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Article

Effect of decomposition of catalyst precursor on Ni/CeO₂ activity for CO methanation

Xiaoshan Zhang, Ning Rui, Xinyu Jia, Xue Hu, Chang-jun Liu *

Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

ARTICLE INFO

Article history:

Received 20 October 2018

Accepted 25 December 2018

Published 5 April 2019

Keywords:

Nickel

CeO₂

Carbon monoxide

Syngas

Methanation

Plasma

ABSTRACT

CO methanation on Ni/CeO₂ has recently received increasing attention. However, the low-temperature activity and carbon resistance of Ni/CeO₂ still need to be improved. In this study, plasma decomposition of nickel nitrate was performed at ca. 150 °C and atmospheric pressure. This was followed by hydrogen reduction at 500 °C in the absence of plasma, and a highly dispersed Ni/CeO₂ catalyst was obtained with improved CO adsorption and enhanced metal-support interaction. The plasma-decomposed catalyst showed significantly improved low-temperature activity with high methane selectivity (up to 100%) and enhanced carbon resistance for CO methanation. For example, at 250 °C, the plasma-decomposed catalyst showed a CO conversion of 96.8% with high methane selectivity (almost 100%), whereas the CO conversion was only 14.7% for a thermally decomposed catalyst.

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1. Introduction

The production of methane from synthetic gas (CO and H₂) is an important process for clean coal utilization. This reaction is called CO methanation. It has important applications in the removal of trace CO for ammonia production and gas purification of fuel cells. Recently, CO methanation has also been exploited for utilization of biomass and waste hydrogen. With the development of solar hydrogen production, methanation has a potential application in energy storage. Various catalysts have been confirmed to be active for CO methanation, including supported noble metal (Pd, Rh, and Ru) and supported nickel (Ni) catalysts [1,2]. Among these catalysts, the supported nickel catalyst is most attractive because it is less expensive but exhibits comparable activity to those supported noble metal catalysts. However, there exist two major challenges in using

supported Ni catalysts for CO methanation. One is that the low-temperature activity needs to be improved, and the other is carbon deposition on the catalyst, which ultimately leads to catalyst deactivation. To design a better catalyst with enhanced carbon resistance for CO methanation, two general mechanisms have been proposed [3]. One mechanism involves the reaction of adsorbed hydrogen (H_{ad}) with adsorbed carbon monoxide (CO_{ad}) to form COH_{ad}, CHO_{ad}, or CHOH_{ad} intermediates, followed by C–O bond breaking. The other mechanism involves direct dissociation of adsorbed CO_{ad} to form surface carbon (C_{ad}) as the methanation intermediate. For the second mechanism, the formed carbon must be highly reactive. The balance between carbon formation and hydrogenation determines the catalytic activity and stability. If carbon formation occurs more rapidly than hydrogenation, carbon accumulation and deposition on the metallic Ni surface occur, ultimately

* Corresponding author. Fax: +86-22-27406490; E-mail: ughg_cjl@yahoo.com, coronacj@tju.edu.cn

This work was supported by the National Natural Science Foundation of China (21476157, 21536008 and 21621004), and the National Key R&D Program of China (2016YFB0600902).

DOI: S1872-2067(19)63289-4 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 40, No. 4, April 2019

leading to catalyst deactivation. Significant efforts have been made toward preparation of Ni catalysts with enhanced carbon resistance and improved low-temperature activity. These efforts include but are not limited to the following: (1) limiting the catalyst size [4–6], (2) using structure-controlled preparation of the catalyst [6–8], (3) improving the Ni-support interaction [9,10], (4) using structured supporting materials [11,12], and (5) improving the support properties [13,14]. In fact, all these efforts aim at better control of the catalyst size and structure. Previous studies have confirmed that using a small catalyst enhances the carbon resistance of Ni catalysts for CO methanation [4–14]. It has also been observed that catalysts with Ni(111) as the principal exposed facet show excellent carbon resistance [6,15,16]. According to the reported works, structure control is more difficult than size control in the preparation of Ni catalysts. At present, the most convenient way to affect the structure of Ni catalysts is indirectly via size control [17]. An increasing number of publications can be found in the literature on the preparation of Ni catalysts with small size (or high dispersion) for CO methanation. For this purpose, decomposition of the catalyst precursor using cold plasma, a type of plasma operated at low temperatures (less than 200 °C), has been found to be a facile and effective way with less use of chemicals in order to make the catalysts in small size or high dispersion [15–18]. Previous studies have confirmed that plasma-decomposed Ni/SiO₂ [4,6,15] and Ni/Ce/SBA-15 [19] catalysts exhibit high dispersion with enhanced activity for CO methanation. In addition, plasma-decomposed Ni/MgAl₂O₄ [20], Ni/TiO₂ [21], Ni-La/Al₂O₃ [22], Ni/CeO₂ [23], Ni/Al₂O₃ [23], and Ni/CeO₂-Al₂O₃ [23,24] show improved activity for CO₂ methanation. Cold plasma contains abundant highly energetic species such as electrons, excited species, and radicals. They can induce more rapid decomposition of the nickel precursor at temperatures below 200 °C than conventional thermal decomposition. Under the influence of cold plasma, rapid nucleation but slow crystal growth is established, which helps to limit the catalyst size while improving the dispersion [15,16,18]. This plasma decomposition method has been applied to preparation of catalysts other than nickel [16,18].

