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Article

ZrO₂-modified Ni/LaAl₁₁O₁₈ catalyst for CO methanation: Effects of catalyst structure on catalytic performance

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ABSTRACT

We report Ni/LaHA@ZrO₂ catalysts prepared by a facile modified successive adsorption and reaction method for CO methanation. N₂ adsorption, X-ray diffraction, transmission electron microscopy, scanning electron microscopy, thermogravimetric analysis, H₂ temperature-programmed reduction, H₂ temperature-programmed desorption, X-ray photoelectron spectroscopy, thermogravimetric analysis, and inductively coupled plasma atomic emission spectrometry were used to characterize the samples. The results indicated that the ZrO₂ nanoparticles were distributed over the surface of the Ni/LaHA@ZrO₂ catalyst and even partially covered some Ni particles, resulting in the coating exerting a confinement effect. The excess ZrO₂ had an adverse effect on the enhancement of CO conversion because of the coverage of the surface Ni particles; however, the Ni/LaHA@ZrO₂ catalyst displayed much higher CH₄ selectivity than Ni/LaHA because of the activation of the byproduct CO₂ molecules by ZrO₂ species. Therefore, even though 20Ni/LaHA@ZrO₂-5 exhibited similar CO conversion as 20Ni/LaHA, the use of the former resulted in a higher CH₄ yield than the use of the latter. A 107-h-lifetime test revealed that the Ni/LaHA@ZrO₂ catalyst was highly stable with superior anti-sintering and anti-coking properties because of its coating structure and the promoter effect of ZrO₂.

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1. Introduction

The CO methanation reaction from syngas has attracted intensive attention from both academia and industry, especially in coal-rich regions and countries such as China [1–4]. This reaction is strongly exothermic and thermodynamically feasi-

ble ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$, $\Delta H_{298\text{K}} = -206.1 \text{ kJ mol}^{-1}$), leading to high demand for methanation catalysts. Ideal catalysts should be highly active at low temperatures ($\sim 300^\circ\text{C}$) and highly stable at high temperatures ($\sim 600^\circ\text{C}$). Some transition metals such as Ru, Rh, Pt, Ni, Fe, and Co have been used in the methanation reaction [5–9]. Among them, Ru-based catalysts

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are the most active; however, the limited resources and high cost of Ru restrict the large-scale industrial application of these catalysts [10]. In addition, both the activity and CH₄ selectivity of Fe- and Co-based catalysts are still relatively low [4]. Hence, Ni is the most favorable choice for CO methanation because of its relatively high activity and low cost [11]. Moreover, many supports such as Al₂O₃ [11], SiO₂ [12], SiC [13], TiO₂ [14], and ZrO₂ [15] have been investigated for Ni catalysts; however, these catalysts often suffer from Ni sintering and coke formation on the surface of the Ni particles during the methanation process. Therefore, considering that the methanation process is generally performed at high temperatures (≥ 400 °C) [1,3,16], together with its strongly exothermic nature, the control of the thermally induced sintering of Ni particles and supports as well as coke formation is critical for maintaining the catalyst activity.

Hexaaluminate (HA) materials are highly stable at high temperatures because of their unique layered structure of alternately stacked spinel blocks separated by mirror planes [5,17] and have been used as catalysts or catalyst supports for high-temperature reactions such as methane catalytic combustion [18,19], methane reforming reaction [20], and CO methanation [5,17]. In addition, the rare-earth oxide La₂O₃ has been widely used as an excellent promoter for various catalysts because of its unique properties, such as neutralization of acid sites [21], stabilization of the support [22–24], enhancement of the catalytic performance [25], and suppression of carbon deposition by activating adsorbed H₂O and CO₂ [26,27]. Lanthanum hexaaluminate (LaAl₁₁O₁₈)-supported Ni catalysts are thus expected to be promising CO methanation catalysts.

To prevent both the sintering of Ni particles and coke formation, several strategies have been employed in the literature, such as the addition of an inorganic oxide via atomic layer deposition [28,29], encapsulation using the precipitation–deposition method [11], or the use of core–shell [30,31], core–sheath [32], or ordered mesoporous structures [33,34]. Although partial success has been achieved, these approaches still have drawbacks, such as poor control of the shell thickness [30], the need for special equipment [28], costly raw materials [33], and complicated and harsh preparation processes [30], which limit their wide and large-scale applications. Recently, we prepared ZrO₂-modified Ni/ α -Al₂O₃ catalysts using a facile modified impregnation method for CO methanation with the construction of a ZrO₂-on-metallic Ni surface coating structure, yielding significant enhancement of the catalytic activity and anti-sintering of Ni particles [35]. However, the anti-coking property was poor and thus required further improvement.

