

文章编号: 0253-2409(2013)08-0972-06

A comparative study on the catalytic properties of high Ni-loading Ni/SiO₂ and low Ni-loading Ni-Ce/SiO₂ for CO methanation

WANG Yong-zhao, LI Feng-mei, CHENG Hui-min, FAN Li-yuan, ZHAO Yong-xiang
(School of Chemistry and Chemical Engineering, Engineering Research Center for Fine Chemicals of Ministry of Education, Shanxi University, Taiyuan 030006, China)

Abstract: Two Ni-based catalysts of 13% Ni/SiO₂ (13Ni/Si) and 7% Ni-2% Ce/SiO₂ (7Ni-2Ce/Si, by weight) were prepared by the incipient-wetness impregnation method and characterized with N₂-sorption, XRD, H₂-TPR, FT-IR, TEM, H₂-TPD and CO-TPD techniques. It was shown that addition of Ce promoter generated an interaction among NiO, CeO₂ and SiO₂, which changed chemical environment of Ni-O-Si bond, enhanced the dispersion and reduction of NiO, and increased the active surface area. In particular, a new type of moderately strong CO adsorption sites was formed on the surface of the 7Ni-2Ce/Si catalyst. As a result, the low Ni-loading 7Ni-2Ce/Si catalyst exhibited higher CO adsorption capacity and CO methanation catalytic activity than the high Ni-loading 13Ni/Si. Under the reaction conditions of 1% CO (volume fraction in H₂ atmosphere), GHSV of 7 000 h⁻¹ and atmospheric pressure, the temperature for complete conversion of CO over the 7Ni-2Ce/Si catalyst was 230 °C, being 30 °C lower than that found over the high Ni loading 13Ni/Si catalyst.

Keywords: CO methanation; Ni-Ce/SiO₂ catalyst; cerium promoter; Ni loading

CLC number: O643 **Document code:** A

CO methanation has been widely applied in many industries such as hydrogen production in the synthesis of ammonia and the preparation of petroleum chemicals and synthesis of natural gas from coke oven gas or syngas^[1]. In recent years, proton exchange membrane fuel cell (PEMFC) has attracted a great deal of attention because of its clean and renewable characteristics^[2-4]. At present, most hydrogen is produced through steam reforming and partial oxidation of methane or methanol. However, this inevitably co-produced 1% ~ 2% of CO, which will poison Pt anodes, and hence, severely decreasing the efficiency of PEMFC. Thus, it is necessary to remove CO from the produced hydrogen gas^[5-7]. In this aspect, methanation has been proved to be an effective way as it does not require addition of reactants and the products are not poisonous to the electrodes and the environment.

In the CO methanation, Ni-based catalysts have been mostly used as results of its high catalytic activity and low cost. However, the Ni loading of this type of catalysts is generally high, making its atomic utilization rate low and the catalyst cost still relatively high. From the theoretical and practical viewpoint, the decrease of Ni loading would be interesting. CeO₂ is widely used to prepare catalysts because of its high storage and supply oxygen

capacity, excellent oxidation-reduction quality and characteristics for improving the dispersion of surface active component^[8]. It was reported that doping appropriate amounts of CeO₂ in the Ni-based catalysts decreased the crystallite size by supplying more "spacers" and inhibited the crystal growth and sintering by the strong interaction between Ni and CeO₂, consequently showing high catalytic activity and stability in some oxidation reactions^[9-13].

Our previous work shows that the 13Ni/Si shows high catalytic activity for CO methanation^[14]. In this work, a low Ni-loading catalyst of 7Ni-2Ce/Si is prepared by using SiO₂ aerogel as support and Ce as promoter. Compared to the 13Ni/Si, it shows significantly improved catalytic properties in CO methanation due to the increase in the Ni dispersion and active surface area.

1 Experimental

1.1 Catalyst preparation

A desired amount of acetic acid, water, tetraethoxysilane (TEOS) and anhydrous ethanol were stirred to form a uniform mixture, which was then transferred into a Teflon-lined stainless steel autoclave and heated to the temperature larger than *t_c* (243 °C) and the pressure higher than *p_c* (6.36 MPa) for hydrolysis of TEOS. The product was calcined at

Received date: 2013-05-27; **Received in revised form:** 2013-06-17.

