催化剂的性能之间的关系的研究鲜见报道. 本文以不同温度下氧化处理的SiC为载体, 采用浸渍法制备镍基甲烷化催化剂, 考察SiC载体表面氧化程度对催化剂性能的影响.

2. 实验部分

2.1. 催化剂的制备

采用硅粉和活性炭粉的直接化合反应合成SiC^[14]. 称取等化学计量比的金属硅粉(纯度99.9%, 上海中油企发粉体材料有限公司)和活性炭粉(CP, 科密欧试剂), 加入一定量的羟丙基甲基纤维素、桐油和去离子水, 在捏合机(HyN1L型, 如皋市华宇机械厂)中充分搅拌均匀形成泥料. 所得泥料用双螺杆挤条机(F-26III型, 华南理工大学机械厂)挤成 $\phi 3$ mm的圆柱体, 经110 °C干燥过夜后, 在Ar气中于1400 °C反应2 h, 形成自烧结的碳化硅圆柱体, 将其敲碎并筛分, 取40–60目颗粒用作载体, 标记为S. 将载体S分别在空气中500, 700和900 °C氧化处理4 h, 所

得载体依次标记为S-500, S-700和S-900. 采用等体积浸渍法, 用一定量的1 mol/L的 $\text{Ni}(\text{NO}_3)_2$ 水溶液分别浸渍上述四种载体, 浸渍后在110 °C干燥4 h, 500 °C焙烧2 h, 所得催化剂依次标记为NS, NS-500, NS-700和NS-900, NiO负载量均为9 wt%.

2.2. 催化剂的表征

热重-差示扫描量热(TG-DSC)分析在德国NETZSCH公司STA 449 F3型同步热分析仪上进行. 样品置于刚玉坩埚内, 在空气气氛中以10 °C/min由室温升至1000 °C.

样品的比表面积和孔结构在美国Quantachrome公司NOVA 2200e型比表面和孔径分析仪上测定. 测试前样品在300 °C动态真空中脱气2 h, 之后在液氮温度下进行 N_2 吸附-脱附实验. 由多点BET法计算比表面积(A_{BET}), 总孔容(V_p)取 $p/p_0 = 0.97$ 处的吸附体积, 平均孔径(D_p)由公式 $D_p = 4V_p/A_{\text{BET}}$ 计算.

傅里叶变换红外光谱(FT-IR)测试在美国Thermo Scientific公司Nicolet 6700型光谱仪上进行, 分辨率为4 cm^{-1} , 扫描次数为32, 扫描范围为4000–650 cm^{-1} . 样品粉末与KBr粉末按固定质量比混匀, 压片后置于不锈钢池体中间, 记录样品片在空气中的谱图.

氨程序升温脱附(NH_3 -TPD)实验在美国Quantachrome公司ChemBET Pulsar型自动化学吸附仪上进行. 样品先在300 °C下用He吹扫0.5 h以除去表面杂质, 冷却至室温后将气体切换为0.5% NH_3/N_2 混合气, 室温下吸附1 h, 然后将气体切换回He并升温至120 °C, 吹扫1 h以除去表面物理吸附的 NH_3 . 待仪器基线稳定后, 在He气氛下以10 °C/min升至900 °C, TCD检测脱附的 NH_3 .

X射线衍射(XRD)测定在日本Rigaku公司RINTD/MAX-2500PC型X射线衍射仪上进行. 激发光源为Cu K_α 射线($\lambda = 0.15406 \text{ nm}$), 管电压40 kV, 管电流200 mA, 扫描范围 $2\theta = 20^\circ\text{--}80^\circ$, 扫描速度5°/min, 步长0.02°. 利用JCPDS标准谱图确定样品的晶相组成.

氢程序升温还原(H_2 -TPR)在美国Quantachrome公司的ChemBET Pulsar型自动化学吸附仪上进行. 样品先在300 °C下用Ar吹扫0.5 h以除去表面杂质, 然后冷却至室温, 将气体切换为10% H_2/Ar 混合气, 以10 °C/min升至900 °C. 尾气经冷阱去除还原过程中生成的水气后, 用TCD连续检测.