Following our previous works on catalysis [6,35–40], in this work, ZrO₂-modified Ni/LaAl₁₁O₁₈ catalysts were prepared using a modified successive adsorption and reaction method to overcome the technical barriers of sintering and coking. To the best of our knowledge, no reports on this type of CO methanation reaction route are available in the literature. To better understand the effect of the catalyst structure on the catalytic activity and stability, a series of tests and characterizations were performed. The results revealed that the coating of ZrO₂ nanoparticles over the Ni/LaAl₁₁O₁₈ catalyst could suppress

both Ni sintering and coke formation.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of LaHA support

The LaHA support was prepared using a coprecipitation method with carbon black as the hard template, similar to a method previously described in the literature [17]. First, 0.165 mol Al(NO₃)₃·9H₂O and 0.015 mol La(NO₃)₂·6H₂O were dissolved in 300 mL of deionized water at 60 °C; then, 10 g carbon black was added, and the mixture was stirred for 5 h to obtain a precursor slurry. Next, a (NH₄)₂CO₃ aqueous solution (3 mol L^{−1}) was heated to 60 °C and added to the above precursor slurry while controlling the pH at approximately 8.0. After vigorous stirring for 4 h, the mixture was filtered and dried at 100 °C. The calcination process was divided into two parts. First, the mixture was calcined in an Ar flow at 1350 °C for 12 h at a heating rate of 5 °C min^{−1}. During this process, the inclusion of carbon black prevented the agglomeration of LaHA particles at high temperature. Second, the carbon black was removed in air at 900 °C for 3 h to obtain the LaHA support.

2.1.2. Preparation of 20Ni/LaHA catalyst

The 20Ni/LaHA catalyst was prepared using the wet impregnation method [11]. Stoichiometric amounts of polyethylene glycol (average MW = 20000) and Ni(NO₃)₂·6H₂O were dissolved in deionized water, followed by the addition of LaHA powder; then, the slurry was vigorously stirred at room temperature overnight. During this process, polyethylene glycol was used as the dispersant for Ni²⁺ ions in the aqueous solution, with a mass ratio of polyethylene glycol:Ni(NO₃)₂·6H₂O of 1:10. After evaporation of the solvent at 80 °C, the mixture was calcined at 350 °C for 2 h in air to obtain the 20Ni/LaHA catalyst with a NiO loading of 20 wt%.

2.1.3. Preparation of ZrO₂-modified 20Ni/LaHA catalyst

The ZrO₂-modified 20Ni/LaHA catalyst (20Ni/LaHA@ZrO₂) was prepared using a modified successive adsorption and reaction method [35,41]. First, 0.05 mol L^{−1} zirconium *n*-butoxide (Zr(OBu)₄) anhydrous toluene solution and 0.1 mol L^{−1} ethanol aqueous solution were prepared. For each cycle, the milled 20Ni/LaHA (1.00 g) was first spread into a thin layer in a sand core funnel and immersed in a Zr(OBu)₄ anhydrous toluene solution (5 mL, 0.05 mol L^{−1}) for 1 min to allow adsorption of Zr(OBu)₄ onto the surface of 20Ni/LaHA. After being filtrated and washed twice with anhydrous toluene, the powder was dried at 150 °C for 10 min. Then, 5 mL ethanol aqueous solution (0.1 mol L^{−1}) was added sequentially, and the powder was immersed in the solution for 1 min. During this process, the pre-adsorbed Zr(OBu)₄ on the surface of 20Ni/LaHA could react with H₂O to form the desired ZrO₂ precursor. The powder was then filtrated and dried at 150 °C in an oven. To obtain the desired amount of ZrO₂, the above modification cycle could be repeated several times (Fig. 1). Finally, to control the crystalline phase of ZrO₂ [35], the obtained samples were calcined at 400

Fig. 1. Illustration of one cycle of the modified successive adsorption and reaction method used to prepare the Ni/LaHA@ZrO₂ catalyst.

°C in air for 2 h and denoted as 20Ni/LaHA@ZrO₂-*x* (*x* = 5 and 10), where *x* represents the number of cycles.

2.2. Catalyst characterization

A surface area and pore size analyzer (Quantachrome, NOVA 3200e) was used to determine the specific surface area and pore size distribution using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO MPD using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. A Quantachrome chemBET pulsar TPR/TPD was used to record both H₂ temperature-programmed reduction (H₂-TPR) and H₂ temperature-programmed desorption (H₂-TPD) profiles. Transmission electron microscopy (TEM; JEM-2010F) was used to examine the morphology of the catalysts at a working voltage of 200 kV. Field-emission scanning electron microscopy (FE-SEM; JSM-6700F, JEOL, Japan) coupled with liquid-nitrogen-cooled energy-dispersive X-ray spectroscopy (EDS) was used for elemental analysis and morphological observation. The surface chemical composition was analyzed using X-ray photoelectron spectroscopy (XPS; VG ESCALAB 250, Thermo Electron, UK) with a non-monochromatized Al K α X-ray source (1486 eV). Inductively coupled plasma atomic emission spectrometry (ICP-AES; Thermo Scientific iCAP 6300) was used to determine the exact composition of the catalysts. Finally, a Seiko Instruments EXSTAR TG/DTA 6300 was used to record the thermogravimetric (TG) analysis results.