However, there has been no investigation of plasma decomposition for preparation of Ni/CeO₂ for CO methanation. According to the reported works in the literature, Ni/CeO₂ shows better activity for methanation of CO and CO₂ [23,25–27] than Ni catalysts supported by other oxides, because of its unique Ce–O–Ni interaction [25]. The enhanced CO₂ adsorption on CeO₂ improves the activity of Ni/CeO₂ for CO₂ methanation [26,27]. Because a previous study has confirmed that plasma-decomposed Ni/CeO₂ exhibits improved activity for CO₂ methanation [23], it is essential to investigate the properties of plasma-decomposed Ni/CeO₂ for CO methanation. The reason is not only that plasma-decomposed Ni/CeO₂ may show improved activity for CO methanation, but also that CO₂ methanation may take the pathway of CO methanation [20,21]. In this work, we attempt to use cold plasma decomposition to prepare Ni/CeO₂ for CO methanation. Significantly improved activity is demonstrated.

2. Experimental

2.1. Catalyst preparation

Incipient wetness impregnation was employed for catalyst preparation. Dielectric barrier discharge (DBD) was applied for plasma decomposition of the catalyst precursor. DBD plasma is a conventional cold plasma that has been extensively used for ozone generation, polymer surface treatment, TV monitors, UV lighting, and many other applications. The CeO₂ support was prepared by calcining Ce(NO₃)₃·6H₂O (Tianjin Kemiou Chemical Reagent, AR) at 500 °C for 3 h. An aqueous solution of nickel nitrate (Ni(NO₃)₂·6H₂O, Tianjin Kemiou Chemical Reagent, AR) was used for the impregnation operation. After impregnation, the obtained sample was held at room temperature for 12 h and then dried at 110 °C for 12 h. The sample was then separated into two parts. One part was calcined at 500 °C for 3 h, where a heating rate of 10 °C/min was used to reach 500 °C. The resulting sample is denoted as NiO/CeO₂-C. The other part was decomposed by the DBD plasma. Plasma decomposition was operated for 1 h. The temperature for plasma decomposition kept below 150 °C, as measured by thermal imaging. The obtained sample is denoted as NiO/CeO₂-DBD. After hydrogen reduction, the samples are labeled Ni/CeO₂-C and Ni/CeO₂-DBD, respectively. The Ni loading is 10 wt% for Ni/CeO₂-C and Ni/CeO₂-DBD.

The DBD plasma setup has been described in detail in our previous work [28]. The plasma is normally generated between two steel plate electrodes, one grounded and the other supplied with a high voltage. For a typical DBD plasma, the electrodes are covered by a dielectric material (quartz in this work). The diameter of the steel plates applied in this work was 50 mm. The steel electrodes were covered by quartz plates with a thickness of 2.5 mm and diameter of 90 mm. Air was directly applied as the plasma-forming gas. A high-voltage generator (CTP-2000K; Corona Laboratory, Nanjing, China) was employed to generate the plasma. An average voltage of 14 kV with a sinusoidal waveform at a frequency of approximately 22 kHz was applied. The average input power was 200 W.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of the catalysts were recorded by a Rigaku D/max-2500 diffractometer equipped with a Ni-filtered Cu K_α radiation source ($\lambda = 1.54056$ Å) over a 2θ range of 10° to 90° at a scanning speed of 4°/min. The X-ray source was operated at 40 kV and 200 mA. Phase identification was made by comparison with the Joint Committee on Powder Diffraction Standards.

The specific surface area of the catalyst was evaluated by the Brunauer–Emmett–Teller (BET) method using N₂ adsorption (AUTOSORB-1-C). Prior to the measurements, samples were evacuated at 200 °C for 2 h.

H₂ temperature-programmed reduction (H₂-TPR) was carried out using an AutoChem1 II 2920 instrument. A 100 mg sample of NiO/CeO₂-C or NiO/CeO₂-DBD was pretreated with He (30 mL/min) at 200 °C for 1 h. Next, H₂-TPR measurement

was performed from room temperature to 800 °C at a heating rate of 10 °C/min under a 5% H₂/He gas mixture (30 mL/min). The amount of hydrogen consumed was analyzed using a thermal conductivity detector (TCD).

CO temperature-programmed desorption (CO-TPD) was conducted using a TPDRO 1100 apparatus (Thermo Finnigan, LLC) equipped with a TCD to obtain CO signals. Approximately 100 mg of the sample was pretreated in helium (30 mL/min) from 50 to 500 °C at a heating rate of 10 °C/min. Hydrogen (30 mL/min) was then introduced to reduce the catalyst for 1 h. Next, the temperature was decreased to 50 °C in helium (30 mL/min). Then 5 vol% CO/He (30 mL/min) flowed through the sample for 30 min. The catalyst was then purged with helium (30 mL/min) for 1 h. The TCD signal was then collected under a helium (30 mL/min) stream by ramping from 50 to 900 °C at a heating rate of 10 °C/min. CaO and NaOH were used to remove CO₂ and H₂O in the exhaust gas before the TCD detector.

CO pulse chemisorption was conducted using the same equipment as used for CO-TPD. A sample of NiO/CeO₂ (100 mg) was heated from room temperature to 500 °C at 10 °C/min under helium (30 mL/min) and then reduced by hydrogen (30 mL/min) at 500 °C for 1 h, followed by helium (30 mL/min) purging at 500 °C for 1 h. Next, the sample was cooled to 50 °C in flowing helium. Then 5% CO/He was pulsed over the catalyst at 50 °C. The signals were collected by a TCD.

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was carried out on a Tensor 27 spectrometer (Bruker) with a high-temperature reaction chamber (Praying Mantis, Harrick) with ZnSe windows. The sample (approximately 25 mg) was reduced under H₂ (20 mL/min) for 1 h at 500 °C before characterization. It was then placed in the sample cup of the high-temperature cell. The sample was reduced *in situ* at 300 °C for 1 h using flowing 5% H₂ (20 mL/min; Ar-balanced), followed by purging with Ar (20 mL/min) for 1 h. Then the sample was cooled to 250 °C. At this point, a background spectrum was recorded. Next, 1.1% CO/Ar (20 mL/min) was flowed through the sample cell at 250 °C for 30 min, and the spectrum was recorded. The spectrum was recorded at a resolution of 4 cm⁻¹ and 64 scans, and the background spectrum was subtracted. The data were in Kubelka-Munk units, which are linear with respect to the concentration of surface species.