Foundation items: National Natural Science Foundation of china(21073114) ; Youth Scientific and Technological Foundation of Shanxi Province (2010021008-3)

Corresponding author: ZHAO Yong-xiang; WANG Yong-zhao, Fax: +86-351-7011688, E-mail: catalyst@sxu.edu.cn; yxzha@sxu.edu.cn.

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>)。

400 °C for 3 h in air to obtain the SiO₂ aerogel support^[1]. The 13Ni/Si and 7Ni-2Ce/Si catalysts were prepared by impregnating the SiO₂ aerogel support with a certain amount of Ni(NO₃)₂·6H₂O or “Ni(NO₃)₂·6H₂O and Ce(NO₃)₃·6H₂O” mixture aqueous solution, followed by subsequently drying at 80 °C and 120 °C and calcining at 400 °C for 3 h, respectively, in air. For comparison, 7Ni/Si, 7Ni-6Ce/Si and 13Ce/Si were also prepared according to the same procedures.

1.2 Apparatus and method for catalytic test

The catalytic activity of the samples for CO methanation was evaluated at atmospheric pressure in a continuous-flow quartz microreactor with an i. d. of 4 mm. 0.1 g sample sieved to 40 ~ 60 mesh was set into the microreactor, and a thermocouple was inserted into the catalyst bed to measure and control the reaction temperature. The concentration and temperature gradients and pressure drop over the catalyst bed were negligible. The feed gas consisting of 1% of CO and 99% of H₂ flowed through the catalyst bed at a rate of 60 mL/min. Quantitative analysis of CO and CH₄ was performed on an on-line gas chromatograph equipped with a 3 m column packed with carbon molecular sieve, a methanator and a flame ionization detector (FID). Prior to the test, all the samples were pretreated at 400 °C for 3 h in a H₂ flow and then cooled to the designed temperature. The reaction temperature was raised from 100 to 300 °C at a rate of 2 °C/min. The reaction products were detected on an on-line Micromeritics Autochem II 2920 Chemisorb. It was found that the products contained only CH₄ and H₂O. Thus, the CO conversion was calculated by the following equations:

$$x = \left(1 - \frac{S'_{CO}}{S_{CO}}\right) \times 100\% \quad (1)$$

x : CO conversion

S'_{CO} : the peak area of CO in the tail gas

S_{CO} : the peak area of CO in the feed gas

1.3 Catalyst characterization

N₂ adsorption-desorption isotherms were measured at -196 °C on a Micromeritics ASAP 2020 specific surface area and porosity analyzer. The specific surface area (A_{BET}) was determined from the N₂ adsorption isotherm. The pore-structural parameters were obtained from the adsorption branch by the BJH method in terms of a cylindrical pore model. Prior to the adsorption experiments, the samples were degassed at 150 °C for 24 h under high vacuum conditions. X-ray diffraction (XRD) patterns were recorded in the range of 10 ~ 80 °C at a scanning speed of 6°/min on a Bruker D8-Advance

X-ray diffractometer with a Cu $K\alpha$ target operated at 40 kV and 40 mA. Average crystallite sizes of the samples were evaluated from X-ray line broadening analysis (XLBA) by the Scherrer equation ($d = 0.89 \lambda / \beta \cos \theta$). H₂ temperature-programmed reduction (H₂-TPR) experiments were carried out in a tubular quartz reactor, where 30 mg of sample (40 ~ 60 mesh) was loaded in the thermostatic zone. The reduction was conducted in a N₂ flow containing 5% H₂ (flow rate of 20 mL/min) at a heating rate of 10 °C/min. The consumption of H₂ was detected with a TCD. Fourier transform infrared (FT-IR) spectra of the samples were obtained on a Bruker TENSOR 27 spectrometer in the range of 400 ~ 1 400 cm⁻¹ by the KBr pellet method (1% of sample). Transmission electron microscopy (TEM) images were measured on a JEM-2100 Transmission electron microscope operated at 200 kV by ultrasonically dispersing powder sample in ethanol and depositing it onto a standard copper grid covered with a holey carbon film.