2.3. Catalytic measurement

The CO methanation reaction was performed at atmospheric pressure in a quartz-tube fixed-bed reactor, in which a thermocouple was inserted into the furnace chamber to control the reaction temperature. The effect of mass and heat transfer were examined and eliminated before the catalytic tests. First, 0.1 g catalyst (20–40 mesh) diluted with 5.0 g quartz sand (20–40 mesh) was loaded into the quartz tube (I.D. 8 mm) and reduced at 650 °C in pure H₂ (100 mL min⁻¹) for 2 h. After being cooled to the starting reaction temperature (300 °C) in H₂ flow, the mixed H₂ and CO as well as N₂ (as an internal standard) (H₂/CO/N₂ = 3/1/1, mole ratio, 200 mL min⁻¹) were introduced into the reactor at a weight hourly space velocity (WHSV) of 120 L g⁻¹ h⁻¹ [6,13]. The activity test was conducted in the temperature range of 300–600 °C using an interval of 50 °C. The temperature-programmed heating rate was 5 °C min⁻¹, and to reach steady state, the catalyst remained at each temperature for 1 h before the product analysis (Micro GC 3000A, Agilent Technologies). The lifetime test of CO methanation was performed at 550 °C, 0.1 MPa, and 120 L g⁻¹ h⁻¹. The CO conversion, CH₄ selectivity, and CH₄ yield were defined as follows [6]:

$$\text{CO conversion} = 100\% \times (V_{\text{CO,in}} - V_{\text{CO,out}})/V_{\text{CO,in}} \quad (1)$$

$$\text{CH}_4 \text{ selectivity} = 100\% \times V_{\text{CH}_4,\text{out}}/(V_{\text{CO,in}} - V_{\text{CO,out}}) \quad (2)$$

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

where $V_{\text{m,in}}$ and $V_{\text{m,out}}$ ($\text{m} = \text{CO or CH}_4$) are the volume flow rates (mL s⁻¹) of CO or CH₄ at the inlet and outlet of the reactor, respectively, at standard temperature and pressure (STP).

3. Results and discussion

3.1. Catalyst characterization

Fig. 2(a) presents the N₂ adsorption isotherms of the as-synthesized samples, which are Type-IV isotherms with H4 hysteresis loops. The hysteresis loops of the samples were very small because of the small pore volumes. However, the onsets

Fig. 2. N₂ adsorption isotherms (a) and PSD curves (b) of as-synthesized catalysts.

of the relative pressure of the hysteresis loops of all the samples appeared at relatively high positions, indicating that macropores over 50 nm in size dominated the samples. Moreover, the PSD curves provide further evidence of the pore diameters. The PSD curves of LaHA and 20Ni/LaHA are almost horizontal lines, whereas those of the Ni/LaHA@ZrO₂ catalysts are upward sloping lines. These results indicate that LaHA and 20Ni/LaHA contained hardly any pores, whereas 20Ni/LaHA@ZrO₂-5 and 20Ni/LaHA@ZrO₂-10 were dominated by large pores after the addition of ZrO₂ species (Fig. 2(b)). The BET specific surface areas and pore volumes of the samples are listed in Table 1. The LaHA support had a very low surface area of 4.5 m² g⁻¹, suggesting that it is difficult to obtain high-surface-area LaHA via the hard-template method using carbon black under severe conditions at 1350 °C for 12 h in Ar. Investigation of high-surface-area LaHA will be performed in our future work. In addition, after being loaded with NiO and ZrO₂, the surface areas of the 20Ni/LaHA and Ni/LaHA@ZrO₂-5 catalysts increased to 9.1 and 26.6 m² g⁻¹, respectively, because the addition of NiO and ZrO₂ nanoparticles led to a much coarser LaHA support surface. However, excess ZrO₂ had an adverse effect on the surface area because ZrO₂ usually has a low surface area and excess ZrO₂ may block some of the pores

between NiO and the LaHA support [35]. The exact NiO and ZrO₂ contents of the above samples were determined by ICP-AES, and the results are listed in Table 1. The real Ni loading of 20Ni/LaHA@ZrO₂ was slightly less than 20 wt% because of the addition of ZrO₂ to 20Ni/LaHA, and the ZrO₂ loading was 3.92 and 7.31 wt% for 20Ni/LaHA@ZrO₂-5 and 20Ni/LaHA@ZrO₂-10, respectively. In short, the measured components of the as-synthesized catalysts were consistent with the corresponding theoretical values.

