

Ni/CaO-ZrO₂-Al₂O₃ catalyst for CO₂ methanation: Enhanced low-temperature activity and high-temperature sintering resistance

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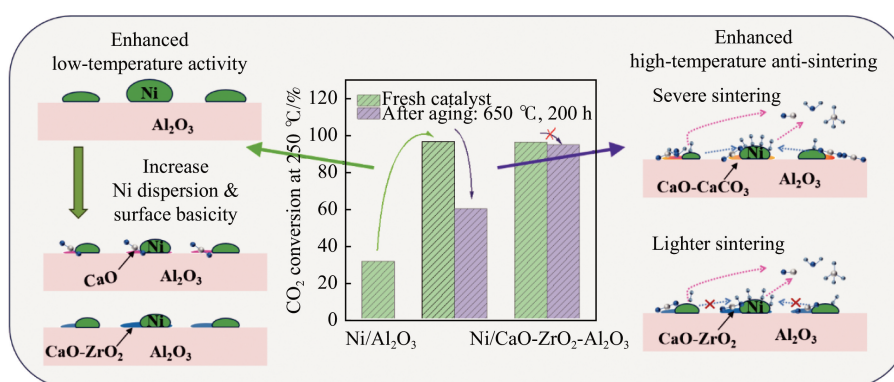
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Abstract: Ni/Al₂O₃ is regarded as one of the most promising catalysts for industrial application in CO₂ methanation, but is still plagued by issues of inadequate low-temperature activity and thermal sintering. In response to these challenges, an Ni/CaO-ZrO₂-Al₂O₃ catalyst with

high low-temperature activity and robust high-temperature sintering resistance was prepared by introducing Ca and Zr promoters. Under the reaction conditions of 250 °C and a space velocity of 30000 mL/(g·h), the CO₂ conversion and methane space-time yield reached 96% and 257.5 mmol/(g·h), respectively. In addition, the Ca-Zr dual-promoted Ni/CaO-ZrO₂-Al₂O₃ catalyst exhibited a smaller increase in the Ni particle size and less activity loss than the Ca-promoted catalyst in a 200 h aging test at 600 °C. The Ca and Zr promoters can not only improve the Ni dispersion but also enhance the surface basicity, resulting in excellent low-temperature activity. Moreover, the Zr promoter suppresses the transformation of Ca species into CaCO₃ through solid-phase reaction under operating conditions, thereby inhibiting Ni sintering and ensuring high-temperature stability. This work provides a new promoter design strategy for the development of high-performance Ni-based catalysts for CO₂ methanation.

Key words: methanation; Ni/Al₂O₃ catalyst; low-temperature activity; sintering resistance



CO₂ methanation plays a critical role in the power-to-gas technology, involving the reaction of captured CO₂ with green hydrogen produced from excess electricity generated by renewable energy sources to form methane, which can be easily stored and transported^[1]. Moreover, because methane can be transported through the existing natural gas pipeline infrastructure, CO₂ methanation is considered a promising method for achieving CO₂ resource utilization and the efficient storage of green energy^[2].

The catalyst is pivotal for the CO₂ methanation reaction.

In the low-temperature region below 300 °C, CO₂ methanation is severely limited kinetically due to the high activation energy required for CO₂ dissociation, leading to suboptimal CO₂ conversion on most catalysts^[3–5]. At elevated temperatures, although the reaction rate increases substantially, the equilibrium conversion decreases with rising temperature due to the exothermic characteristics of CO₂ methanation, whereas conducting the reaction under high pressure can significantly alleviate the thermodynamic constraints because of the volume-shrinking nature of this

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reaction^[6–7]. It has been reported that the equilibrium CO₂ conversion can approach 100% under the conditions of 3 MPa, H₂/CO₂ = 4 (molar ratio) and 200–400 °C^[6–7]. However, the exothermic nature of CO₂ methanation can cause sintering of the active metal particles, leading to a significant loss of activity under high-temperature conditions^[8–10]. In industrial applications, the catalyst deactivation caused by sintering can be aggravated by localized hotspots due to insufficient heat transfer^[11]. Therefore, the development of catalysts with both high low-temperature activity and robust high-temperature sintering resistance is essential for the industrial implementation of CO₂ methanation.

CO₂ methanation catalysts can be primarily categorized into Ni-based catalysts and noble metal-based catalysts such as Ru, Rh and Pt. Noble metal-based catalysts exhibit considerable methanation activity in the low-temperature region of 250 °C due to their strong H₂ dissociation capability. For instance, 5% Ru/CeO₂ catalysts demonstrate a CO₂ conversion as high as 80% and selectivity of exceeding 90% to methane at 250 °C, 0.1 MPa and 3600 mL/(g·h)^[12]. While the Ni-based catalysts generally show lower activity compared to the noble metal-based ones, their performance can surpass that of noble metals if optimized through precise adjustment of components^[13–14] or structural modifications^[15]. Considering their cost-effectiveness, the Ni-based catalysts are regarded as the most promising candidates for industrial applications. Among them, Al₂O₃ supports are widely employed due to their commercial availability and strong CO₂ adsorption capacity^[16]; in particular, the Ni/Al₂O₃ catalysts have been commercially utilized for CO_x hydrogenation pretreatment in the ammonia synthesis^[17].

For the Ni/Al₂O₃ catalysts, the addition of alkaline earth promoters like Mg and rare earth promoters like La and Ce is commonly adopted to enhance their catalytic activity^[18]. However, the MgO promoters tend to form solid solutions with NiO, which results in a decrease in the Ni reducibility^[19] or the oxidative deactivation of the catalyst^[20]. Despite their effectiveness, rare earth promoters limit their industrial application due to their high cost. In contrast, Ca, another alkaline earth metal, offers a promising alternative owing to its low cost and stronger basicity. Although Ca promoters are less studied in conventional CO₂ methanation, they have been extensively investigated in the field of Dual Functional Materials (DFMs) for integrated CO₂ capture and methanation^[21]. In DFMs studies, CaO not only acts as a CO₂ adsorbent for capture, but also serves as a promoter that enhances CO₂ methanation activity. Wu et al.^[22] prepared a series of Ni/Ca_xMg_{1-x}CO₃ DFMs and found that Ni/CaCO₃ material exhibited the highest activity and stability over 15 ICCU-methanation cycles, which was attributed to its stronger alkalinity and thermally stable CaCO₃ phase. In their study on Ni/AlCaO_x DFMs, Li et al.^[23] demonstrated that adding Ca can weaken the strong Ni-Al interaction and promote NiO reduction by facilitating electron transfer between Ni

and H₂, thus achieving excellent CO₂ adsorption and catalytic properties. These findings highlight the potential of Ca promoters to enhance the low-temperature activity of CO₂ methanation. Nevertheless, their long-term stability remains underexplored^[24–26].