H₂ or CO temperature-programmed desorption (H₂- or CO-TPD) experiments were carried out on a Micromeritics Autochem II 2920 Chemisorb. 100 mg of sample (40 ~ 60 mesh) was in situ reduced in a H₂ flow for 3 h at 400 °C, and then swept with 99.999% Ar (or He) for 1 h at 410 °C to obtain clean surface. Then, the sample was cooled down to 50 °C and allowed to adsorb H₂ or CO for 2 h or 0.5 h. After that, the sample was swept with Ar or He until the baseline was stable. Finally, the temperature was elevated at a rate of 10 °C/min in a Ar or He flow (20 mL/min). The desorbed H₂ or CO was detected by an on-line quadrupole mass spectrometer (HIDEN HPR-20 QIC) with the minimum dwell time of 3 ms.

2 Results and discussion

2.1 Catalytic test for CO methanation

Figure 1 shows the dependence of CO conversions obtained over different catalysts in CO methanation on the reaction temperature. Except for 13Ce/Si, the CO conversions of other samples significantly increased with increasing reaction temperature from 120 to 250 °C. At the same reaction temperature, the CO conversions of 7Ni-2Ce/Si and 7Ni-6Ce/Si were nearly the same. The reaction over these two catalysts started at 120 °C and completed at 210 °C. In contrast, the CO conversion obtained over the 7Ni/Si at 210 °C was only 46%. Although an increase in the Ni content from 7% to 13% could increase the CO conversion, it is still lower than that obtained over the 7Ni-2Ce/SiO₂. The 7Ni/Si and

13Ni/Si gave a total conversion of CO at 290 and 240 °C respectively. This indicates that the addition of Ce promoter to the Ni/Si catalysts considerably improved their catalytic activities for CO methanation. Thus, a detailed characterization of the 7Ni-2Ce/Si and 13Ni/Si samples was conducted in the following for investigating the reason.

2.2 Characterization of catalysts

2.2.1 N₂ physisorption

The physical properties attained from the N₂ adsorption/desorption isotherm of 13Ni/Si, 7Ni/Si and 7Ni-2Ce/Si were listed in Table 1. Clearly, the surface area and the pore volume increased with the Ni content decreasing, while the pore diameter decreased. It seems that these physical properties are independent of the Ce content.

Table 1 Surface area and pore structure parameters of 13Ni/Si, 7Ni-2Ce/Si and 7Ni/Si

Catalyst	BET surface area $A / (\text{m}^2 \cdot \text{g}^{-1})$	Pore volume $v / (\text{cm}^3 \cdot \text{g}^{-1})$	Average pore radius d / nm
13Ni/Si	527	0.31	3.08
7Ni-2Ce/Si	631	0.34	2.84
7Ni/Si	628	0.34	2.82

2.2.2 XRD characterization

The XRD patterns of the 13Ni/Si and the 7Ni-2Ce/Si are shown in Figure 2.

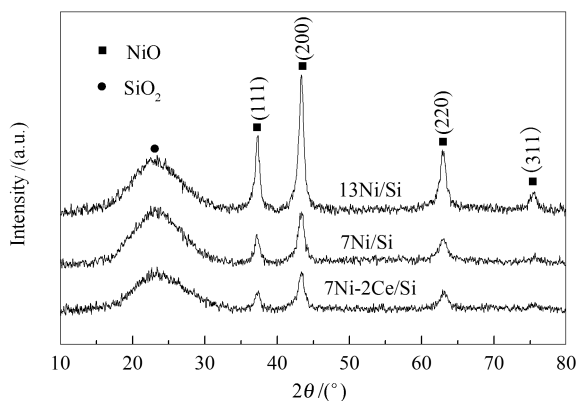


Figure 2 XRD patterns of the 13Ni/Si and 7Ni-2Ce/Si catalysts

The peaks attributed to cubic NiO (37.2°, 43.3°, 62.9°, 75.1°) and amorphous silica ($2\theta = 22.9$) were observed for both the samples, but the characteristic peaks of CeO₂ were not observed, indicative of a high dispersion of CeO₂. In addition, the lower intensity of the diffraction peaks of NiO species in the 7Ni-2Ce/Si than those in the 13Ni/Si and the 7Ni/Si, indicating that the former sample has a small crystal size. Indeed, the average crystallite size, estimated by the Scherrer equation, of the NiO species in the 7Ni-2Ce/Si is 7.5 nm, which is smaller than those of the 13Ni/Si (11.5 nm) and the 7Ni/Si (9.2 nm). This shows that the dispersion degree of