Fig. 3(a) presents XRD patterns of the LaHA support and as-synthesized Ni-based catalysts. The peaks at 32.1°, 34.0°, 36.1°, 42.8°, 45.0°, 60.0°, and 67.3° correspond to (110), (112), (114), (025), (026), (0211), (220), and (116) planes of LaAl₁₁O₁₈ (JCPDS 00-033-0699). In addition, the two peaks at 23.4° and 48.0° correspond to (111) and (024) planes of perovskite LaAlO₃ (JCPDS 01-082-0478), respectively, indicating that the as-synthesized LaHA sample contained a small amount of the LaAlO₃ phase [42,43]. As previously reported, it is difficult to obtain pure LaHA [19,44] because the solid-state formation of LaHA by the reaction between LaAlO₃ and Al₂O₃ is extremely slow even at high temperatures. After the NiO addition, new diffraction peaks at 43.3° and 62.8° appeared in their XRD patterns, which correspond to the (012) and (110) planes

Table 1
Physicochemical parameters of the samples.

Sample	S_{BET} (m ² g ⁻¹)	V_p (cm ³ g ⁻¹)	Content ^a (wt%)		Ni crystallite size ^b (nm)	Ni dispersion ^c (%)
			NiO	ZrO ₂		
LaHA	4.5	0.01	—	—	—	—
20Ni/LaHA	9.1	0.02	20.01	—	11.2	10.9
20Ni/LaHA@ZrO ₂ -5	26.6	0.11	19.22	3.92	9.7	9.1
20Ni/LaHA@ZrO ₂ -10	20.6	0.08	18.56	7.31	9.6	8.6

^aThe exact composition of the as-synthesized catalysts was determined by ICP-AES.

^bEstimated from the XRD diffraction peak ($2\theta = 44.6^\circ$) using the Debye–Scherrer equation. The Ni crystallite sizes were calculated after peak fitting at 44.6° because of the overlapping Ni with LaHA peaks at 45.5° .

^cNi dispersion calculated based on the H₂-TPR and H₂-TPD results according to Ref. [35].

Fig. 3. XRD patterns of as-synthesized samples (a) and samples reduced at 650 °C (b). (1) LaHA; (2) 20Ni/LaHA; (3) 20Ni/LaHA@ZrO₂-5; (4) 20Ni/LaHA@ZrO₂-10.

of NiO (JCPDS 00-044-1159), respectively. For the 20Ni/LaHA@ZrO₂-x samples, weak peaks appeared at 30.1° and 50.1°, corresponding to the (111) and (202) planes of tetragonal ZrO₂ (JCPDS 01-079-1767), respectively. The XRD patterns of the 650 °C-reduced samples are presented in Fig. 3(b). The tetragonal phase of the ZrO₂ species was retained after the reduction at 650 °C for 1 h. Meanwhile, the diffraction peak corresponding to the (111) plane of metallic Ni (JCPDS 01-070-1849) appeared at approximately 44.6°. In addition, the Ni crystallite sizes were calculated using the Debye–Scherrer equation after peak fitting at 44.6°, and the results are presented in Table 1. Overall, the Ni particle sizes of the 20Ni/LaHA@ZrO₂ catalysts were slightly smaller than that of 20Ni/LaHA because the steric hindrance of the ZrO₂ nanoparticles restricted the sintering of Ni particles during the reduction process at high temperature [45].

The morphologies of the reduced catalysts are shown in Fig. 4. Overall, the LaHA support consisted of a bulk solid with a relatively smooth surface, which is consistent with the lack of pores previously observed in the N₂ adsorption results. For 20Ni/LaHA, the Ni nanoparticles were dispersed over the LaHA support with an average Ni size of 12.3 nm (Fig. 4(a)). After the addition of ZrO₂, lumpy ZrO₂ particles were distributed on the surface of both the LaHA support and Ni species (Fig. 4(b)–(c)). For 20Ni/LaHA@ZrO₂-10, the ZrO₂ species even covered the dominating surface of the 20Ni/LaHA catalyst at high ZrO₂ loading (Fig. 4(c)). The average Ni particle sizes of 20Ni/LaHA@ZrO₂-5 (Fig. 4(b)) and 20Ni/LaHA@ZrO₂-10 (Fig. 4(c))

were 10.5 and 10.0 nm, respectively. This unique distribution of ZrO₂ species was beneficial for restraining the growth and migration of Ni particles during the reduction and catalytic reaction at high temperatures.

The lattice spacings of approximately 0.25, 0.28, and 0.47 nm in the HRTEM images of the reduced catalysts (Fig. 4(d)–(f)) correspond to the (114), (110), and (011) planes of LaAl₁₁O₁₈ [46], respectively, and those of approximately 0.31 and 0.20 nm correspond to the tetragonal ZrO₂ (101) plane [34,47–49] and metallic Ni (111) plane [32], respectively. The ZrO₂ species were clearly located near the Ni particles (Fig. 4(e)) and even covered the surface of metallic Ni (Fig. 4(f)), which was beneficial for improving the interaction between Ni species and the support. Combined with the N₂ adsorption, XRD, and TEM characterization results, these findings indicate that the 20Ni/LaHA@ZrO₂ catalysts with the coating structure were successfully synthesized using the modified successive adsorption and reaction method.