In addition to enhancing the low-temperature activity, the incorporation of promoters can also effectively improve the high-temperature sintering resistance of Ni/Al₂O₃ catalysts. These promoters mainly prevent the migration, agglomeration, and growth of Ni particles at elevated temperatures by strengthening the metal-support interaction or spatially confining the Ni particles^[27]. Jiang et al.^[28] investigated the effects of Zr, Fe and Ce promoters on Ni-based catalysts and found that the Zr-modified Ni/Al₂O₃ catalyst possessed the highest Ni dispersion and the most optimal metal-support interaction. Consequently, the Zr-modified Ni/Al₂O₃ catalyst demonstrated superior CO methanation activity and high stability under challenging conditions of 600 °C and 1 MPa. Furthermore, Lin et al.^[29] reported that the Zr promoter inhibited the sintering of the Al₂O₃ support itself, which gave the Ni/ZrO₂-Al₂O₃ catalysts a better stability in the CO₂ methanation. To date, despite the individual promise of Ca and Zr, the co-modification of Ni/Al₂O₃ catalysts with both Ca and Zr promoters for CO₂ methanation has not yet been explored.

In this study, the low-temperature activity and high-temperature stability of Ni/Al₂O₃ catalysts for CO₂ methanation were enhanced through the incorporation of Ca and Zr promoters. It was found that the Ni/Al₂O₃ catalysts co-doped with Ca and Zr exhibited excellent low-temperature activity, similar to those doped with single Ca. However, with respect to the high-temperature stability, only the Ca-Zr co-doped Ni/CaO-ZrO₂-Al₂O₃ catalyst showed exceptional sintering resistance. The mechanisms behind the effects of Ca and Zr promoters were elucidated using various characterization techniques, including XRD, TEM, H₂-TPR, H₂-TPD, N₂ sorption XPS and TG. The findings provide a novel promoter design strategy for the development of high-performance Ni-based catalysts for CO₂ methanation.

1 Experimental

1.1 Materials

All reagents were of analytical grade and used without further treatment. Ni(NO₃)₂·6H₂O and Ca(NO₃)₂·4H₂O were purchased from Tianjin Damao Chemical Reagent Factory. Al(NO₃)₃·9H₂O and Na₂CO₃·10H₂O were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Zr(NO₃)₄·5H₂O was procured from Meryer (Shanghai) Biochemical Technology Co., Ltd.

1.2 Catalyst preparation

All catalysts were synthesized *via* the coprecipitation

method. A designed quantity of Ni(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, and corresponding promoter precursors (Ca(NO₃)₂·4H₂O or Zr(NO₃)₄·5H₂O) were dissolved in deionized water to obtain a mixed nitrate solution with a total metal ion concentration of 0.3 mol/L. The nitrate solution and 1.0 mol/L Na₂CO₃ solution were simultaneously added dropwise into 100 mL of deionized water at 35 °C under continuous stirring, while maintaining the pH value at 9.0 ± 0.5. After completion of the titration, the resulting slurry was stirred for an additional 10 min. The precipitates were filtered, washed, and dried at 110 °C for 12 h, followed by calcination in a muffle furnace at 450 °C for 6 h. Based on the promoter composition, the catalysts were designated as NA (no promoter), NAC (Ca-promoted), NAZ (Zr-promoted) and NACZ (Ca-Zr co-promoted), and the spent catalysts after the aging test were labeled with the suffix '-S'. For example, the spent Ni/CaO-ZrO₂-Al₂O₃ catalyst after the aging test was denoted as NACZ-S. In all catalysts, the Ni loading was 40%, and the content of each promoter was 6% (calculated as oxides).

1.3 Characterization

N₂ adsorption-desorption characterization was performed on a BSD-660M A6S|B3M physisorption analyzer. Prior to analysis, samples were degassed under vacuum at 300 °C for 4 h, followed by N₂ adsorption at -196 °C. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Focus instrument equipped with a Cu K α radiation source, with a scan speed of 8(°)/min. X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo Scientific K-Alpha instrument. A monochromatic Al target ($E = 1486.68$ eV) was employed, and all spectra were calibrated against C 1s (284.8 eV).

CO₂/H₂ temperature programmed desorption (CO₂-TPD, H₂-TPD) were conducted on a Xianquan TP-5080E chemisorption analyzer. Prior to the test, calcined samples underwent an *in situ* reduction at 650 °C in pure H₂ for 2.5 h. After that, the samples were saturated with the corresponding gas at room temperature, purged with He for 30 min, and subsequently desorbed from room temperature to 900 °C at a heating rate of 10 °C/min with real-time signal monitoring by TCD. The catalyst basicity was evaluated by the CO₂-TPD results, while the Ni dispersion (D_{Ni}) was determined by the H₂-TPD results, calculated as^[20]:

$$D_{Ni}(\%) = \frac{2 \times V_{ad} \times M \times SF}{m \times w \times V_m} \times 100\% \quad (1)$$

where V_{ad} refers to the H₂ chemisorption capacity of H₂-TPD; M is the molar mass of Ni; SF represents the stoichiometric factor, which is 1 for Ni/H; m is the mass of tested catalyst (50 mg); w is the mass fraction of Ni (40%); V_m denotes the molar volume of gas under standard conditions.

Field emission transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission

electron microscopy (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDS) were performed using a JEOL JEM-F200 instrument at an acceleration voltage of 200 kV. Particle size distributions were obtained by measuring at least 50 Ni particles using Nano Measurer software. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449F3 simultaneous thermal analyzer. During testing, an appropriate sample quantity was heated in air from 30 to 800 °C at a heating rate of 10 °C/min.

H₂ temperature programmed reduction (H₂-TPR) experiments were conducted on a Xianquan TP-5076 instrument. 50 mg of catalyst was loaded and reduced with the temperature rising from 30 to 900 °C at a rate of 10 °C/min in 5% H₂/Ar (30 mL/min), while monitoring the signal in real time using TCD.

1.4 Catalytic performance test

The CO₂ methanation activity of the catalyst was evaluated in a micro fixed-bed reactor. Prior to the performance test, the catalyst was reduced under a flow of pure H₂ (20 mL/min) by heating to 650 °C at 2 °C/min and holding for 2.5 h to obtain the fresh catalyst. 100 mg of fresh catalyst (40–60 mesh) uniformly mixed with 100 mg of quartz sand (40–60 mesh) was loaded into a stainless-steel reactor tube. The reaction was carried out under the following conditions: 3 MPa, CO₂/H₂/N₂ = 6:24:1 (molar ratio), total gas flow rate of 50 mL/min (WHSV = 30000 mL/(g·h)), and reaction temperature of 200–325 °C. The composition of feedstock and products was analyzed online using a FULI GC9790II gas chromatograph. The CO₂ conversion (x_{CO_2}), CH₄ selectivity (s_{CH_4}), and methane space-time yield (STY_{CH₄}) were calculated using the following equations:

$$x_{CO_2} = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100\% \quad (2)$$

$$s_{CH_4} = \frac{F_{CH_4,out}}{F_{CO_2,in} - F_{CO_2,out}} \times 100\% \quad (3)$$

$$STY_{CH_4} = \frac{F_{CO_2,in} \times x_{CO_2} \times s_{CH_4}}{m} \times 100\% \quad (4)$$

where $F_{CO_2,in}$ and $F_{CO_2,out}$ denote the inlet and outlet molar flow rates of CO₂, respectively, $F_{CH_4,out}$ represents the outlet molar flow rate of CH₄ (mol/min), and m is the mass of the catalyst sample loaded in the reactor.