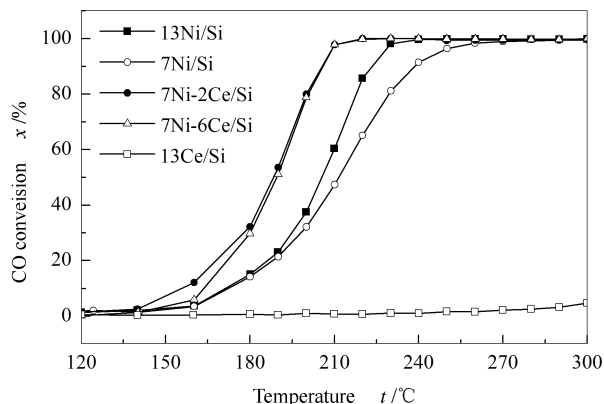


Figure 1 Effect of reaction temperature on the activities of catalysts
reaction conditions: 1% CO in H₂, GHSV of 7 000 h⁻¹, atmospheric pressure

NiO species increased with the decrease of the Ni loading in the sample and by the addition of Ce promoter.

2.2.3 H₂-TPR characterization

The H₂-TPR profiles of the 13Ni/Si and the 7Ni-2Ce/Si are shown in Figure 3.

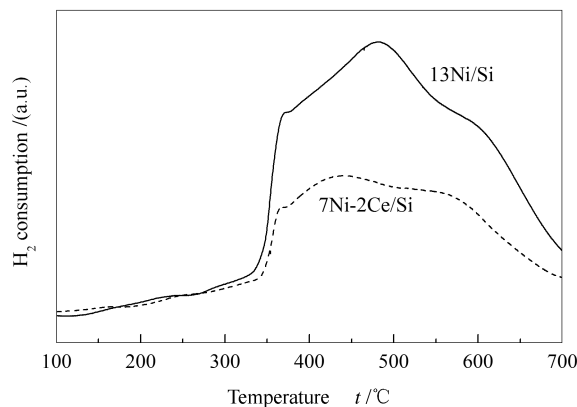


Figure 3 H₂-TPR profiles of the 13Ni/Si and 7Ni-2Ce/Si catalysts

An intense H₂ consumption peak at 490 °C was observed with two shoulder ones at 370 and 580 °C in the profile of the 13Ni/Si^[14]. In contrast, the two reduction peaks at high temperatures shifted to 450 and 550 °C respectively for the 7Ni-2Ce/Si, indicative of a weak interaction between NiO species and support. In addition, the partial bonding among the NiO, CeO₂ and Si-OH makes the electron cloud around NiO asymmetrical and more reactive^[15], consequently, improving the reduction degree of NiO

species.

2.2.4 FT-IR characterization

In order to further understand the difference between the structures of the 13Ni/Si and the 7Ni-2Ce/Si, the FT-IR spectra of the 13Ni/Si, 7Ni-2Ce/Si and SiO₂ support were measured. The absorption peaks characteristic of SiO₂ appeared at 1 084, 960, 804 and 467 cm⁻¹ (Figure 4), which can be assigned to asymmetric and symmetric stretching vibration of Si-O-Si bond, the stretching vibration of Si-OH and the bending vibration of cyclic Si-O-Si, respectively. When Ni²⁺ was impregnated on the SiO₂, the 1 084 cm⁻¹ absorption peak shifted to 1 095 cm⁻¹, and the vibration peaks at 960, 804 and 467 cm⁻¹ decreased in intensity. This indicates that Ni²⁺ entered into the SiO₂ framework^[16], and the Ni-O-Si structure was formed^[17]. A further impregnation of Ce onto the support shifted 960 cm⁻¹ peak to 966 cm⁻¹ and decreased the peaks at 1 095, 966, 804 and 467 cm⁻¹ in intensity, indicating that an interaction occurred among the NiO, CeO₂ and SiO₂, which could change the chemical environment of the Ni-O-Si bond.