To obtain more information about the real state of the Ni and Zr species over LaHA, elemental mappings and an EDS spectrum of 20Ni/LaHA@ZrO₂-10 were obtained, and the results are presented in Fig. 5. The Ni and ZrO₂ components were homogeneously dispersed on the LaHA support with the majority of ZrO₂ species located near Ni particles, providing a physical barrier for Ni species. In addition, some Ni species were covered by ZrO₂ species.

Fig. 6(a) presents the H₂-TPR profiles of the catalysts. No obvious reduction peaks were observed over either LaHA or

Fig. 4. TEM and HRTEM images of reduced catalysts. (a, d) 20Ni/LaHA; (b, e) 20Ni/LaHA@ZrO₂-5; (c, f) 20Ni/LaHA@ZrO₂-10.

Fig. 5. EDS element layered image (a), EDS spectrum (b), SEM image (c), and elemental mapping images of Al (d), O (e), La (f), Ni (g), and Zr (h) of 20Ni/LaHA@ZrO₂-10.

Fig. 6. H₂-TPR (a) and H₂-TPD (b) profiles of the samples.

the pure ZrO₂ (data not shown), and all the hydrogen-consuming peaks of the catalysts were attributed to the NiO reduction. A weak reduction peak at approximately 298 °C and a broad strong peak in the range of 323–781 °C are ob-

served in the 20Ni/LaHA profile, which correspond to NiO with weak (298 °C) or middle/strong (323–781 °C) interactions with the support [11,40]. After the addition of ZrO₂, the weak reduction peak at low temperature (298 °C) disappeared, and

the broad one shifted to higher temperature. Therefore, higher ZrO_2 loadings appear to lead to higher reduction temperatures for Ni/LaHA@ZrO_2 catalysts. This result may have been observed because the NiO species were partially covered by some ZrO_2 particles, resulting in significantly increased difficulty of the reduction of NiO species. However, the strong interaction between Ni species and the LaHA support is crucial for the enhanced thermal stability of Ni particles at high temperature. In addition, the H_2 consumptions [6] of $20\text{Ni/LaHA@ZrO}_2\text{-5}$ and $20\text{Ni/LaHA@ZrO}_2\text{-10}$ equaled the stoichiometric amounts determined by ICP (Table 1), which indicates the complete reduction of the ZrO_2 -covered NiO species over $20\text{Ni/LaHA@ZrO}_2\text{-5}$ and $20\text{Ni/LaHA@ZrO}_2\text{-10}$ samples. To completely reduce the NiO species, the reduction process was performed in a H_2 flow at 650°C for 1 h.

The H_2 -TPD profiles of all the catalysts are presented in Fig. 6(b). There was a negligible H_2 desorption peak over the pure ZrO_2 and LaHA support (data not shown), and thus, all the hydrogen desorption peaks in the H_2 -TPD profiles of the catalysts could be assigned to the metallic Ni species. Overall, the H_2 -TPD profiles of all the catalysts were similar, with a single peak at approximately 213°C , which can be attributed to the chemisorbed hydrogen on the highly dispersed Ni nanoparticles [6,39]. The intensity of the H_2 desorption peak decreased with increasing ZrO_2 addition, and $20\text{Ni/LaHA@ZrO}_2\text{-10}$ had the smallest integrated peak area among the catalysts. In addition, Table 1 lists the calculated Ni dispersion of the catalysts based on the H_2 -TPR and H_2 -TPD results. As expected, the ZrO_2 coating caused a decrease of Ni dispersion, and among the catalysts, $20\text{Ni/LaHA@ZrO}_2\text{-10}$ exhibited the lowest Ni dispersion of 8.6%, indicating that some ZrO_2 particles were distributed on the surface of Ni particles, decreasing the Ni dispersion of the catalysts. This result provides further evidence of the coverage of some exposed Ni particles by ZrO_2 particles and the efficient quantity of Ni particles over the 20Ni/LaHA@ZrO_2 catalysts during the CO methanation reaction.