X-ray photoelectron spectroscopy (XPS) analyses were performed using a Perkin Elmer PHI-1600 spectrometer with Mg K_α ($h\nu = 1254$ eV) radiation. The binding energies were calibrated using a reference C 1s peak (284.6 eV).

High-resolution scanning transmission electron microscopy (HRSTEM) analyses were performed on a Philips Tecnai G2F20 system operated at 200 kV. The sample powder was ultrasonically dispersed in ethanol for 30 min. A drop of the suspension was deposited on a copper grid coated with carbon and then dried in air.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on a Netzsch STA 449 F3 system under flowing air at 100 mL/min and a heating rate of 10 °C/min from 35 to 700 °C.

2.3. Activity test

CO methanation was carried out under atmospheric pressure in a quartz-tube fixed-bed reactor. The catalyst (50 mg, 40–60 mesh) with 100 mg of SiC was loaded into the quartz tube. Before reaction, the sample was heated to 500 °C under argon (20 mL/min). Then the sample was reduced at 500 °C for 1 h under hydrogen (20 mL/min). After reduction, the temperature was decreased to 235 °C in flowing argon (20 mL/min). Then the reaction was carried out under a gas flow of 40 mL/min at a carbon monoxide/hydrogen ratio of 1:6. The effluent was analyzed online by a gas chromatograph (GC; Agilent 6890, USA) with a 2 m carbon molecular sieve (TDX-01) column and a TCD using argon as the carrier gas. A cold trap was placed before the GC to remove water from the effluent. For the stability test, CO methanation was performed continuously at 300 °C for 10 h.

The CO conversion rate ($\text{mol}_{\text{CO}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$) is calculated by the following equation:

$$\text{CO conversion rate} = F_{\text{inCO}} \cdot X_{\text{CO}} / W \quad (1)$$

where F_{inCO} ($\text{mol}_{\text{CO}}/\text{h}$) is the inlet mole flow rate of CO, X_{CO} (%) is the CO conversion, and W (g) is the catalyst weight.

The CO conversion (X_{CO} , %) and CH₄ selectivity (S_{CH_4} , %) are calculated using formulas based on carbon balance:

$$X_{\text{CO}} = (F_{\text{CO,in}} - F_{\text{CO,out}}) / F_{\text{CO,in}} \times 100\% \quad (2)$$

$$S_{\text{CH}_4} = F_{\text{CH}_4,\text{out}} / (F_{\text{CO,in}} - F_{\text{CO,out}}) \times 100\% \quad (3)$$

where $F_{\text{CO,in}}$ (mL/min) and $F_{\text{CO,out}}$ (mL/min) are the inlet and outlet flow rates of CO, respectively, and $F_{\text{CH}_4,\text{out}}$ (mL/min) is the outlet flow rate of CH₄.

The CO methanation activity was characterized by the turnover frequency (TOF) of Ni surface atoms (expressed as moles of CO converted per second per mole surface Ni atoms). The TOF (s^{-1}) was calculated from data at low CO conversion ($X_{\text{CO}} < 10\%$ at 235 °C) using the following equation:

$$\text{TOF} = F_{\text{inCO}} \cdot X_{\text{CO}} / (m_{\text{Ni}} \cdot D)$$

where m_{Ni} is the number of supported metallic Ni particles, and D is the Ni dispersion.

3. Results and discussion

3.1. Catalytic activity

Fig. 1 shows the CO conversion and CH₄ selectivity of Ni/CeO₂-C and Ni/CeO₂-DBD. Ni/CeO₂-DBD exhibits superior CO conversion. In particular, at 250 °C, the CO conversion reaches 96.8% over Ni/CeO₂-DBD. However, it is only 14.7% over Ni/CeO₂-C. At 235 °C, the CO conversions of Ni/CeO₂-C and Ni/CeO₂-DBD are below 15%. A dramatic increase in CO conversion from 11.3% at 235 °C to 96.8% at 250 °C is observed over Ni/CeO₂-DBD. At 300 °C, both the CO conversion and CH₄ selectivity reach 100% for Ni/CeO₂-DBD. From 300 to 500 °C, the CO conversion remains high for both catalysts. Obviously, the low-temperature activity over the DBD-decomposed Ni catalyst was significantly improved compared to that over Ni/CeO₂-C. The activity of Ni/CeO₂-DBD is even higher than that over most of the reported catalysts, as shown in Table S1 (Supporting Information). The TOF values

Fig. 1. (a) CO conversion and (b) CH₄ selectivity of Ni/CeO₂-C and Ni/CeO₂-DBD. Gas hourly space velocity (GHSV) = 48000 mL g_{cat}⁻¹ h⁻¹; CO/H₂ = 1:6.

for CO conversion at 235 °C are 0.07 and 0.09 s⁻¹ over Ni/CeO₂-C and Ni/CeO₂-DBD, respectively. It is obvious that Ni/CeO₂-DBD shows a higher TOF value, which indicates higher low-temperature activity of Ni/CeO₂-DBD.

3.2. Catalyst characterization

The XRD patterns of the Ni/CeO₂-C and Ni/CeO₂-DBD catalysts are presented in Fig. 2. The diffraction peaks at 28.6°, 33.1°, 47.5°, and 59.3° represent the CeO₂(111), (200), (220), and (311) lattice planes, respectively (PDF #34-0394). The peaks at 44.4° and 51.7° can be assigned to Ni(111) and Ni(200), respectively (PDF #65-2865). As shown in Fig. 2, Ni/CeO₂-C exhibits more intense and narrower nickel peaks, suggesting a larger crystallite size than Ni/CeO₂-DBD. The nickel crystallite sizes of Ni/CeO₂-C and Ni/CeO₂-DBD are 24.4 and 12.0 nm, respectively, according to calculations using the Scherrer equation for the Ni(111) plane.