To evaluate the high-temperature sintering resistance of catalysts, selected catalysts were subjected to prolonged aging under accelerated deactivation conditions. The aging test was conducted at 600 °C, 0.1 MPa, CO₂/H₂/N₂ = 6:24:1 (molar ratio) and a WHSV of 15000 mL/(g·h) for 200 h. After the aging treatment, the catalytic performance was re-evaluated at 3 MPa, WHSV = 30000 mL/(g·h) and 200–325 °C. The activity loss was determined by comparing the performance of the aged catalysts with that of fresh samples.

2 Results and discussion

2.1 Catalytic performance

The effects of Ca and Zr promoters on the performance of Ni/Al₂O₃ catalysts in the CO₂ methanation are shown in Figure 1. Within the temperature range of 200–325 °C, the CO₂ conversion over all catalysts increased with rising temperature. Above 275 °C, the conversion gradually approached the thermodynamic equilibrium curve, resulting in a noticeable plateau (Figure 1(a)). Within the 200–250 °C temperature range, significant differences in the CO₂ conversion were observed among these tested catalysts, with the activity order being: NACZ ≥ NAC > NAZ > NA. The activity disparity was most evident at 250 °C, where the CO₂ conversion over the NA catalyst achieved only 31.7%, compared to 68.2%, 96.2% and 96.1% over NAZ, NAC and NACZ, respectively. The addition of either Ca or Zr alone significantly enhanced the activity relative to NA, with Ca exhibiting a more pronounced promoting effect. The NACZ catalyst incorporated both Ca and Zr showed no significant difference in activity compared to NAC. Figure 1(b) displays the corresponding selectivity to CH₄ for each catalyst, with minimal variation among various samples. Both NAC and NACZ catalysts maintained a selectivity of

close to 100% to CH₄ throughout the temperature range. At 250 °C, the methane space-time yields over NAC and NACZ reached 257.5 mmol/(g·h), which ranks among the highest values reported for Ni/Al₂O₃ catalysts (Table 1).

To analyze the effects of promoters on the high-temperature stability of Ni/Al₂O₃ catalysts, the most active NAC and NACZ catalysts underwent a 200 h aging test at 600 °C (Figure 2). The CO₂ methanation performance during the aging process is shown in the inset of Figure 2(a). The CO₂ conversion and CH₄ selectivity over the NAC and NACZ catalysts were approximately 68% and 40%, respectively, and remained stable without any observed decline. After aging, all catalysts exhibited CO₂ conversion comparable to their fresh counterparts in the 275–325 °C range, but showed varying degrees of activity loss in the 200–250 °C range (Figure 2(a)). Within 200–250 °C, the CO₂ conversion over the NAC-S catalyst decreased more significantly relative to its fresh counterpart than the NACZ-S catalyst. At 250 °C, the CO₂ conversion loss of the NAC-S catalyst reached 37.5%, whereas that of the NACZ-S catalyst was nearly negligible. The CH₄ selectivity over all catalysts remained close to 100% after aging (Figure 2(b)). The results indicate that the Zr promoter imparts exceptional high-temperature stability to the NACZ catalyst.

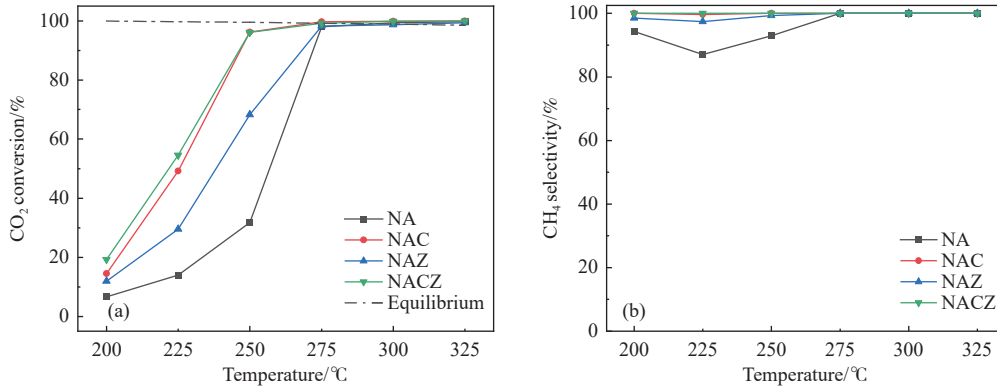


Fig. 1 Influence of Ca and Zr promoters on the performance of Ni/Al₂O₃ catalyst in the CO₂ methanation:

(a) CO₂ conversion; (b) CH₄ selectivity

Reaction condition: WHSV = 30000 mL/(g·h), CO₂/H₂/N₂ (molar ratio)= 6:24:1, 3 MPa.

Table 1 Activity of Ni/Al₂O₃ catalysts reported in literature

Sample	Loading w/%	Temperature/°C	Pressure/MPa	WHSV/(mL·g ⁻¹ ·h ⁻¹)	STY _{CH₄} /(mmol·g ⁻¹ ·h ⁻¹)	Ref.
Ni/Al ₂ O ₃	40	250	0.19	30000	61.6	[30]
Ni ₂ Mn/Al ₂ O ₃	20	250	2.5	10000	80.0	[31]
Ni/5CeO ₂ -Al ₂ O ₃	40	250	0.19	30000	112.9	[32]
Ni/Al ₂ O ₃ -ZrO ₂	25	250	0.1	15000	15.1	[33]
Ni/20La ₂ O ₃ -Al ₂ O ₃	30	250	—	30000	95.6	[34]
Ni/CaO-ZrO ₂ -Al ₂ O ₃	40	250	3	30000	257.5	this work

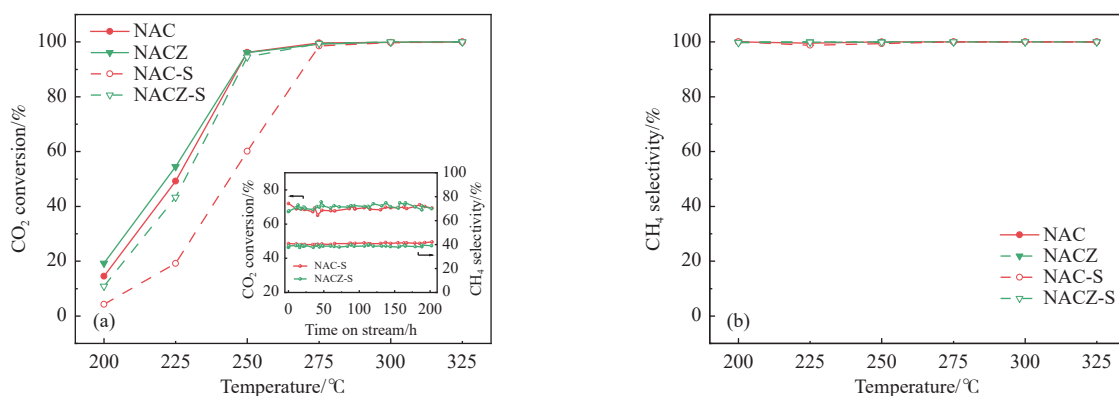


Fig. 2 Catalytic performances of the NAC and NACZ catalysts after aging in the CO₂ methanation: (a) CO₂ conversion, with the inset showing the catalytic performances during the aging test; (b) CH₄ selectivity
Aging conditions: WHSV = 15000 mL/(g·h), 600 °C, CO₂/H₂/N₂ (molar ratio) = 6:24:1, 0.1 MPa;
Reaction conditions: WHSV of 30000 mL/(g·h), CO₂/H₂/N₂ (molar ratio) = 6:24:1, 3 MPa

2.2 Mechanism for the enhanced low-temperature activity

To investigate the enhancement effect of Ca and Zr promoters on the low-temperature activity of Ni/Al₂O₃ catalysts, N₂ adsorption-desorption measurements were conducted on fresh catalysts. As shown in Figure 3(a), all catalysts exhibited type IV isotherms, characteristic of typical mesoporous materials^[13]. Figure 3(b) displays the pore size distribution curves of the fresh catalysts. The main peaks for all catalysts were located within the mesoporous range of 4–10 nm, accompanied by shoulder peaks in the micropore region below 2 nm. The introduction of Ca and Zr promoters increased the micropore content. Table 2 lists the textural parameters of catalysts. It was evident that the addition of Ca or Zr markedly enhanced the specific surface

area of catalysts, likely due to the increased number of micropores. A larger specific surface area of the support facilitates uniform dispersion of the active species and consequently improves the catalytic activity^[35].