To determine the surface chemical composition of the cata-

lysts, XPS measurements of the as-synthesized and reduced $20\text{Ni/LaHA@ZrO}_2\text{-10}$ were performed, and the XPS spectra of $\text{Ni } 2p$, $\text{La } 3d$, and $\text{Zr } 3d$ are presented in Fig. 7. In Fig. 7(a), for the as-synthesized sample, the $\text{Ni } 2p$ peaks at approximately 855.7 and 862.0 eV correspond to Ni^{2+} ; in addition, the weak peak at approximately 852.8 eV is attributed to Ni^0 resulting from the slight reduction of surface NiO species during the XPS measurement [33]. After the reduction at 650°C , strong Ni^0 peaks appeared at 852.8 eV, suggesting the presence of metallic Ni on the surface of the reduced $20\text{Ni/LaHA@ZrO}_2\text{-10}$. However, the Ni^{2+} peaks at 855.7 and 862.0 eV were still present, originating from the rapid oxidation of Ni^0 in air during the sample transfer [33]. Hence, it was difficult to determine whether the ZrO_2 -covered NiO species were completely reduced based on the XPS analysis. In Fig. 7(b), for the as-synthesized $20\text{Ni/LaHA@ZrO}_2\text{-10}$ catalyst, the peaks at 835.9 and 839.1 eV are attributed to $\text{La } 3d$ [50], with these peaks shifting to lower energies (835.4 and 838.9 eV, respectively) for the reduced catalyst. This result indicates that La_2O_3 was partially reduced from La_2O_3 to La_2O_x ($x < 3$) during the 650°C reduction process. La_2O_x can transfer partial electrons to metallic Ni , resulting in an increase in the d-electron density of the surface Ni atoms, which can promote CO dissociation on the catalyst surface, leading to a relatively high catalytic performance [40,51]. Similarly, the peaks at 182.0 and 184.4 eV are attributed to $\text{Zr } 3d$ over the as-synthesized $20\text{Ni/LaHA@ZrO}_2\text{-10}$, and these peaks shifted to lower energies (181.8 and 184.2 eV, respectively) after the reduction at 650°C (Fig. 7(c)) [52]. The shift in the XPS binding energy of $\text{Zr } 3d$ may originate from the partial surface Zr^{4+} species being reduced to a lower valence state [52]. This observation indicates that the presence of a high amount of metallic Ni species promotes the reduction of the Zr oxidation state.

3.2. Catalytic activity

The catalytic activity of the catalysts for the CO methanation

Fig. 7. $\text{Ni } 2p$ (a), $\text{La } 3d$ (b), and $\text{Zr } 3d$ (c) XPS spectra of the as-synthesized (1) and reduced (2) $20\text{Ni/LaHA@ZrO}_2\text{-10}$ catalysts.

reaction was determined in the temperature range of 260–600 °C at 0.1 MPa and 120 L g⁻¹ h⁻¹, and the results are presented in Fig. 8. The CO conversion of all the catalysts exhibited a volcano-shaped trend with increasing reaction temperature, indicating that high temperature has an adverse effect on this reaction [3,16]. This finding may be related to CO methanation being a strongly exothermic reaction. The 20Ni/LaHA@ZrO₂-5 and 20Ni/LaHA catalysts exhibited similar CO conversion in the entire temperature range even using a WHSV of as high as 120 L g⁻¹ h⁻¹ at 0.1 MPa, and 20Ni/LaHA@ZrO₂-10 had the lowest CO conversion. In addition, the CO thermodynamic equilibrium data calculated using the Gibbs free energy minimization method are presented in Fig. 8(a) as a reference [6]. The CO conversions on 20Ni/LaHA@ZrO₂-5 and 20Ni/LaHA nearly reached equilibrium at 400 °C but were less than the equilibrium value at other temperatures. This result may have occurred because the WHSV was too high in this work. However, the CH₄ selectivity of the catalysts had the opposite sequence compared with their CO conversion. The addition of ZrO₂ improved the CH₄ selectivity, with 20Ni/LaHA@ZrO₂-10 exhibiting the highest selectivity. The main byproduct detected by GC was CO₂ due to the side reactions such as the water–gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$), CO Boudouard reaction ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$), and inverse methane CO₂ reforming reaction ($2\text{CO} + 2\text{H}_2 \rightarrow \text{CO}_2 + \text{CH}_4$) [6]. As previously reported, ZrO₂ can activate CO₂ molecules to form CO and oxygen intermediates on the

metallic Ni surface [34,47,53,54]; thus, the addition of ZrO₂ considerably improves the CH₄ selectivity. The 20Ni/LaHA@ZrO₂-5 catalyst exhibited the best catalytic performance, with CO conversion and CH₄ yield reaching 96% and 72%, respectively, at 400 °C. The CO conversion and CH₄ selectivity of 20Ni/LaHA@ZrO₂-5 catalyst were higher than those of 20Ni/BaAl₁₂O₁₉ with the same NiO loading under similar operation conditions at 0.1 MPa [5]. However, excess ZrO₂ was adverse for the catalytic performance, and the activity of 20Ni/LaHA@ZrO₂-10 decreased with further increasing of the ZrO₂ loading. Overall, the coating amount of ZrO₂ is crucial for the catalytic performance, and only the appropriate amount of ZrO₂ can remarkably enhance the CO methanation reaction.