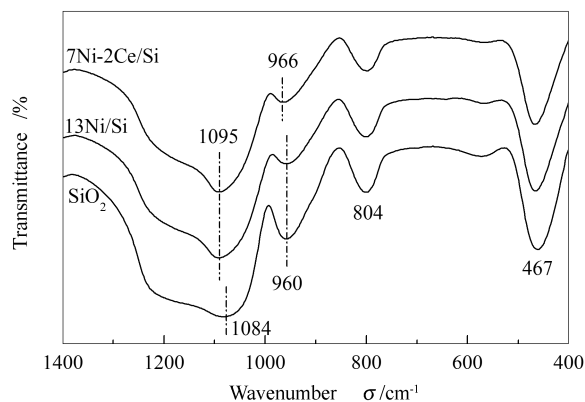


Figure 4 FT-IR spectra of the 13Ni/Si, 7Ni-2Ce/Si and SiO₂

2.2.5 TEM characterization

Figure 5 shows the TEM images of the 13Ni/Si and the 7Ni-2Ce/Si. Slight aggregations of NiO species occurred in the 13Ni/Si catalyst (Figure 5 (a)), while this species had a uniform distribution on the surface of the 7Ni-2Ce/Si (Figure 5 (b)). The NiO crystallite sizes of the 13Ni/Si and the 7Ni-2Ce/Si are 10 ~ 13 nm and 5 ~ 8 nm respectively, being in agreement with the results obtained from the XRD measurements (Figure 2).

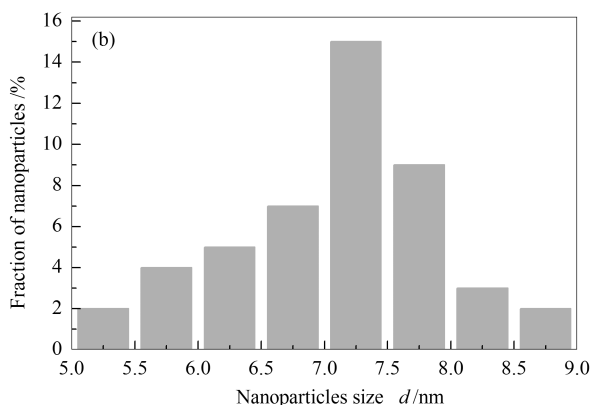
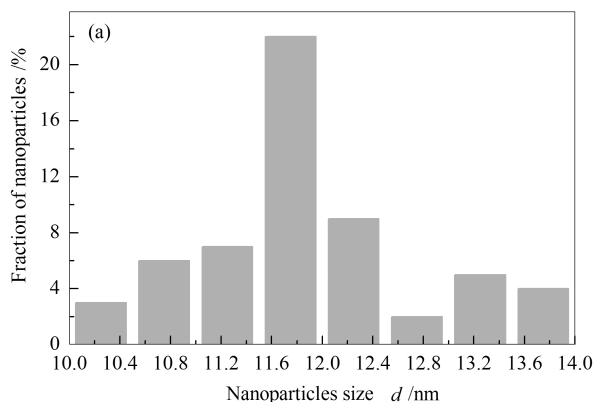
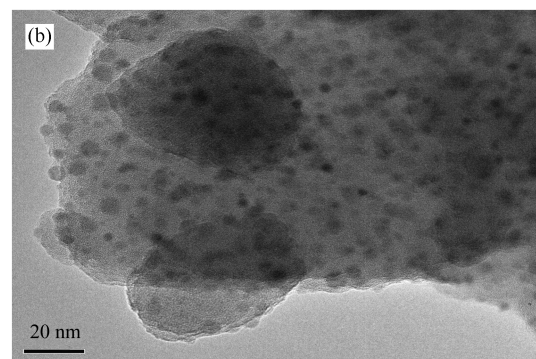
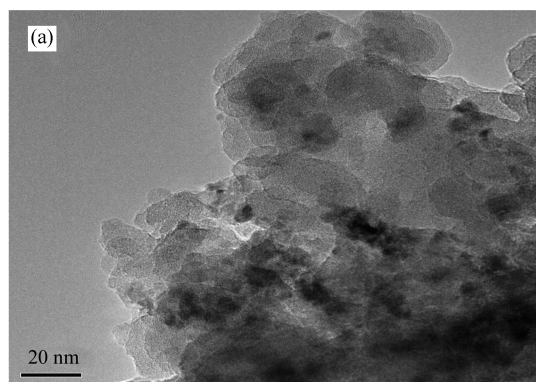