氢化学吸附在美国Quantachrome公司的ChemBET Pulsar型自动化学吸附仪上进行. 样品先在纯 H_2 气流中

500 °C下还原2 h, 之后在相同温度下用Ar吹扫1 h以除去样品表面吸附的 H_2 , 并在Ar气氛下冷却至室温. 待TCD基线稳定后, 用仪器自带的定量环(50 μL)向系统中自动脉冲纯 H_2 气体直至吸附饱和. 假定每个Ni原子吸附一个H原子, 样品完全还原并且Ni晶粒均为球形, 计算出Ni金属的比表面积, 再由此计算Ni晶粒的平均粒径.

2.3. 催化剂的评价

甲烷化反应在连续流动固定床管式反应器(内衬刚玉管, 内径8 mm)中进行, 将一定量的催化剂装填于反应器的等温区. 反应前催化剂在500 °C用纯 H_2 还原4 h. 原料气湿基组成为: 6.2% H_2 , 2.0% CO , 3.8% H_2O , 88.0% Ar, 空速40000 h^{-1} , 压力3.0 MPa, 反应温度300–500 °C. 气体流量由美国Brooks公司5850E型质量流量计控制, 水蒸气由美国SSILabAlliance公司Series II型高压泵定量输送去离子水至汽化器中气化而得. 反应尾气用安捷伦GC7890A型气相色谱仪在线分析, TDX-01色谱柱, TCD和FID双检测器.

3. 结果与讨论

3.1. 表面氧化对载体性质的影响

3.1.1. TG-DSC结果

图1是所制载体S在空气气氛中的TG-DSC曲线. 由图可见, SiC载体在500 °C前失重仅为0.35%, 这归因于载体表面吸附水的脱除. 载体S从500 °C开始缓慢增重, 到700 °C时累计增重约0.4%, 之后明显增重, 到1000 °C时累计增重达3%. 载体增重由表面氧化形成的 SiO_xC_y 或 SiO_2 引起. 这表明SiC载体从500 °C开始缓慢氧化, 700 °C后氧化程度明显提高.

3.1.2. 比表面积和孔结构

表1为不同温度氧化处理的载体比表面积、孔容和平均孔径. 可以看出, 随着氧化温度的提高, 载体的比表面积和孔容均下降, 平均孔径整体上变化不大. 与载体S相比, S-500的比表面积和孔容略微下降, 表明氧化程度较轻; S-700的比表面积下降约23%, 孔容下降约15%, 推测发生了中等程度的氧化; S-900的比表面积和孔容都下降过半, 表明发生了严重氧化. 比表面积和孔容下降可能是由于载体氧化后形成的表面硅氧化物层堵塞了部分小孔, 或载体中细小颗粒在氧化后团聚长大.

3.1.3. FT-IR结果

图2是不同温度氧化处理的载体的FT-IR谱图. 可以看出, 各载体呈现相似的透射谱带, 其中816 cm^{-1} 附近强而宽的透射峰归属于Si–C键的伸缩振动, 是SiC的特征

峰; 1238和1100 cm^{-1} 处谱峰对应于Si–O键的非对称伸缩振动^[38]. 载体S的Si–O振动峰强度非常弱, 说明其硅氧化物的含量非常少. 随着氧化温度的提高, S-500, S-700和S-900的Si–O振动峰强度依次明显增加, 表明载体中硅氧化物的含量随氧化温度的提高而增加. 这与热重和物理吸附的分析结果一致.

3.1.4. NH_3 -TPD结果

图3是不同载体的 NH_3 -TPD曲线. 新鲜制备的载体S在300和676 $^{\circ}\text{C}$ 附近出现 NH_3 的脱附峰, 分别对应于表面硅氧化物的弱酸中心和强酸中心. S-500和S-700分别在660和612 $^{\circ}\text{C}$ 附近出现较宽的脱附峰, 且峰面积都明显高于S的, 这表明随着氧化温度的升高, 载体的酸强度减弱但总酸量增加. S-900只在600 $^{\circ}\text{C}$ 附近出现较弱的脱附峰, 酸强度和酸量都明显下降. SiC载体的酸性来源于表面 SiO_xC_y 或 SiO_2 中的羟基物种^[39]. 在一定范围内, 随着载体氧化温度的提高, 表面硅氧化物及羟基物种数量增加, 总酸量增加; 但过高温度(900 $^{\circ}\text{C}$)下的氧化使载体表面形成了活性较弱的氧化硅物种, 其表面羟基较少, 因而对 NH_3 的吸附能力变差, 酸量下降.