Table 1 shows the specific surface area of the Ni/CeO₂-C and Ni/CeO₂-DBD catalysts. Compared to that of pure CeO₂, the surface area of the supported catalysts is reduced. Ni/CeO₂-DBD shows a larger surface area and pore volume

than Ni/CeO₂-C, because Ni/CeO₂-DBD has a smaller Ni size and higher Ni dispersion. This is consistent with the results of XRD analysis and CO pulse chemisorption, as discussed below.

The metal dispersion was determined by CO pulse chemisorption [29]. The surface area of Ni was calculated by assuming the stoichiometric ratio of CO/Ni_{surface} to be 1. The Ni dispersions obtained from CO pulse chemisorption are also shown in Table 1. The values for Ni/CeO₂-C and Ni/CeO₂-DBD are 3.73% and 6.30%, respectively. This result supports the XRD finding that Ni dispersion on CeO₂ is significantly enhanced by DBD plasma decomposition. From the Ni surface area, the diameter of the Ni particles can be obtained using a hemisphere model. The results are shown in Table 1.

In addition, the number of active metal sites of the catalysts was estimated by CO pulse chemisorption. When the interaction between the metal and support is ignored, the relative value of the CO uptake can be used to calculate the number of active sites for the catalysts [30], as each adsorbed CO molecule corresponds to one metal active site. The CO uptake is 52.8 and 78.8 μmol/g_{cat} for Ni/CeO₂-C and Ni/CeO₂-DBD, respectively. This result demonstrates that Ni/CeO₂-DBD has more metal active sites, which are beneficial for CO methanation.

The reducibility and metal-support interaction were estimated using H₂-TPR. The H₂-TPR profiles of NiO/CeO₂-C and NiO/CeO₂-DBD are shown in Fig. 3. The reduction temperature

Fig. 2. XRD patterns of Ni/CeO₂-C and Ni/CeO₂-DBD catalysts.

Table 1
Structural properties of Ni/CeO₂ catalysts.

Sample	<i>S</i> _{BET} ^a (m ² /g _{cat})	<i>V</i> _{pore} ^a (cm ³ /g _{cat})	Ni disper- sion ^b (%)	<i>D</i> _{Ni} ^b (nm)	<i>D</i> _{Ni} ^c (nm)	CO uptake ^b (μmol/g _{cat})
Ni/CeO ₂ -C	37.39	0.13	3.73	27.2	24.4	52.8
Ni/CeO ₂ -DBD	66.50	0.19	6.30	16.1	12.0	78.8
CeO ₂	88.67	0.20	—	—	—	—

^a BET surface area and pore volume are determined by the nitrogen adsorption isotherms at -196 °C.

^b Ni dispersion, Ni particle diameter, and CO uptake are estimated from CO pulse chemisorption at 50 °C.

^c Nickel crystallite size is estimated from XRD-based Scherrer equation for the Ni(111) plane.

of NiO is related to the particle size of NiO and the metal-support interaction [31]. Two broad peaks at 429 °C (for NiO/CeO₂-C) and 423 °C (for NiO/CeO₂-DBD) can be attributed to surface reduction of CeO₂ [32]. The peak at 127 °C for both catalysts can be attributed to reduction of adsorbed oxygen species [33,34]. NiO/CeO₂-C exhibits three NiO reduction peaks. The peak at 169 °C can be ascribed to reduction of free bulk NiO [35]. Further, the peak at 250 °C can be identified as the reduction peak of NiO interacting weakly with CeO₂ [32]. The peak at 293 °C can be attributed to reduction of NiO interacting strongly with the support [34]. However, NiO/CeO₂-DBD exhibits four NiO reduction peaks. There is a smaller peak at 184 °C, which is identified as free NiO. The peak position for NiO particles interacting weakly with CeO₂ is shifted to a lower temperature of 220 °C compared with that of NiO/CeO₂-C, indicating the presence of more easily reduced NiO. This reducible NiO is beneficial for methanation at low reaction temperature [36]. A shoulder peak centered at 257 °C appears for Ni/CeO₂-DBD, which can be assigned to the moderate interaction between NiO and the support. This peak is absent for NiO/CeO₂-C. The last peak for NiO reduction is clearly shifted to a higher temperature of 330 °C with a larger area for NiO/CeO₂-DBD, which implies stronger interaction between NiO and the support.

CO-TPD analyses were carried out to analyze the interaction between the catalyst and CO. The TPD profiles are shown in Fig. 4. Ni/CeO₂-C exhibits an intense peak at 500 °C and a broad peak centered at 677 °C, in good agreement with the literature [37]. Ni/CeO₂-DBD exhibits three peaks at 518, 662, and 752 °C. For the two catalysts, the peaks at 500 and 518 °C are attributed to CO desorption from CeO₂. The peaks observed at 662, 677, and 752 °C are desorption peaks of CO adsorbed on the metallic Ni [25,37]. The CO desorption temperatures of Ni/CeO₂-DBD are higher than those of Ni/CeO₂-C. This indicates that the CO adsorption strength is enhanced over Ni/CeO₂-DBD. Moreover, the amount of CO desorbed from Ni/CeO₂-DBD (area under the curve) is slightly higher than that of Ni/CeO₂-C. This suggests stronger adsorption of CO over Ni/CeO₂-DBD. The improved CO adsorption can be interpreted as enhanced metal-support interaction [25,27], which further

Fig. 4. CO-TPD profiles of Ni/CeO₂-C and Ni/CeO₂-DBD.

promotes electron transfer from the support to nickel. For partial electron transfer from the support to the metal, the electron donation effect can strengthen the bond between the metal and carbon because of electron donation from the metal to the antibonding π orbital of the adsorbed CO. Consequently, the C–O bond of CO adsorbed on the metal can be weakened. Therefore, CO dissociation is enhanced, and the adsorbed C is hydrogenated to methane, promoting CO methanation.