Figure 5 TEM images of (a) 13Ni/Si and (b) 7Ni-2Ce/Si catalysts

2.2.6 H₂-TPD characterization

The H₂-TPD profiles of the 13Ni/Si, 7Ni/Si and

7Ni-2Ce/Si are shown in Figure 6. All the catalysts exhibited two hydrogen desorption peaks at the

temperature lower than 350 °C and the temperature higher than 400 °C, which are attributed to the desorption of H₂ adsorbed on the active metal surface and of spillover H₂ desorbed on the support surface respectively^[18-20]. Nevertheless, a shoulder peak was also observed around 180 °C for the 13Ni/Si and 7Ni/Si samples, which is, however, absent in the profile of the 7Ni-2Ce/Si. This peak could be assigned to the desorption of H₂ adsorbed on surface of large Ni crystals. Generally, the more intense the lower-temperature peak is, the better the hydrogenation performance of the catalyst is. Although the Ni loading of the 13Ni/Si was about 1.86 times of that of the 7Ni-2Ce/Si, its hydrogen desorption amount is just slightly larger than that of the 7Ni-2Ce/Si but much higher than that of the 7Ni/Si catalyst, supporting the higher activity of the 7Ni-2Ce/Si.

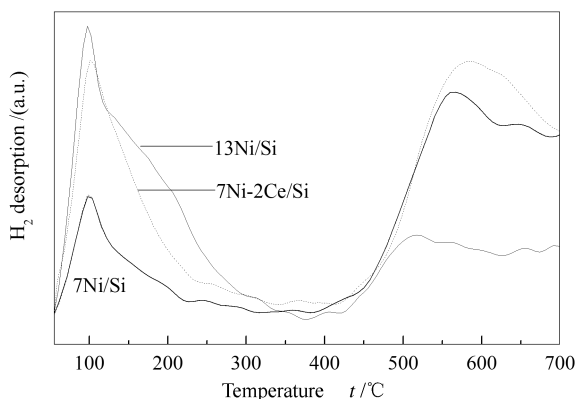


Figure 6 H₂-TPD profiles of the 13Ni/Si, 7Ni-2Ce/Si and 7Ni/Si catalysts

2.2.7 CO-TPD characterization

Figure 7 shows the CO-TPD profiles of the 13Ni/Si and the 7Ni-2Ce/Si. One CO desorption peak at about 130 °C is present in the profile of the 13Ni/Si, while there are two peaks around 130 and 170 °C for the 7Ni-2Ce/Si. This shows the presence of two types of CO adsorption sites on the surface of the 7Ni-2Ce/Si, while of only one type on the surface of the 13Ni/Si. The CO adsorption sites corresponding to 170 °C improved the CO adsorption

ability on the 7Ni-2Ce/Si. In combination with the XRD result, it can be deduced that the appropriate interaction among the NiO, CeO₂ and SiO₂ enhanced the dispersion of NiO species, promoted the formation of a new type of moderately strong CO adsorption sites, improved the CO adsorption capacity, and consequently, increased the catalytic activity of the 7Ni-2Ce/Si. Therefore, the 7Ni-2Ce/Si with low Ni loading exhibited higher CO methanation catalytic activity than the 13Ni/Si catalyst with high Ni loading.