3.2. 催化剂的表征结果

3.2.1. 比表面积和孔结构

表2为由四种不同载体制备的催化剂的比表面积、孔容和平均孔径. 与对应的载体相比, 催化剂NS和NS-500的比表面积减小, 而催化剂NS-700和NS-900的比表面积略微增加, 各催化剂的孔容和平均孔径均增大. 载体中微孔和介孔的孔壁对比表面积起主要贡献, 大孔(> 50 nm)对比表面积的贡献较小. 孔容则主要由孔的数量和大小分布决定. 在催化剂制备过程中, 载体的部分小孔被镍粒子堵塞, 使得比表面积和孔容下降; 另一方面, 部分镍粒子负载到载体的大孔表面上从而形成新的介孔, 引起比表面积和孔容增大. 这两个因素共同作用决定了催化剂的比表面积和孔容.

3.2.2. XRD结果

图4为还原态催化剂的XRD谱. 图中位于35.6°, 41.3°, 51.9°, 71.7°和75.4°处的衍射峰归属于 β -SiC (JCPDS 29-1129), 44.4°, 51.8°和76.4°处的衍射峰是Ni的特征峰(JCPDS 87-0712). 此外NS-900在21.7°处还出现了一个宽的衍射峰, 归属于方英石相(JCPDS 71-0785), 这表明900 $^{\circ}\text{C}$ 氧化后载体表面生成一定量的惰性 SiO_2 , 证实了3.1.4节中S-900严重氧化形成活性较弱的氧化硅物种的推论. 另外, 从NS到NS-900, 镍的衍射峰逐渐变窄变强, 根据Ni(111)面的衍射峰由谢乐公式估算出镍晶

粒的大小分别为13, 15, 16和19 nm. 这表明随着载体氧化温度的提高, 其负载的镍粒子尺寸逐渐增大.

3.2.3. H_2 -TPR结果

图5是不同Ni/SiC催化剂的 H_2 -TPR谱. 由图可见, NS和NS-500的还原曲线相似, 都在410 $^{\circ}\text{C}$ 附近出现强还原峰, 并在520 $^{\circ}\text{C}$ 附近伴有肩峰, 前者是与载体相互作用较弱的表面氧化镍物种的还原, 后者对应于与载体有中等相互作用且较难还原的镍硅混合氧化物物种. 此外, 726 $^{\circ}\text{C}$ 处较弱的还原峰归属于与载体发生强相互作用的表面硅酸镍的还原^[40]. 相比之下, NS-700在410 $^{\circ}\text{C}$ 附近的还原峰变强, 520 $^{\circ}\text{C}$ 处的肩峰基本消失, 730 $^{\circ}\text{C}$ 处的还原峰强度减弱; 而NS-900只出现更强的低温还原峰, 高温还原峰完全消失. 由此可见, 随着SiC氧化温度的提高, 其负载的Ni催化剂更容易还原. 这是因为高温氧化降低了载体表面硅氧化物的吸附活性, 减弱了氧化镍与载体间的相互作用.

3.2.4. 氢化学吸附结果

表3为新鲜催化剂和500 $^{\circ}\text{C}$ 反应50 h后催化剂的氢化学吸附结果. 可以看出, 随着载体氧化温度的提高和比表面积的下降, 新鲜催化剂的镍分散度和活性表面积下降, 镍粒子尺寸变大. 反应后, NS催化剂的镍分散度和活性表面积明显下降, 镍粒子明显增大, 而其它三种催化剂的变化相对较小. 这是因为NS催化剂中镍粒子相对较小, 表面能较大, 更易在反应中受热长大, 而且未氧化的SiC载体上硅氧化物较少, 对镍粒子的固定作用较弱, 高温下镍粒子易在表面迁移并聚集长大; 而氧化后的载体具有表面 SiO_xC_y 或 SiO_2 层, 其对镍粒子具有较强的锚定作用^[14,37], 能有效抑制镍粒子迁移, 但载体的过度氧化使表面硅氧化物对镍粒子的锚定作用减弱, 因此反应后NS-900的镍粒子增大幅度超过NS-500和NS-700的.