To determine the phase composition of the catalysts, XRD analysis was performed. Figure 4(a) shows the XRD patterns of the calcined samples, revealing discrete reflections at 37.2°, 43.3° and 62.9°, which were assigned to NiO (PDF#047-1049). No diffraction peaks associated with Al or Ca species were observed. The XRD patterns of the reduced catalysts are presented in Figure 4(b). After reduction at 650 °C in H₂, the NiO diffraction peaks disappeared, whereas the metallic Ni diffraction peaks (PDF#004-0850) emerged at 44.5°, 51.8° and 76.2°, indicating that NiO was almost completely reduced to metallic Ni.

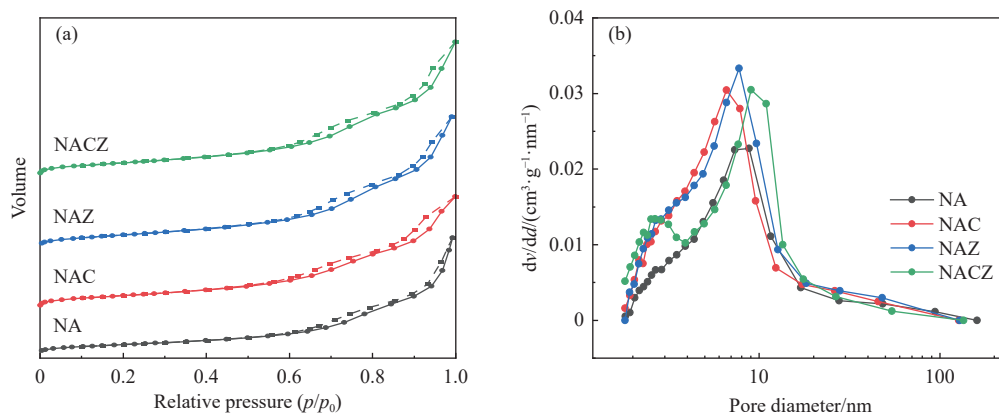


Fig. 3 (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of fresh catalysts

Table 2 Textural properties of catalysts

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	Pore volume/(mL·g ⁻¹)	Average pore size/nm
NA	106	0.40	11.8
NAC	136	0.39	8.9
NAZ	149	0.47	9.8
NACZ	137	0.38	9.0

Compared with the unmodified NA catalyst, the Ni diffraction peaks of the catalysts with promoters exhibited varying degrees of broadening, suggesting a decrease in the grain size of Ni species. The Ni grain size calculated using the Scherrer formula followed the order: NAC < NACZ < NAZ < NA (Table 3). These results indicate that the introduction of Ca significantly decreases the Ni grain size of NAC, while the effect of Zr is slightly less pronounced.

The element distribution and Ni particle size was further investigated by EDS and TEM techniques. As shown in Figure 5(a), the NA catalyst exhibited a non-uniform distribution of Ni and Al, with noticeable Al enrichment

observed within the dashed circle. In contrast, the NAC and NACZ catalysts showed highly homogeneous distributions of Ni, Al and Ca, indicating the promoting effect of Ca on the Ni dispersion. The Ni dispersion in the NAZ catalyst was slightly less uniform, with numerous isolated Zr particles present. This suggests that the Zr promoter primarily acts as a separator and increases the specific surface area. The Ni particle sizes of the catalysts, as summarized in Figure 5 and Table 3, followed the order: NAC < NACZ < NAZ < NA, which is consistent with the XRD results.

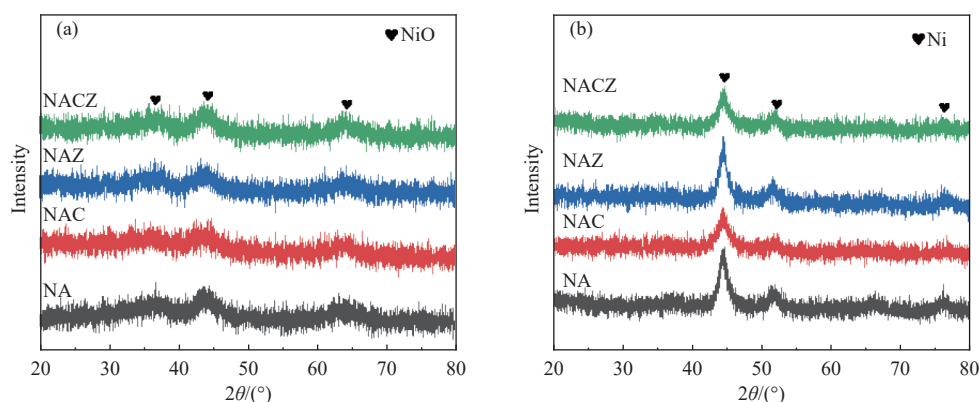


Fig. 4 XRD patterns of catalysts at different stages: (a) calcined, (b) reduced

Table 3 Ni size and Ni dispersion of catalysts

Sample	Ni size/nm		Ni dispersion ^c /%
	grain size ^a	particle size ^b	
NA	6.7	8.2	3.0
NAC	4.6	6.7	15.2
NAZ	6.4	7.5	3.5
NACZ	5.2	7.0	10.6

Notes: ^a: Calculated from the XRD patterns using the Scherrer equation; ^b: Statistically obtained from TEM images; ^c: Determined by chemical adsorption in the H₂-TPD measurements.