A 107-h-lifetime test of 20Ni/LaHA@ZrO₂-5 and 20Ni/LaHA was performed using the harsh conditions of 550 °C, 120 L g⁻¹ h⁻¹, and 0.1 MPa, and the results are displayed in Fig. 9. The CO conversion and CH₄ yield over 20Ni/LaHA decreased by 5.7% and 5.3%, respectively; however, the CH₄ selectivity remained comparable with a decrease of only 1.8%. In contrast, the CO conversion and CH₄ yield over 20Ni/LaHA@ZrO₂-5 remained constant over the entire lifetime test. Clearly, the addition of ZrO₂ to 20Ni/LaHA significantly improved its stability, especially at high temperature and WHSV.

To investigate the reasons for the high stability of the 20Ni/LaHA@ZrO₂-5 catalyst, both spent catalysts were characterized using TEM, XRD, and TG analysis. The average Ni na-

Fig. 8. Catalytic properties of the catalysts. (a) CO conversion; (b) CH₄ selectivity; (c) CH₄ yield.

Fig. 9. Lifetime test of 20Ni/LaHA and 20Ni/LaHA@ZrO₂-5. (a) CO conversion; (b) CH₄ selectivity; (c) CH₄ yield.

noparticle sizes of the spent 20Ni/LaHA (Fig. 10(a)) and 20Ni/LaHA@ZrO₂-5 (Fig. 10(b)) were 19.1 and 10.8 nm, respectively. Unlike that of the spent 20Ni/LaHA@ZrO₂-5, the size of Ni particles over the spent 20Ni/LaHA was not uniform, and some of the particles were as large as 35.1 nm. In addition, Fig. 9(c) presents XRD patterns of the spent 20Ni/LaHA and 20Ni/LaHA@ZrO₂-5 catalysts after the lifetime test. The calculated Ni particle sizes of the spent 20Ni/LaHA and 20Ni/LaHA@ZrO₂-5 were 21.1 and 10.2 nm, respectively. Compared with the aforementioned TEM (Fig. 4) and XRD (Fig. 3, Table 1) results of the reduced catalysts, the sintering of Ni particles over 20Ni/LaHA was severe, whereas 20Ni/LaHA@ZrO₂-5 exhibited superior anti-sintering performance. Carbon deposition often occurs on Ni catalysts because of the CO Boudouard reaction and CH₄ cracking reaction [55]; thus, the amount of carbon deposited on the spent catalysts was measured by TG analysis, and the results are presented in Fig. 9(d). The decrease of the mass loss percentage of the spent 20Ni/LaHA catalyst was larger than that of 20Ni/LaHA@ZrO₂-5, indicating the higher resistance of 20Ni/LaHA@ZrO₂-5 to coking formation. The coke resistance of 20Ni/LaHA@ZrO₂-5 can be attributed to the following reasons (Fig. 11): (1) ZrO₂ can enhance CO₂ dissociation to generate oxygen intermediates, which facilitates the removal of carbon formed on the Ni particles by CO₂ reduction ($\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$) [35,47] and (2) the formation of the carbon filament can be suppressed over 20Ni/LaHA@ZrO₂-5 because it is difficult for carbon to lift Ni particles from the support matrix because of the confinement

Fig. 11. Schematic diagram of effect of catalyst structure on stability. (a) 20Ni/LaHA@ZrO₂; (b) 20Ni/LaHA.

effect of the partial ZrO₂-covered structure. In short, the sintering of Ni particles and coking led to a decrease of the activity of 20Ni/LaHA in the lifetime test, and 20Ni/LaHA@ZrO₂-5 exhibited high catalytic activity and stability as well as greatly improved resistance to Ni sintering.

4. Conclusions

We conducted a systematic investigation of Ni/LaHA@ZrO₂ catalysts synthesized using a modified successive adsorption and reaction method to produce synthetic natural gas via the CO methanation reaction. After the addition of ZrO₂, the ZrO₂ nanoparticles were distributed over the surface of the Ni/LaHA

Fig. 10. TEM images of spent 20Ni/LaHA (a) and 20Ni/LaHA@ZrO₂-5 (b); (c) XRD patterns of the catalysts after lifetime tests; (d) TG curves of the spent catalysts in air.

catalyst and even partially covered some Ni particles, resulting in the coating exerting a confinement effect. The Ni/LaHA@ZrO₂ catalyst with the addition of an appropriate amount of ZrO₂ even exhibited slightly higher CO conversion and CH₄ yield than Ni/LaHA. Moreover, the CH₄ selectivity was significantly enhanced after the addition of ZrO₂ because of the activation of the byproduct CO₂ molecules. However, excess ZrO₂ had an adverse effect on the enhancement of the catalytic activity because of the coverage of the surface Ni particles. Life-time tests at 0.1 MPa, 550 °C, and 120 L·g⁻¹·h⁻¹ revealed that the Ni/LaHA@ZrO₂ catalyst was highly stable with superior anti-sintering and anti-coking properties. It is expected that the confinement structure and the promoter effect of ZrO₂ species led to the high stability of the Ni/LaHA@ZrO₂ catalyst.