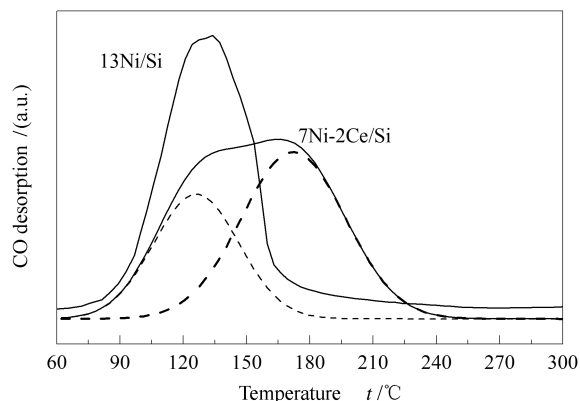


Figure 7 CO-TPD profiles of the 13Ni/Si and 7Ni-2Ce/Si catalysts

3 Conclusions

The addition of Ce led to an interaction among the NiO, CeO₂ and SiO₂. Although this does not have strong effects on the texture properties of the catalyst, but significantly increased the NiO dispersion degree and the active surface area and decreased the interaction of the active component with the support. In addition, a new type of moderately strong CO adsorption sites was formed on the surface of the 7Ni-2Ce/Si catalyst. This results in the 7Ni-2Ce/Si with high CO adsorption and activation ability, and hence, with high catalytic activity for CO methanation despite that its H₂ desorption amount was smaller than that of the 13Ni/Si. The work provides an effective way for decreasing the Ni loading of Ni-based catalysts but improving their catalytic properties such as CO methanation activity.

References

- [1] WU R F, ZHANG Y, WANG Y Z, GAO C G, ZHAO Y X. Effect of ZrO₂ promoter on the catalytic activity for CO methanation and adsorption performance of the Ni/SiO₂ catalyst[J]. Journal of Fuel Chemistry and Technology, 2009, **37**(5): 578-582.
- [2] PARK E D, LEE D, LEE H C. Recent progress in selective CO removal in a H₂-rich stream[J]. Catal Today, 2009, **139**(4): 280-289.
- [3] WANG N, SUN Z J, WANG Y Z, GAO X Q, ZHAO Y X. Preparation of bimetallic Ni-Fe/ γ -Al₂O₃ catalyst and its activity for CO methanation[J]. Journal of Fuel Chemistry and Technology, 2011, **39**(3): 219-223.
- [4] WANF B W, SHANG Y G, DING G Z, WANG H Y, WANG E D, LI Z H, MA X B, QIN S D, SUN Q. Ceria-alumina composite support on the sulfur-resistant methanation activity of Mo-based catalyst[J]. Journal of Fuel Chemistry and Technology, 2012, **40**(11): 1390-1396.
- [5] GALLETI C, SPECCHIA S, SARACCO G and SPECCHIA V. CO selective methanation over Ru/ γ -Al₂O₃ catalysts in H₂-rich gas for PEMFC applications[J]. Chem Eng Sci, 2010, **65**(1): 590-596.
- [6] DAGLE R A, WANG Y, XIA G G, STROHM J J, HOLLADAY J, PALO D R. Selective CO methanation catalysts for fuel processing applications[J]. Appl Catal A: Gen, 2007, **326**(2): 213-218.