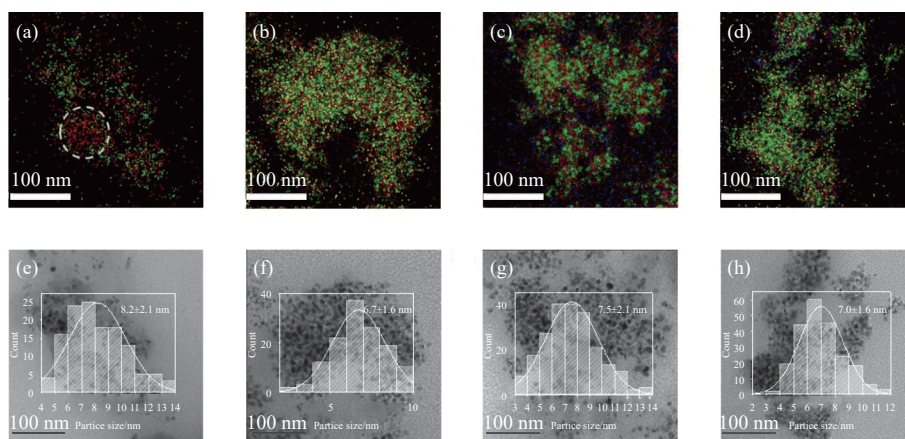


Fig. 5 TEM-EDX elemental mapping of (a) NA, (b) NAC, (c) NAZ and (d) NACZ, in which the green, red, yellow and blue dots represent Ni, Al, Ca and Zr elements, respectively; TEM images of the fresh catalysts, with the insets showing the Ni particle size distribution: (e) NA, (f) NAC, (g) NAZ, (h) NACZ

The introduction of Ca or Zr reduced Ni particle size and improved Ni dispersion, with Ca exhibiting a greater effect than Zr. These findings are also in good agreement with the Ni dispersion derived from H₂-TPD measurements (Table 3). The NAC catalyst exhibited the highest Ni dispersion (15.2%), whereas the undoped NA catalyst showed the lowest (3.0%).

The CO₂ adsorption capacities of the fresh catalysts were measured and correlated with methane space-time yield, as summarized in Figure 6(a). The addition of all promoters enhanced the catalyst alkalinity, though the enhancement effects varied with different promoters. Ca significantly increased the number of basic sites, while Zr showed a comparatively weaker effect. The simultaneous addition of Ca and Zr maximized the number of basic sites. The total CO₂ adsorption capacity ranked as follows: NACZ > NAC > NAZ > NA, consistent with the low-temperature activity observed at 200–250 °C.

Figure 6(b) displays the O 1s spectra. All samples contained two types of oxygen species: lattice oxygen (O_{lat}, 530.7–530.9 eV) and adsorbed oxygen (O_{ads}, 531.7–531.9 eV). The amount of adsorbed oxygen observed was positively correlated with the concentration of oxygen vacancy content^[10], which was known to promote CO₂ adsorption and activation. Both Ca and Zr dopants individually increased the proportion of adsorbed oxygen, with the most significant enhancement observed when Ca and Zr were added simultaneously.

The above results indicate that CO₂ adsorption and activation constitute the rate-determining step of the reaction. The co-addition of Ca and Zr simultaneously increases the specific surface area and promotes elemental dispersion, thereby enhancing the dispersion of metal Ni. Additionally, it comprehensively increases basicity and the number of oxygen vacancies of the NACZ catalyst. Both factors contribute to promoting the adsorption and activation of CO₂. Therefore, the NACZ catalyst, despite with a lower Ni dispersion than the NAC catalyst, exhibited comparable activity due to its higher density of basic sites and oxygen vacancies.

2.3 Mechanism for the enhanced high-temperature anti-sintering performance

Figure 7(a) shows the XRD patterns of spent catalyst samples after the aging test. Apparently, the Ni diffraction peaks became significantly sharper after the high-temperature aging. As given in Table 4, the Ni grain size increased by 149% for NAC-S and 108% for NACZ-S, indicating the sintering of Ni species during aging. However, the NAC catalyst underwent more pronounced sintering compared to NACZ, demonstrating that Zr addition effectively suppressed the Ni grain sintering and growth. Additionally, CaCO₃ diffraction peaks were observed at approximately 29° in both NAC-S and NACZ-S samples, attributed to the reaction of Ca species with CO₂ under the reaction atmosphere. A ZrO₂ diffraction peak, which was absent in the fresh NACZ and NAZ catalyst, was detected in NACZ-S (Figure 7(b)). This ZrO₂ diffraction peak exhibited splitting, with new humps appearing at lower angles, which was attributed to the expansion of the ZrO₂ unit cell due to the partial incorporation of Ca²⁺ into the ZrO₂ lattice^[36]. These findings indicate the occurrence of a solid-state reaction between Ca²⁺ and ZrO₂ under the reaction atmosphere, which may explain how the Zr promoter enhances the high-temperature sintering resistance of NACZ.

Figure 8 and Table 4 present the elemental distributions and Ni particle sizes of the spent catalysts after aging tests. Ni agglomeration was observed in both NAC-S and NACZ-S catalysts, with a clear separation of Ni and Al elements in NAC-S. This indicates that the support in NAC exhibits a weaker binding affinity for metallic Ni compared with that in NACZ. The TEM images further confirmed the aggregation and sintering of Ni particles. The average Ni particle size in NAC-S increased dramatically from 6.7 to 15.7 nm, whereas that in NACZ-S only increased from 7.0 to 10.8 nm (a moderate increase of 54%), demonstrating the superior sintering resistance of NACZ.

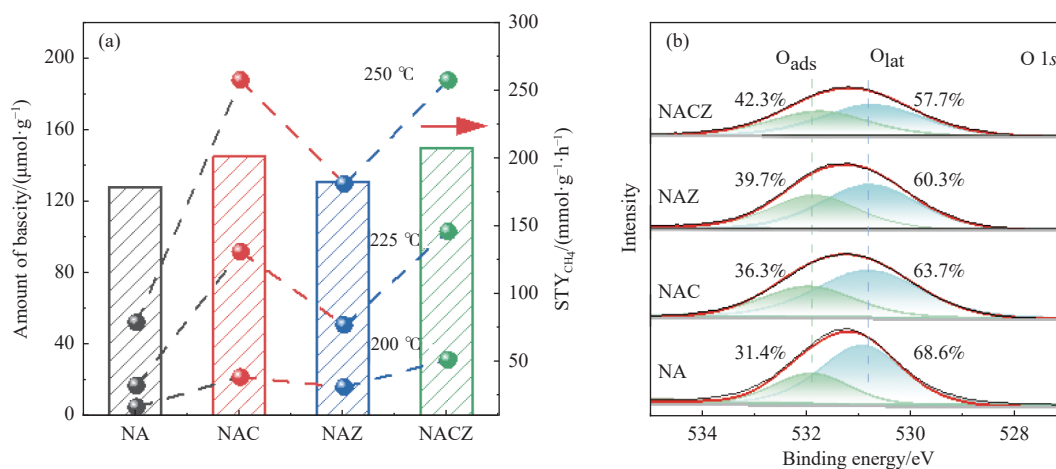


Fig. 6 (a) Correlation between alkalinity content and methane space-time yield of various catalysts; (b) XPS O 1s spectra

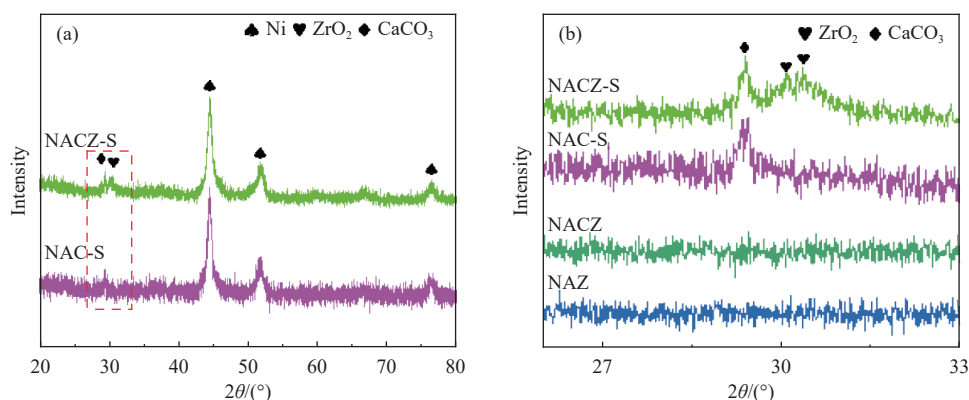


Fig. 7 (a) XRD patterns of spent catalysts after aging test, (b) magnified view of the selected region