DRIFT spectroscopy was conducted to clarify the surface species of the catalysts. Fig. 5 presents the spectra of Ni/CeO₂-C and Ni/CeO₂-DBD under a CO-containing gas (1.1 vol% CO in Ar) at 250 °C. The spectrum was collected after 30 min of adsorption. The bands at 2110 and 2174 cm⁻¹ originate from gaseous CO. Bridged CO and linear CO on Ni appear at 1926 and 2068 cm⁻¹ for Ni/CeO₂-DBD, respectively [38,39]. On the surface of CeO₂, the bands contain monodentate carbonates (m-CO₃²⁻) (1371, 1392, and 1477 cm⁻¹), bidentate carbonates (b-CO₃²⁻) (1290, 1329, 1566, and 1588 cm⁻¹), and hydrocarbonates (HCO₃⁻) (1427 and 1612 cm⁻¹) [10,39,40]. Ni/CeO₂-DBD exhibits stronger band intensities than Ni/CeO₂-C, indicating that it has more active sites for CO ad-

Fig. 3. H₂-TPR profiles of NiO/CeO₂-C and NiO/CeO₂-DBD.

Fig. 5. DRIFT spectra of Ni/CeO₂-C and Ni/CeO₂-DBD at 250 °C under adsorption with 1.1 vol% CO in Ar (20 mL/min) for 30 min.

sorption. The terminal nickel carbonyl and bridged nickel carbonyl bands of Ni/CeO₂-DBD are obviously red-shifted compared to those of Ni/CeO₂-C. This frequency shift to lower values indicates the electron-donating properties of the support for Ni/CeO₂-DBD [39].

As discussed above, one of the reasons for the higher activity of the plasma-decomposed catalyst is enhanced electron migration from the support to nickel. In addition, the higher surface area and more numerous active sites are also beneficial for CO methanation. As there are more Ni active sites on Ni/CeO₂-DBD, more H atoms are dissociated from H₂ on the Ni surface and can promote the methanation process.

XPS spectra were used to investigate the chemical states of cerium and Ni on the reduced catalyst surface, and the results are shown in Fig. 6. For the Ni/CeO₂-DBD sample, the Ni 2p_{3/2} spectrum consists mainly of signals at 852.4 eV (metallic Ni), 853.7 and 855.5 eV (NiO), and 860.9 eV (a satellite peak of NiO, which results from oxidation of Ni under air exposure) [41]. The Ni⁰/(Ni⁰ + NiO) ratios calculated from the integrated areas under the fitted components are 0.19 and 0.24 for Ni/CeO₂-C and Ni/CeO₂-DBD, respectively. This result demonstrates that Ni/CeO₂-DBD has more reducible Ni species [42]. Dissociation of H₂ and the hydrogenation process would be enhanced on more Ni sites. Compared to those of Ni/CeO₂-C, the Ni 2p_{3/2} peaks for metallic Ni of Ni/CeO₂-DBD are shifted toward lower values by approximately 0.2 eV, indicating increased electron density on Ni [43].

The Ce 3d spectra are rather complex owing to the presence

of both Ce³⁺ and Ce⁴⁺. The peaks can be labeled v₀, v, v', v'', and v''', which correspond to Ce 3d_{5/2}, and u₀, u, u', u'', and u''', which correspond to Ce 3d_{3/2}. The four peaks v₀, u₀, u', and v' are indexed as Ce³⁺, and the other six peaks are attributed to Ce⁴⁺ [36,44,45]. The Ce³⁺ content (%) is calculated from the areas of u' and v' according to the following equation [45,46]:

$$\text{Ce}^{3+} = A_{u'} + A_{v'} / \sum (A_u + A_v) \times 100\% \quad (5)$$

where A_i is the area of the corresponding peaks.

The Ce³⁺/(Ce³⁺+Ce⁴⁺) ratio is 24.53% and 35.39% for Ni/CeO₂-C and Ni/CeO₂-DBD, respectively. The higher Ce³⁺ content of Ni/CeO₂-DBD could be related to the presence of more surface oxygen vacancies [45]. It has been reported that oxygen vacancies can be generated by reduction treatment of ceria in H₂ and that hydrogen spillover can facilitate Ce³⁺ generation [47]. The higher Ce³⁺ content can be attributed to enhanced hydrogen spillover from Ni particles to the support, which facilitates ceria reduction [41]. Rombi *et al.* [48] proposed that partially reduced CeO_x would assist dissociation of CO at the nickel-ceria boundary by accepting oxygen, preventing the formation of CO₂ by reaction of adsorbed oxygen with CO.

3.3. Stability

Ten hour stability tests were conducted over Ni/CeO₂-C and Ni/CeO₂-DBD at 300 °C, as shown in Fig. 7. For Ni/CeO₂-C, the CO conversion changed from 96.8% to 94.4% during the stabil-

Fig. 6. XPS Ni 2p_{3/2} and Ce 3d spectra over (a, c) Ni/CeO₂-C and (b, d) Ni/CeO₂-DBD catalysts.

Fig. 7. Stability test at GHSV = 48000 mL g_{cat}⁻¹ h⁻¹ with CO/H₂ ratio of 1:6 at 300 °C.

ity test. In contrast, Ni/CeO₂-DBD showed superior stability. The CO conversion remained constant at 100% over Ni/CeO₂-DBD.