3.3. 催化剂的低温活性

图6是300 $^{\circ}\text{C}$ 时各Ni/SiC催化剂上的甲烷化反应性能. 由图可见, 所有催化剂都发生不同程度的失活, 大小顺序为: NS-900 > NS > NS-700 > NS-500, 而催化剂的总体活性顺序与此相反. 另外, 反应初期 CH_4 选择性快速下降, 经过约3h的反应稳定期后基本不变, 其中NS-900和NS上的 CH_4 选择性略微高于NS-500和NS-700上的, 但由于前两者的CO转化率远低于后两者的, 总体上前两者的 CH_4 收率仍低于后两者的. 综合考虑CO转化率和 CH_4 收率, 各催化剂的低温甲烷化性能如下: NS-500 > NS-700 > NS > NS-900.

各催化剂在低温下发生失活,但提高反应温度后其甲烷化活性又恢复. Pedersen等^[41]也发现了Ni/Al₂O₃催化剂上类似的低温失活现象,并称之为“ β -失活”.这很有可能是CO在低温下解离生成了活性较差的表面碳物种(β -Cs),低温下表面碳物种的加氢甲烷化速率慢于其生成速率,导致活性位被表面碳物种覆盖而降低活性.此外,低温下CO在镍上的吸附较为牢固,从而占据活性位,导致反应活性下降^[42].当提高反应温度后,表面碳物种的加氢速率大大提高,CO的吸附变弱,被覆盖的活性位重新暴露,因而反应活性恢复.与其它三种催化剂相比,NS-900的低温失活更为严重,这是由于载体过度氧化使负载的镍粒子分散性变差,形成较大的镍粒子.一般认为,甲烷化活性随镍粒子增大而下降^[43,44],因此NS-900催化剂上的表面碳物种加氢速率更慢,使得活性位被碳物种覆盖地更快,失活也更快.对于镍粒径最小的NS催化剂,其失活程度仅次于NS-900的,这可能是由低温下较多的CO牢固地吸附在较小的镍粒子上引起活性位覆盖而造成的.

3.4. 催化剂的高温稳定性

图7是500 °C时各Ni/SiC催化剂上的甲烷化反应性能.由图可见,NS催化剂上CO转化率随反应时间的延长先逐渐下降至某一极小值,后又缓慢增大,而CH₄选择性则持续下降.对于NS-500,NS-700和NS-900催化剂,CO转化率和CH₄选择性在整个反应过程中都基本保持不变,但NS-700和NS-900上的活性和选择性明显高于NS-500的.各催化剂的高温甲烷化性能为: NS-700 $\approx$ NS-900 > NS-500 > NS.

甲烷化反应体系中存在三个独立反应: CO甲烷化、水气变换和CO歧化.在H₂/CO $\geq$ 3且原料气中含有水蒸气的条件下,基本不发生歧化反应,CO转化率主要取决于前两个反应.根据氢化学吸附结果,NS在反应过程中镍粒子明显长大,这种烧结作用很可能是其高温稳定性差的原因.在反应前20 h内CO甲烷化反应占主导,CO转化率和CH₄选择性随着镍粒子的长大而下降;此后镍粒子的长大对甲烷化反应速率的影响变小,因而水气变换反应占据主导地位,随着镍粒子的长大,CO转化率提高,而CH₄选择性则继续下降.对于其它三种催化剂,由于载体氧化形成的表面硅氧化物对镍粒子具有较好的锚定作用,反应后镍粒径变化较小,因而催化剂的高温稳定性较好.

4. 结论

考察了SiC载体的表面氧化程度对其负载的镍基甲烷化催化剂性能的影响.结果表明,随着载体氧化温度的提高,其负载催化剂的比表面积和镍分散度下降,还原性和反应稳定性提高.各催化剂的低温性能顺序为NS-500 > NS-700 > NS > NS-900,高温性能顺序为NS-700 $\approx$ NS-900 > NS-500 > NS,总体上以NS-700的性能最佳.SiC载体的适度氧化能够提高催化剂的低温活性和高温稳定性,而未氧化载体所负载催化剂的高温稳定性较差,SiC过度氧化则会导致其负载的催化剂发生较严重的低温失活.这是由于载体适度氧化后形成了活性的硅氧化物,既能保证镍较好地分散,又提高了对镍粒子的锚定作用.