Table 4 Physicochemical properties of the spent catalysts after aging test

Sample	Ni size/nm		CO ₃ ²⁻ /%
	grain size ^a	particle size ^b	
NAC	4.6	6.7	18.7
NACZ	5.2	7.0	17.4
NAC-S	11.7 (149%)	15.7 (137%)	31.1 (66%)
NACZ-S	10.8 (108%)	10.8 (54%)	19.4 (11%)

Notes: ^a: Calculated from the XRD pattern using the Scherrer equation, with the number in parentheses indicating the increase relative to the corresponding fresh catalyst; ^b: Obtained from the TEM image statistics, with the number in parentheses indicating the increase relative to the corresponding fresh catalyst; ^c: Determined from the XPS results, with the number in parentheses indicating the increase relative to the corresponding fresh catalyst.

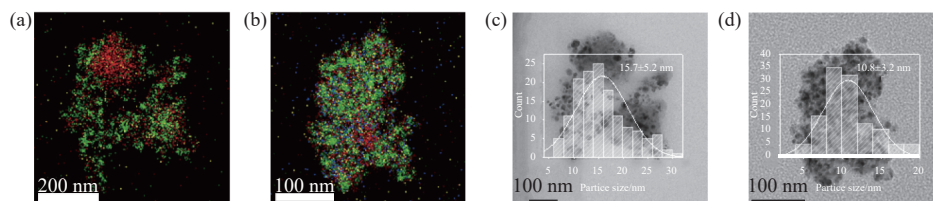


Fig. 8 TEM-EDX elemental mapping of (a) NAC-S, (b) NACZ-S, in which the green, red, yellow and blue dots represent Ni, Al, Ca and Zr elements, respectively; TEM images of the catalysts after aging, with the insets showing the Ni particle size distribution: (c) NAC-S, (d) NACZ-S

Thermogravimetric analysis was conducted to investigate the thermal decomposition of the NAC-S and NACZ-S samples after aging (Figure 9(a)). The thermogravimetric curves of both samples exhibited similar trends. Based on the mass changes observed at specific temperature ranges, the thermogravimetric curve can be divided into four intervals: room temperature to 250, 250–490, 490–600 and 600–700 °C, corresponding to the desorption of adsorbed species, the oxidation of metallic Ni^[33], the combustion of carbon deposits^[20], and the decomposition of CaCO₃, respectively. The mass losses in the 490–600 °C region attributed to carbon combustion were comparable for NAC-S and NACZ-S, at 0.4% and 0.6%, respectively. Combined with the XRD and TEM results, it can be concluded that the stability difference between the NAC and NACZ catalysts is not primarily attributed to carbon deposition but rather to Ni sintering. Furthermore, the mass losses due to CaCO₃ decomposition for NAC-S and NACZ-S were 1.9% and

1.5%, respectively, indicating that more CaCO₃ was formed on NAC-S during aging. The XRD analysis of NACZ-S revealed partial incorporation of Ca into the ZrO₂ lattice during the reaction, potentially explaining the lower CaCO₃ content in NACZ-S. The conversion of Ca species into CaCO₃ may weaken its anchoring effect on Ni, leading to the Ni migration and sintering. The Zr promoter in the NACZ catalyst hindered the formation of CaCO₃, which contributed to its superior sintering resistance.

To investigate the influence of various dopants on the metal-support interaction of the Ni/Al₂O₃ catalysts, H₂-TPR tests were conducted on the calcined samples, as shown in Figure 9(b). Based on the reduction temperature regions, the reduction profiles can be deconvoluted into three types of NiO species: α-NiO (300–410 °C), β-NiO (410–780 °C), and γ-NiO (780–900 °C). The α-NiO species represents bulk free NiO with weak interaction with the Al₂O₃ support, whereas β-NiO exhibits moderate interaction with the Al₂O₃

support. In contrast, γ -NiO corresponds to Ni reduction within the spinel phase, indicating a strong interaction with the Al₂O₃ support^[37]. Except for NACZ, all other catalysts exhibited distinct free NiO hydrogen consumption peaks, indicating that NiO in the NACZ catalyst exhibited the strongest interaction with the support and good dispersion. β -NiO was the predominant form in all catalysts, with the β peak center position in the order of NACZ > NAC > NAZ $\approx$ NA. These results indicate that Ca enhances metal-support interaction, while Zr further synergistically strengthens this effect. A stronger metal-support interaction effectively mitigates high-temperature sintering by suppressing Ni migration^[27].

Figure 10 shows the XPS spectra, to gain deeper insight into the interaction between Ca and Zr promoters. The binding energies of Ca²⁺ and Zr⁴⁺ in the co-doped NACZ catalyst exhibited noticeable shifts compared to those of the catalysts doped with Ca or Zr alone, indicating a strong interaction between Ca and Zr^[38–39]. In the C 1s spectra, the

peak near 289 eV was assigned to CO₃²⁻. As given in Table 4, the CO₃²⁻ content increased in both NAC-S and NACZ-S samples after aging tests, though a lower increase was observed in NACZ-S. This aligns with the XRD and TG results, indicating that Ca species in the NAC catalyst reacted with CO₂ to form CaCO₃, whereas the Zr promoter in the NACZ catalyst reduced CaCO₃ formation. During the conversion of Ca species into CaCO₃, the intermediate CaO* readily drives its grain aggregation on its surface^[40]; CaCO₃ itself is prone to sintering^[41], which collectively leads to severe sintering of interacting Ni and a decline in catalytic activity. In the NACZ catalyst, the formation of Ca-Zr solid solution mitigates such events, thereby alleviating the Ni sintering.

In summary, the introduction of Zr enhances the metal-support interactions and reduces Ni sintering. In addition, Zr inhibits the conversion of Ca species into CaCO₃, thereby alleviating Ca-induced Ni agglomeration.