The catalyst deactivation has two possible explanations: nickel aggregation and carbon deposition. In order to evaluate the properties of the used catalysts, HRSTEM and TGA-DSC analyses were conducted. HRSTEM was conducted to evaluate the Ni particle size of Ni/CeO₂ before and after the stability reaction. The results are presented in Figs. 8 and 9, respectively. The average Ni particle sizes are 12.6 and 30.4 nm for fresh Ni/CeO₂-DBD and Ni/CeO₂-C, respectively. After the reaction, the average Ni particle sizes of Ni/CeO₂-DBD and Ni/CeO₂-C increased to 14.1 and 43.2 nm, respectively. This result shows that aggregation of nickel in Ni/CeO₂-C is one reason for the reduced activity during the stability test.

Further TGA-DSC analyses were performed to study the oxidation reactivity of the carbon formed on the catalysts during the reaction. The TGA-DSC result is shown in Fig. 10. TGA was used for quantitative measurement of the carbon formed on the used catalysts after the stability test. The used Ni/CeO₂-DBD has negligible weight loss between 200 and 700 °C compared with the used Ni/CeO₂-C. Overall, little carbon was deposited on both Ni/CeO₂-C and Ni/CeO₂-DBD. The peaks before 200 °C in the DSC curves are attributed to water removal over the catalysts. Between 200 and 300 °C, the weight increase in the TG curve is attributed to oxidation of Ni to NiO and partial reduc-

Fig. 8. HRSTEM images of (a) Ni/CeO₂-C and (b) Ni/CeO₂-DBD catalysts before reaction.

Fig. 9. HRSTEM images of (a) Ni/CeO₂-C and (b) Ni/CeO₂-DBD catalysts after 10 h stability test.

tion of CeO_{2-x} to CeO₂. Further, the weight increase for the used Ni/CeO₂-DBD is much higher than that for the used Ni/CeO₂-C from 200 to 300 °C, demonstrating that more nickel is oxidized in this temperature range. This result shows that, after the reaction, more active nickel remains in the Ni/CeO₂-DBD catalyst. The peak centered at 321 °C is attributed mainly to carbon dissolved in the Ni particles in the used Ni/CeO₂-C [49]. However, the exothermic peak at higher temperature, centered at 493 °C, is attributed to oxidation of deposited carbon. Over Ni/CeO₂-DBD, there is a weak oxidation peak at 440 °C, which indicates small amounts of carbon oxidized at low temperatures. Carbon oxidation occurs at higher temperatures over Ni/CeO₂-C than over Ni/CeO₂-DBD. This suggests that the carbon deposited after the methanation reaction on Ni/CeO₂-C is more difficult to oxidize. This is consistent with our previous studies of methanation over other supporting materials [6,50]. The carbon formed on Ni/CeO₂-DBD at a lower oxidation temperature is more reactive. During the reaction, the carbon intermediate formed on Ni/CeO₂-DBD can be removed easily by hydrogen atoms that spill over from the Ni particles. Therefore, Ni/CeO₂-DBD is more stable for CO methanation.

4. Conclusions

In this work, plasma decomposition of nickel nitrate at ca.

Fig. 10. TGA-DSC profiles of Ni/CeO₂-C and Ni/CeO₂-DBD after stability test at 300 °C for 10 h.

150 °C was performed. It was followed by hydrogen reduction at 500 °C in the absence of plasma, and a highly dispersed Ni/CeO₂ catalyst was obtained. The obtained Ni/CeO₂ catalyst shows enhanced metal-support interaction, intensified CO adsorption, more oxygen vacancies, better low-temperature activity, better stability, and improved carbon resistance for CO methanation. The methane selectivity of the plasma-decomposed catalyst is also very high (up to 100%). The reaction rate of the plasma-decomposed Ni/CeO₂ catalyst for CO methanation is higher than that on most of the Ni catalysts reported in the literature.