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Graphical Abstract

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ZrO₂-modified Ni/LaAl₁₁O₁₈ catalyst for CO methanation: Effects of catalyst structure on catalytic performance

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The ZrO₂-modified Ni/LaHA catalyst shows slight increment of CH₄ yield and obvious enhancement stability for CO methanation reaction compared with Ni/LaHA catalyst owing to its coating structure as well as the promoter effect of ZrO₂.

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氧化锆改性的Ni/LaAl₁₁O₁₈用于CO甲烷化反应：催化剂结构对催化性能的影响

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摘要: 对于煤制天然气, CO甲烷化技术起着重要作用, 其研究核心之一是高效催化剂的开发。目前, CO甲烷化催化剂主要采用金属Ni作为活性组分, 但存在高温易烧结和易积炭等问题。因此, 如何使其同时具有较高的催化活性和高温稳定性是亟待解决的问题。针对这些问题, 本文以高热稳定性的六铝酸镧(LaAl₁₁O₁₈)为载体, 采用浸渍法负载金属镍, 制备了Ni/LaAl₁₁O₁₈催化剂; 以高化学惰性的ZrO₂为包覆层, 采用改进的连续吸附反应法, 将ZrO₂前驱体液相沉积在Ni/LaAl₁₁O₁₈表面进行改性, 制备了具有包覆结构的Ni/LaAl₁₁O₁₈@ZrO₂甲烷化催化剂。探讨了ZrO₂在Ni/LaAl₁₁O₁₈表面的分布形式以及不同沉积包覆量对催化剂结构、CO甲烷化催化剂活性和稳定性的影响。分别采用氮气物理吸附、X射线衍射、透射电镜、扫描电镜、氢气程序升温还原、氢气程序升温脱附、X射线光电子能谱、热重分析和电感耦合等离子体原子发射光谱法等手段对催化剂进行了系统表征。结果表明, ZrO₂纳米粒子能够同时分布在催化剂活性组分和载体表面, 增加了金属-载体间相互作用力, 高温还原时可以有效抑制活性金属Ni的烧结, 成功构筑了具有显著限域结构的包覆型催化剂。同时, ZrO₂的包覆不利于金属的氢气化学吸附。在常压, 260–600 °C和120 L g⁻¹ h⁻¹条件下对催化剂进行了催化活性测试。结果显示, 与未改性的催化剂相比, 包覆后催化剂上CO转化率略有降低, 但是其CH₄选择性明显提高, 适量的ZrO₂包覆对CH₄得率有较好的促进作用, 但是过量的ZrO₂包覆会因占据过多的金属镍表面使得CO转化率显著降低。在常压, 550 °C和120 L g⁻¹ h⁻¹空速的操作条件下所进行的107 h稳定性测试结果表明, 包覆型Ni/LaAl₁₁O₁₈@ZrO₂催化剂展示了良好的高温稳定性, 具有

优异的抗烧结和抗积碳性能。这主要是因为包覆型催化剂具有良好的“限域”效应,从而显著改善了催化剂的抗烧结性能;同时较强的金属-载体相互作用以及 ZrO_2 助剂对 CO_2 的活化提升了催化剂的消碳能力,增强了 $\text{Ni/LaAl}_{11}\text{O}_{18}@ZrO_2$ 催化剂的抗积碳能力。总之,本文构筑了一种高稳定性的包覆型催化剂 $\text{Ni/LaAl}_{11}\text{O}_{18}@ZrO_2$,可广泛应用到其他多种高温反应中。

关键词: 六铝酸镧; ZrO_2 ; 镍催化剂; 包覆结构; CO 甲烷化

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《催化学报》进入中科院 JCR 期刊分区工程技术大类2区

近日,中国科学院文献情报中心发布 2016 年版中科院JCR期刊分区, *Chinese Journal of Catalysis* (《催化学报》) 在工程技术类 1845 种期刊中排名第 354 位,居工程技术大类2区。中科院 JCR 期刊分区按照学术影响力作为划分方式,将每个学科的所有期刊按照学术影响力 (3年平均JCR影响因子 (IF)) 由高到低降序排列,依次划分为4个区,使每个分区期刊影响力总和相同。由于学科内期刊的3年IF的偏态分布,这使得1区期刊数量极少。为保证期刊1区期刊数量,1区期刊取整个学科数量总数的5%,即3年平均IF最高的5%的期刊为1区期刊。2–4区期刊使用3年平均IF总和相同的方式划分(分区方法详见<https://www.fenqubiao.com>)。

近年,《催化学报》的学术质量及影响力不断提升,这是中国化学会催化委员会委员、《催化学报》编委、审稿专家、作者和读者长期不懈努力和共同支持的结果。衷心感谢各位老师、投稿原创性高质量稿件、学术质量把关以及组约优秀稿件、组办高水平专刊等方面所给予的持续的、巨大的支持!

(《催化学报》编辑部)