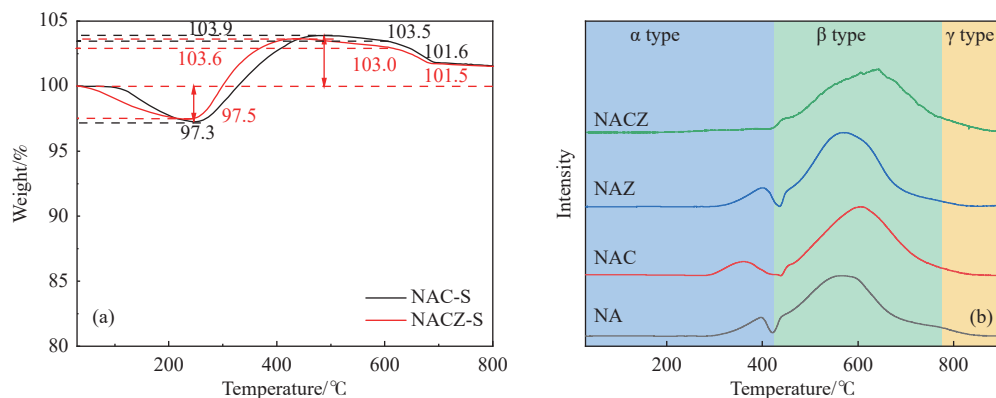


Fig. 9 (a) TG curves of NAC-S and NACZ-S; (b) H₂-TPR profiles of various catalysts

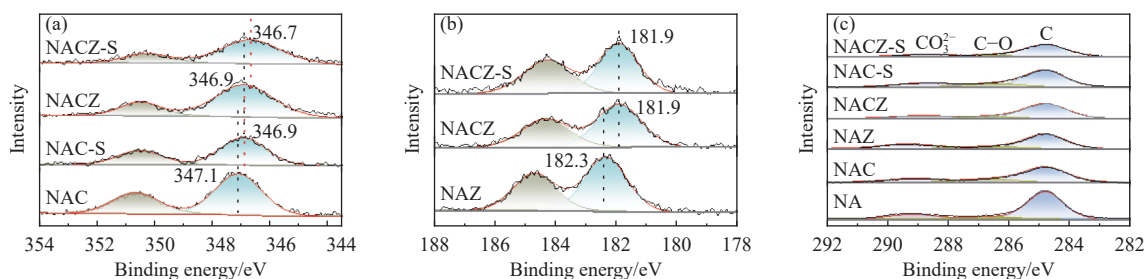


Fig. 10 XPS spectra of (a) Ca 2p, (b) Zr 3d and (c) C 1s

3 Conclusions

An Ni/CaO-ZrO₂-Al₂O₃ catalyst co-doped with both Ca and Zr was prepared, which exhibited high low-temperature activity and robust high-temperature sintering resistance in the CO₂ methanation. At 250 °C and a WHSV of 30000 mL/(g·h), the Ni/CaO-ZrO₂-Al₂O₃ catalyst achieved a CO₂ conversion of 96% and a CH₄ selectivity of 100% and the high performance in CO₂ methanation was preserved after high-temperature aging. In contrast, the Ni/CaO-Al₂O₃ catalyst doped with Ca alone showed

comparable initial activity, but suffered a pronounced activity decline after aging. Physicochemical characterization results reveal that Ca significantly enhances Ni dispersion, while the combined introduction of Ca and Zr increases alkalinity; these synergistic effects account for the excellent low-temperature activity of the Ni/CaO-ZrO₂-Al₂O₃ catalyst. The Ca species in the Ni/CaO-Al₂O₃ catalyst convert into CaCO₃ during the reaction, which may promote the Ni sintering. However, the presence of Zr strengthens the metal-support interaction and forms partial Ca-Zr solid solutions to stabilize Ca species, which can effectively suppress the Ni sintering at high temperature.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] GÖTZ M, LEFEBVRE J, MÖRS F, et al. Renewable power-to-Gas: A technological and economic review[J]. Renewable Energy, 2016, 85: 1371–1390.
- [2] JENTSCH M, TROST T, STERNER M. Optimal use of Power-to-Gas energy storage systems in an 85% renewable energy scenario[J]. Energy Procedia, 2014, 46: 254–261.
- [3] RIANI P, SPENNATI E, GARCIA M V, et al. Ni/Al₂O₃ catalysts for CO₂ methanation: Effect of silica and nickel loading[J]. Int J Hydrogen Energy, 2023, 48(64): 24976–24995.
- [4] KENYOTHA K, KIDKHUNTHOD P, POO-ARPORN Y, et al. Ceria-supported Ni catalyst with high catalytic activity, selectivity and stability for CO₂ conversion to CH₄ by hydrogenation reaction investigated by X-ray absorption spectroscopy[J]. J Phys Chem Solids, 2024, 190: 112009.
- [5] OBEID M, POUPIN C, LABAKI M, et al. Influence of the ultrasound power density in the ultrasound-assisted synthesis of Ni-based LDH catalysts for CO₂ methanation[J]. J Environ Chem Eng, 2024, 12(5): 114059.
- [6] GAO J, WANG Y, PING Y, et al. A thermodynamic analysis of methanation reactions of carbon oxides for the production of synthetic natural gas[J]. RSC Adv, 2012, 2(6): 2358–2368.
- [7] WANG H, GUO S, QIN Z, et al. A thermodynamic consideration on the synthesis of methane from CO, CO₂, and their mixture by hydrogenation[J]. J Fuel Chem Technol, 2024, 52(10): 1453–1461.
- [8] EWALD S, KOLBECK M, KRATKY T, et al. On the deactivation of Ni-Al catalysts in CO₂ methanation[J]. Appl Catal A: Gen, 2019, 570: 376–386.
- [9] UTTAMAPRAKROM W, REUBROYCHAROEN P, CHAROENSIRITANASIN P, et al. Development of Ni-Ce/Al-MCM-41 catalysts prepared from natural kaolin for CO₂ methanation[J]. J Environ Chem Eng, 2021, 9(5): 106150.
- [10] SANI L A, WANG C, ZHANG M, et al. Methanation of CO₂ over Yb-promoted Ni/Al₂O₃ catalysts prepared by solution combustion[J]. Energy Fuels, 2022, 36(10): 5360–5374.
- [11] YANG Y, Ge T, JIANG Y, et al. In-situ growth of nickel-based catalysts on the surface of macroporous Al₂O₃ for CO₂ methanation[J]. J Fuel Chem Technol, 2024, 52(11): 1664–1673.
- [12] WANG C, SUN H, LIU X, et al. Low-temperature CO₂ methanation over Ru/CeO₂: Investigation into Ru loadings [J]. Fuel, 2023, 345: 128238.
- [13] TAN J, WANG J, ZHANG Z, et al. Highly dispersed and stable Ni nanoparticles confined by MgO on ZrO₂ for CO₂ methanation[J]. Appl Surf Sci, 2019, 481: 1538–1548.
- [14] ZHANG J, REN B, FAN G, et al. Exceptional low-temperature activity of a perovskite-type AlCeO₃ solid solution-supported Ni-based nanocatalyst towards CO₂ methanation[J]. Catal Sci Technol, 2021, 11(11): 3894–3904.
- [15] SONG C, LIU J, WANG R, et al. Engineering MO_x/Ni inverse catalysts for low-temperature CO₂ activation with high methane yields[J]. Nat Chem Eng., 2024, 1: 638–649.
- [16] LEE W, LI C, PRAJITNO, et al. Recent trend in thermal catalytic low temperature CO₂ methanation: A critical review[J]. Catal Today, 2021, 368: 2–19.
- [17] NETSKINA O, MUCHA S, VESELOVSKAYA J, et al. CO₂ methanation: Nickel-alumina catalyst prepared by solid-state combustion[J]. Materials, 2021, 14(22): 6789.
- [18] YOUNAS M, LOONG KONG L, BASHIR M J K, et al. Recent advancements, fundamental challenges, and opportunities in catalytic methanation of CO₂[J]. Energy Fuels, 2016, 30(11): 8815–8831.
- [19] MILLET M M, TARASOV A V, GIRGSDIES F, et al. Highly dispersed Ni⁰/Ni₄Mg_{1-x}O catalysts derived from solid solutions: How metal and support control the CO₂ hydrogenation[J]. ACS Catal, 2019, 9(9): 8534–8546.
- [20] XING R, JIANG Y, LI J, et al. Ni/MgO-Al₂O₃ catalysts for CO₂ methanation: Deactivation mechanism study[J]. Ind Eng Chem Res, 2025, 64(27): 13653–13662.
- [21] LU B, FAN Y, ZHI X, et al. Material design and prospect of dual-functional materials for integrated carbon dioxide capture and conversion[J]. Carbon Capture Sci Technol, 2024, 12: 100207.
- [22] WU X, CHANG R, TAN M, et al. An investigation of the Ni/carbonate interfaces on dual function materials in integrated CO₂ capture and utilisation cycles[J]. Appl Catal B: Environ, 2023, 338: 123053.
- [23] LI L, ZHANG Y, FENG J, et al. Ni-Ca-Al synergistic effect in dual-function materials for integrated CO₂ capture and conversion[J]. ACS Sustainable Chem Eng, 2024, 12(2): 925–937.
- [24] LIANG C, HU X, WEI T, et al. Methanation of CO₂ over Ni/Al₂O₃ modified with alkaline earth metals: Impacts of oxygen vacancies on catalytic activity[J]. Int J Hydrogen Energy, 2019, 44(16): 8197–8213.
- [25] DIAS Y, BERNARDI F, PEREZ - LOPEZ O W. Improving low-temperature CO₂ methanation by promoting Ni-Al LDH-derived catalysts with alkali metals[J]. ChemCatChem, 2023, 15(22): e202300834.
- [26] DIAS Y, PEREZ-LOPEZ O W. Tuning the Ca content of Ni-Ca-Al layered-double hydroxide catalysts for low-temperature CO₂ methanation[J]. J Mater Chem. A, 2024, 12(39): 26820–26832.
- [27] XING R, LI J, ZHANG X, et al. Deactivation mechanism and solution review of Ni-based catalysts for CO₂ methanation[J]. Chem Ind Eng Prog, 2026, 45(3): 1475–1487.
- [28] JIANG P, ZHAO J, HAN Y, et al. Highly active and dispersed Ni/Al₂O₃ catalysts for CO methanation prepared by the cation-anion double-hydrolysis method: Effects of Zr, Fe, and Ce promoters[J]. Ind Eng Chem Res, 2019, 58(27): 11728–11738.
- [29] LIN J, MA C, WANG Q, et al. Enhanced low-temperature performance of CO₂ methanation over mesoporous Ni/Al₂O₃-ZrO₂ catalysts[J]. Appl Catal B: Environ, 2019, 243: 262–272.
- [30] GAC W, ZAWADZKI W, ROTKO M, et al. Effects of support composition on the performance of nickel catalysts in CO₂ methanation reaction[J]. Catal Today, 2020, 357: 468–482.
- [31] CHEN Y, HOU Z, WANG C, et al. An active manganese promoted Ni/Al₂O₃ catalyst for low temperature CO₂ methanation[J]. Catal Lett, 2024, 154(3): 943–951.