References

- [1] J. Gao, Q. Liu, F. Gu, B. Liu, Z. Zhong, F. Su, *RSC Adv.*, **2015**, 5, 22759–22776.
- [2] S. Tada, R. Kikuchi, *Catal. Sci. Technol.*, **2015**, 5, 3061–3070.
- [3] B. Miao, S. S. K. Ma, X. Wang, H. B. Su, S. H. Chan, *Catal. Sci. Technol.*, **2016**, 6, 4048–4058.
- [4] B. R. Zhao, Z. P. Chen, Y. J. Chen, X. X. Ma, *Int. J. Hydrogen Energy*, **2017**, 42, 27073–27083.
- [5] P. P. Li, M. Y. Zhu, J. M. Dan, L. H. Kang, L. F. Lai, X. Y. Cai, J. S. Zhang, F. Yu, Z. Tian, B. Dai, *Chem. Eng. J.*, **2017**, 326, 774–780.
- [6] X. L. Yan, Y. Liu, B. R. Zhao, Z. Wang, Y. Wang, C. J. Liu, *Int. J. Hydrogen Energy*, **2013**, 38, 2283–2291.
- [7] H. Wang, K. Xu, X. Y. Yao, D. H. Ye, Y. Pei, H. R. Hu, M. H. Qiao, Z. H. Li, X. X. Zhang, B. N. Zong, *ACS Catal.*, **2018**, 8, 1207–1211.
- [8] S. S. Li, D. D. Gong, H. G. Tang, Z. Ma, Z. T. Liu, Y. Liu, *Chem. Eng. J.*, **2018**, 334, 2167–2178.
- [9] M. Tao, X. Meng, Y. H. Lv, Z. C. Bian, Z. Xin, *Fuel*, **2016**, 165, 289–297.
- [10] M. V. Konishcheva, D. I. Potemkin, P. V. Snytnikov, O. A. Stonkus, V. D. Belyaev, V. A. S. obyanin, *Appl. Catal. B*, **2018**, 221, 413–421.
- [11] Y. H. Lv, Z. Xin, X. Meng, M. Tao, Z. C. Bian, *Microporous Mesoporous Mater.*, **2018**, 262, 89–97.
- [12] Y. Han, B. Wen, M. Y. Zhu, *Catalysts*, **2017**, 7, 21.
- [13] S. S. Li, H. G. Tang, D. D. Gong, Z. Ma, Liu Y, *Catal. Today*, **2017**, 297, 298–307.
- [14] Q. Liu, F. N. Gu, X. P. Lu, Y. J. Liu, H. F. Li, Z. Y. Zhong, G. W. Xu, F. B. Su, *Appl. Catal. A*, **2014**, 488, 37–47.
- [15] X. L. Yan, B. R. Zhao, Y. Liu, Y. N. Li, *Catal. Today*, **2015**, 256, 29–40.
- [16] C. J. Liu, M. Y. Li, J. Q. Wang, X. T. Zhou, Q. T. Guo, J. M. Yan, Y. Z. Li, *Chin. J. Catal.*, **2016**, 37, 340–348.
- [17] C. Vogt, E. Groeneveld, G. Kamsma, M. Nachtegaal, L. Li, C. J. Kiely, Berben P H, Meirer F, *Nat. Catal.*, **2018**, 1, 128–134.
- [18] Z. Wang, Y. Zhang, E. C. Neyts, X. X. Cao, X. S. Zhang, B. W. L. Jang, C. J. Liu, *ACS Catal.*, **2018**, 8, 2093–2110.
- [19] L. Bian, L. J. Zhang, Z. T. Zhu, Z. H. Li, *Mol. Catal.*, **2018**, 446, 131–139.
- [20] Z. G. Fan, K. H. Sun, N. Rui, B. R. Zhao, C. J. Liu, *J. Energy Chem.*, **2015**, 24, 655–659.
- [21] R. Zhou, N. Rui, Z. G. Fan, C. J. Liu, *Int. J. Hydrogen Energy*, **2016**, 41, 22017–22025.
- [22] F. Guo, W. Chu, H. Y. Xu, T. Zhang, *Chin. J. Catal.*, **2007**, 28, 429–434.
- [23] L. Bian, L. Zhang, R. Xia, Z. H. Li, *J. Nat. Gas Sci. Eng.*, **2015**, 27, 1189–1194.
- [24] Y. Xu, Y. Chen, J. Li, J. Zhou, M. Song, X. Q. Zhang, Y. X. Yin, *Int. J. Hydrogen Energy*, **2017**, 42, 13085–13091.
- [25] B. Nematollahi, M. Rezaei, E. N. Lay, *J. Rare Earths*, **2015**, 33, 619–628.
- [26] C. Fukuhara, K. Hayakawa, Y. Suzuki, W. Kawasaki, R. Watanabe, *Appl. Catal. A*, **2017**, 532, 12–18.
- [27] S. Tada, T. Shimizu, H. Kameyama, T. Haneda, R. Kikuchi, *Int. J. Hydrogen Energy*, **2012**, 37, 5527–5531.
- [28] Y. Tan, H. Liu, X. Y. Liu, A. Q. Wang, C. J. Liu, T. Zhang, *Chin. J. Catal.*, **2018**, 39, 929–936.
- [29] B. Nematollahi, M. Rezaei, E. N. Lay, *Int. J. Hydrogen Energy*, **2015**, 40, 8539–8547.
- [30] L. R. Winter, E. Gomez, B. Yan, S. Yao, J. G. Chen, *Appl. Catal. B*, **2018**, 224, 442–450.
- [31] A. Vita, C. Italiano, L. Pino, P. Frontera, M. Ferraro, V. Antonucci, *Appl. Catal. B*, **2018**, 226, 384–395.
- [32] W. Liu, W. Wang, K. Tang, J. Guo, Y. Ren, S. Wang, L. Feng, Y. Yang, *Catal. Sci. Technol.*, **2016**, 6, 2427–2434.
- [33] S. Mahammadunnisa, P. Manoj Kumar Reddy, N. Lingaiah, C. Subrahmanyam, *Catal. Sci. Technol.*, **2013**, 3, 730–736.

Graphical Abstract

Chin. J. Catal., 2019, 40: 495–503 doi: S1872-2067(19)63289-4

Effect of decomposition of catalyst precursor on Ni/CeO₂ activity for CO methanation

Xiaoshan Zhang, Ning Rui, Xinyu Jia, Xue Hu, Chang-jun Liu *
Tianjin University

Plasma-decomposed Ni/CeO₂ was prepared and characterized. The catalyst shows superior low-temperature activity. At 250 °C, the CH₄ yield on this plasma-decomposed catalyst is 95.6%, whereas it is only 13.6% for the thermally decomposed catalyst.