- [7] TRIMM D L. Minimisation of carbon monoxide in a hydrogen stream for fuel cell application[J]. Appl Catal A: Gen, 2005, **296**(1): 1-11.
- [8] SONG L, CHEN T H, LI Y X, LIU H B, KONG D J, CHEN D. Performance of palygorskite supported Cu-Mn-Ce catalyst for catalytic oxidation of toluene[J]. Chinese Journal of Catalysis, 2011, **32**(4): 652-656.
- [9] WANG W, WANG J B, ZHU W P, YANG S X, HE W J, CHUN X. Catalytic wet air oxidation of acetic acid and phenol with Ru/ZrO₂-CeO₂ catalysts[J]. Journal of Molecular Catalysis(China), 2007, **21**(5): 401-405.
- [10] ZHAO B X, LIU L X, ZHANG Y Z, CAO X, ZHANG X L, JIN Q T. Effect of doped CeO₂ loading on catalytic activity of Cu-Ni-Ce/SiO₂ catalyst[J]. Journal of Molecular Catalysis(China), 2008, **22**(6): 507-512.
- [11] LIAO Q L, LIANG Z C, QIN Y N, TIAN J X. Promoting effects of La₂O₃ and CeO₂ on catalytic activity of Ni catalysts[J]. Journal of the Chinese Society of Rare Earths, 1995, **13**(1): 35-38.
- [12] JIN R C, CHEN Y X, LI W Z, JI Y Y, QIN Y S, JIANG Y. Ni/ α -Al₂O₃ catalyst for the partial oxidation of methane to syngas[J]. Acta Physico-Chimica Sinica, 1998, **14**(8): 737-741.
- [13] ZHENG W Q, ZHANG J, GE Q J, XU H Y, LI W Z. Effects of CeO₂ addition on Ni/Al₂O₃ catalysts for the reaction of ammonia decomposition to hydrogen[J]. Appl Catal B: Environ, 2008, **80**(1/2): 98-105.
- [14] LI F M, WANG Y Z, ZHANG Z, ZHAO Y X. Promoting effects of Ce promoter on catalytic activity of Ni/SiO₂ catalyst for CO methanation[J]. Ind Catal, 2011, **19**(11): 70-74.
- [15] WEI S Q, LI L B, SHUANG Y C, XU H Y, XU G L. Study on performance of co-precipitated Ni-La₂O₃/ZrO₂ catalyst for CO₂ methanation[J]. Nat Gas Chem Ind, 2004, **29**(5): 10-13.
- [16] WANG Y Z, WU R F, ZHAO Y X. Effect of ZrO₂ promoter on structure and catalytic activity of the Ni/SiO₂ catalyst for CO methanation in hydrogen-rich gases[J]. Catal Today, 2010, **158**(3/4): 470-474.
- [17] TOHJI K, UDAGAWH Y, TANABE S, UENO A. Catalyst preparation procedure probed by EXAFS spectroscopy. 1. Nickel on silica[J]. J Am Chem Soc, 1984, **106**(3): 612-617.
- [18] VELU S, GANGWAL S K. Synthesis of alumina supported nickel nanoparticle catalysts and evaluation of nickel metal dispersions by temperature programmed desorption[J]. Solid State Ion, 2006, **177**(7/8): 803-811.
- [19] GAO X Q, WANG Y Z, LI H T, ZHAO Y X. Effect of manganese promoter on the catalytic performance of Ni/ γ -Al₂O₃ catalyst for CO₂ methanation[J]. Journal of Molecular Catalysis(China), 2011, **25**(1): 49-53.
- [20] LU G Z, WANG R. Effect of CeO₂ on the adsorption capacity of NO, CO on the Cu-Mn-O catalyst[J]. Journal of the Chinese Society of Rare Earths, 1993, **11**(4): 311-316.

高镍负载量 Ni/SiO₂ 和低镍负载量 Ni-Ce/SiO₂ 催化 CO 甲烷化的比较研究

王永钊, 李凤梅, 程慧敏, 范莉渊, 赵永祥

(山西大学化学化工学院 精细化学品教育部工程研究中心, 山西 太原 030006)

摘要: 采用等体积浸渍法制备了高镍负载量的 13% Ni/SiO₂ (13Ni/Si) 催化剂和低镍负载量的 7% Ni-2% Ce/SiO₂ (7Ni-2Ce/Si) 催化剂。通过 N₂ 物理吸附、XRD、FT-IR、TEM、H₂-TPR/TPD 等技术对催化剂进行表征, 在连续流动微反装置上考察了催化剂的 CO 甲烷化活性。结果表明, 在 7Ni-2Ce/Si 催化剂中 NiO、CeO₂ 和 SiO₂ 之间产生的相互作用, 改变了 Ni-O-Si 键的化学环境, 促进了氧化镍物种的分散和还原, 进而提高了催化剂的活性比表面积, 同时在催化剂表面形成了新的中等强度的 CO 吸附中心。与高镍负载量的 13Ni/Si 催化剂相比, 低镍负载量的 7Ni-2Ce/Si 表现出更高的 CO 吸附能力和甲烷化活性。常压下, 在 CO 体积分数 1% 和空速 7 000 h⁻¹ 的反应条件下, 低镍负载量的 7Ni-2Ce/Si 催化剂上 CO 完全甲烷化最低温度为 230 °C, 比高镍负载量的 13Ni/Si 低了 30 °C。

关键词: CO 甲烷化; Ni-Ce/SiO₂ 催化剂; CeO₂ 助剂; 镍负载量

中图分类号: O643 **文献标识码:** A