- [32] GAC W, ZAWADZKI W, ROTKO M, et al. CO₂ methanation in the presence of Ce-promoted alumina supported nickel catalysts: H₂S deactivation studies[J]. Top Catal, 2019, 62: 524–534.
- [33] WANG H, WU J, BAO Y, et al. CO₂ methanation over Ni/Al₂O₃-ZrO₂ catalysts: Optimizing metal-oxide interfaces by calcinating-induced phase transformation of support[J]. J Environ Chem Eng, 2023, 11(2): 109538.
- [34] XU L, ZHANG W, SHEN L, et al. Enhanced low-temperature CO₂ methanation over a Ni-based catalyst supported on La₂O₃-Al₂O₃ composite supports[J]. Catal Sci Technol, 2025, 15(16): 4741–4749.
- [35] AZIZ M A A, JALIL A A, TRIWAHYONO S, et al. Highly active Ni-promoted mesostructured silica nanoparticles for CO₂ methanation[J]. Appl Catal B: Environ, 2014, 147: 359–368.
- [36] HARIYANTO B, ELY S, HILMI A R, et al. Thermal-induced structural behavior in CaO-doped ZrO₂ nanocrystals: A high-temperature synchrotron XRD and XAS study[J]. Nano-Struct Nano-Objects, 2025, 42: 101470.
- [37] WU H, ZOU M, GUO L, et al. Effects of calcination temperatures on the structure-activity relationship of Ni-La/Al₂O₃ catalysts for syngas methanation[J]. RSC Adv, 2020, 10(7): 4166–4174.
- [38] TAN J, REN H, ZHAO Z, et al. Ca²⁺ doped metal organic frameworks for enhanced photocatalytic ammonia synthesis[J]. Chem Eng J, 2023, 466: 143259.
- [39] YU H, SUN J, CHEN X, et al. Synthesis of a novel acid-base bifunctional Zn/Ca-Zr catalyst for biodiesel application: Experimental and molecular simulation studies[J]. Renewable Energy, 2023, 217: 119138.
- [40] WEI L, HAN R, HAN G, et al. Modulating the evolution of metastable CaO* for the near-theoretical performance breakthrough of Ni/CeO₂-CaO in integrated CO₂ capture and methanation[J]. Adv Sci, 2025, 12(26): 2503086.
- [41] SUN H, JIN X, LIU T, et al. Porous hollow Ni/CaO dual functional materials for integrated CO₂ capture and methanation[J]. Carbon Capture Sci Technol, 2024, 13: 100259.

CO₂ 甲烷化: 高低温活性和抗烧结的 Ni/CaO-ZrO₂-Al₂O₃ 催化剂

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摘 要: Ni/Al₂O₃ 是 CO₂ 甲烷化最具工业应用前景的催化剂体系之一, 然而低温活性不足、高温易烧结等问题限制了其应用。针对上述挑战, 通过引入 Ca 与 Zr 助剂, 制备了具有高活性和抗烧结的 Ni/CaO-ZrO₂-Al₂O₃ 催化剂, 在 250 °C、空速 30000 mL/(g·h) 的反应条件下, CO₂ 转化率高达 96%, 甲烷时空收率达 257.5 mmol/(g·h)。对催化剂进行 200 h 的 600 °C 高温老化试验结果表明, 高温老化后, 引入 Ca、Zr 双助剂的 Ni/CaO-ZrO₂-Al₂O₃ 催化剂的 Ni 尺寸增幅低于单一 Ca 助剂的 Ni/CaO-Al₂O₃ 催化剂, 同时活性损失程度更低。Ca 与 Zr 助剂一方面提高了 Ni 分散度; 另一方面增强了表面碱性, 从而获得优异的低温活性。此外, 由于在反应环境下 Zr 与 Ca 发生固相反应, 减少了含 Ca 物种向 CaCO₃ 的转化, 进而抑制高温反应中表面 Ni 的烧结。该研究为开发高性能 CO₂ 甲烷化 Ni 基催化剂提供了新的助剂设计策略。

关键词: 甲烷化; Ni/Al₂O₃ 催化剂; 低温活性; 抗烧结性能

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