- [34] P. Zhao, F. Qin, Z. Huang, C. Sun, W. Shen, H. Xu, *Catal. Sci. Technol.*, **2018**, 8, 276–288.
- [35] K. Tang, W. Liu, J. Li, J. Guo, J. Zhang, S. Wang, S. Niu, Y. Yang, *ACS Appl. Mater. Interfaces*, **2015**, 7, 26839–26849.
- [36] J. Ashok, M. L. Ang, S. Kawi, *Catal. Today*, **2017**, 281, 304–311.
- [37] E. T. Saw, U. Oemar, X. R. Tan, Y. Du, A. Borgna, K. Hidajat, S. Kawi, *J. Catal.*, **2014**, 314, 32–46.
- [38] M. V. Konishcheva, D. I. Potemkin, S. D. Badmaev, P. V. Snytnikov, E. A. Paukshtis, V. A. Sobyannin, V. N. Parmon, *Top. Catal.*, **2016**, 59, 1424–1430.
- [39] G. Blyholder, *J. Phys. Chem.*, **1964**, 68, 2772–2777.
- [40] K. Pokrovski, K. T. Jung, A. T. Bell, *Langmuir*, **2001**, 17, 4297–4303.
- [41] M. Li, H. Amari, A. C. van Veen, *Appl. Catal. B*, **2018**, 239, 27–35.
- [42] Y. Yu, Y. M. Chan, Z. Bian, F. Song, J. Wang, Q. Zhong, S. Kawi, *Int. J. Hydrogen Energy*, **2018**, 43, 15191–15204.
- [43] A. Lewera, L. Timperman, A. Roguska, N. Alonso-Vante, *J. Phys. Chem. C*, **2011**, 115, 20153–20159.
- [44] D. Chen, Q. Ma, L. Wei, N. Li, Q. Shen, W. Tian, J. Zhou, J. Long, *J. Anal. Appl. Pyrolysis*, **2018**, 130, 169–180.
- [45] N. Wang, W. Z. Qian, W. Chu, F. Wei, *Catal. Sci. Technol.*, **2016**, 6, 3594–3605.
- [46] M. S. P. Francisco, V. R. Mastelaro, P. A. P. Nascente, A. O. Florentino, *J. Phys. Chem. B*, **2001**, 105, 10515–10522.
- [47] A. Trovarelli, C. deyleitenburg, G. Dolcetti, J. L. Lorca, *J. Catal.*, **1995**, 151, 111–124.
- [48] E. Rombi, M. G. Cutrufello, L. Atzori, R. Monaci, A. Ardu, D. Gazzoli, P. Deiana, I. Ferino, *Appl. Catal. A*, **2016**, 515, 144–153.
- [49] X. L. Yan, Y. Liu, B. R. Zhao, Y. Wang, C. J. Liu, *Phys. Chem. Chem. Phys.*, **2013**, 15, 12132–12138.
- [50] Y. Zhang, W. Wang, Z. Y. Wang, X. T. Zhou, Z. Wang, C. J. Liu, *Catal. Today*, **2015**, 256, 130–136.

Ni/CeO₂前驱体分解方法对CO甲烷化活性的影响

张晓珊, 芮 宁, 贾忻宇, 胡 雪, 刘昌俊*

天津大学化工学院天津化学化工协同创新中心, 天津300072

摘要: CO甲烷化制备合成天然气是煤化工的重要过程之一,也是合成氨过程和燃料电池除去痕量CO的重要反应。CO甲烷化催化剂包括贵金属催化剂和镍基催化剂。其中,镍基催化剂由于具有较好的活性以及较低的成本受到广泛的重视。目前,镍基CO甲烷化催化剂仍需解决的问题是提高低温活性以及抗积碳性能。目前的改进方法主要包括:(1)控制催化剂尺寸;(2)控制催化剂结构;(3)提高Ni-载体的相互作用;(4)使用结构可控的载体;(5)改进载体性质。其中,通过控制催化剂尺寸来控制催化剂结构是一种有效的改进方式。使用冷等离子体来分解镍前驱体是一种快速有效的制备尺寸小、分散度好的镍基催化剂的方法。

本文使用常压介质阻挡放电等离子体(150 °C左右)分解硝酸镍前驱体,得到的催化剂再经过500 °C氢气还原得到高分散Ni/CeO₂催化剂。作为对比,同时采用常规热焙烧方法分解硝酸镍制备了催化剂。对催化剂进行了X射线衍射(XRD)、CO脉冲化学吸附、CO程序升温脱附(CO-TPD)、CO红外漫反射光谱(CO-DFTIR)及X射线光电子能谱(XPS)等分析,同时进行了CO甲烷化反应活性和300 °C下稳定性测试,发现等离子体分解制备得到的催化剂具有更好的CO低温甲烷化性能、更高的CH₄选择性、更好的低温稳定性和抗积碳性能。在250 °C时,等离子体分解法制备的催化剂上的CO转化率能达到96.8%,CH₄选择性接近100%,但是热焙烧分解制备的催化剂上却只有14.7%的CO转化率。在低温(300 °C)稳定性测试中,等离子体分解制备的催化剂具有优异的稳定性。与常规热焙烧方法得到的催化剂相比,等离子体制备得到的催化剂具有高的Ni分散度、更高的CO吸附性能以及更强的金属-载体相互作用。由于金属-载体相互作用被加强,部分电子由载体转移到金属Ni上,增强了金属与CO反键 π 轨道之间的电子密度,C-O键更易断裂,有利于甲烷化的发生。此外,XPS分析表明等离子体制备的催化剂表面有更多的Ce³⁺,证明了更多氧空位的存在。在Ni-载体界面上CO的O原子更容易被CeO₂的氧空位捕获而解离。更高的分散度提供了更多的Ni比表面积,也有利于加氢过程的进行,从而提高甲烷化活性。CO甲烷化稳定性测试之后催化剂的TG-DSC表征结果表明,等离子体分解制备的催化剂具有更少的积碳及更多的活性镍组分,同时催化剂上积碳的氧化温度更低,表明积碳具有更好的反应活性。

综上所述,等离子体低温分解制备的Ni/CeO₂表现出了更大的比表面积、更高的Ni分散度、增强的CO吸附性能和更多的氧空位,促进了CO甲烷化活性的提高。与文献数据相比,该催化剂具有更高的CO转化速率。

关键词: 镍; 氧化铈; 一氧化碳; 合成气; 甲烷化; 等离子体

收稿日期: 2018-10-20. 接受日期: 2018-12-25. 出版日期: 2019-04-05.

*通讯联系人. 传真: (022)27406490; 电子信箱: ughg_cjl@yahoo.com, coronacj@tju.edu.cn

基金来源: 国家自然科学基金(21476157, 21536008, 21621004); 国家重点研发计划(2016YFB0600902).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).