The Effect of Si on CO₂ Methanation over Ni-xSi/ZrO₂ Catalysts at Low Temperature

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Abstract: A series of Ni-xSi/ZrO₂ (x = 0, 0.1, 0.5, 1 wt%), the controlled contents of Si) catalysts with a controlled nickel content of 10 wt% were prepared by the co-impregnation method with ZrO₂ as support and Si as a promoter. The effect of different amounts of Si on the catalytic performance was investigated for CO₂ methanation with the stoichiometric H₂/CO₂ molar ratio (4/1). The catalysts were characterized by BET, XRF, H₂-TPR, H₂-TPD, H₂-chemisorption, CO₂-TPD, XRD, TEM, XPS, and TG-DSC. It was found that adding the appropriate amount of Si could improve the catalytic performance of Ni/ZrO₂ catalyst at a low reaction temperature (250 °C). Among all the catalysts studied, the Ni-0.1Si/ZrO₂ catalyst showed the highest catalytic activity, with H₂ and CO₂ conversion of 73.4% and 72.5%, respectively and the yield of CH₄ was 72.2%. Meanwhile, the catalyst showed high stability and no deactivation within a 10 h test. Adding the appropriate amount of Si could enhance the interaction between Ni and ZrO₂, and increase the Ni dispersion, the amount of active sites including surface Ni³⁺, oxygen vacancies, and strong basic sites on the catalyst surface. These might be the reasons for the high activity and selectivity of the Ni-0.1Si/ZrO₂ catalyst.

Keywords: CO₂ methanation; Ni-xSi/ZrO₂; Si promotion; oxygen vacancies

1. Introduction

With the release of a large amount of CO₂ into the atmosphere, the greenhouse effect has increased in recent years [1,2]. Facing this great challenge, there are three main ways to control CO₂ emissions: 1. Reducing CO₂ emissions, 2. Capture and storage of CO₂, and 3. Chemical conversion and utilization of CO₂ [3–5]. Converting CO₂ into value-added chemicals is by far the most cost-effective method [6–8]. Clean and renewable energy resources (wind, solar, and tidal energy) produce discontinuous electricity, which is not capable of being connected to the grid. Whereas, hydrogen can be generated by electrolysis using this discontinuous electricity [9–11]. With this H₂ supply, the CO₂ methanation reaction is attracting more and more interest due to the use of both carbon dioxide and hydrogen obtained from renewable energy. Compared with hydrogen, methane has many advantages, which could be easily liquefied, stored, transported, and used by the natural gas infrastructure [12,13]. In 1902, Sabatier et al. came up with the CO₂ methanation reaction (also called the Sabatier reaction) firstly, CO₂ + 4 H₂ → CH₄ + 2 H₂O, ΔG = −130.8 KJ mol⁻¹, ΔH = −165 KJ mol⁻¹ [14]. It can be seen that the CO₂ methanation reaction is highly exothermic, which is thermodynamically favorable but kinetically constrained [15]. Meanwhile, the heat released during the reaction will lead to the sintering of metal particles and deactivation of the catalysts [9,16]. Therefore, designing a high active and stable catalyst operating at low temperature is important [17]. Many studies have shown that VIII metals exhibit a catalytic performance for CO₂ methanation, especially Ru [18], Rh [19], Pd [20], and Ni [21]. Although noble metal catalysts exhibit a higher catalytic activity and CH₄ selectivity at low temperature, their
Catalysts and CO₂ methanation reaction due to its abundance, low cost, and high activity [23–25]. Moreover, the properties of support play an important role in catalytic performance including the surface properties, the ability to disperse the active phase, and metal-support interaction. It is crucial to choose an appropriate support in preparing effective catalysts [26,27]. Many different metal oxides, such as CeO₂ [28], MgO [29], Al₂O₃ [30], TiO₂ [31,32], SiO₂ [9,33], ZrO₂ [34–38], and Y₂O₃ [39], have been used as support to promote CO₂ methanation. ZrO₂ becomes the most promising support and is getting increased attention since it has a higher concentration of oxygen defects [5]. Xu et al. [35] studied the CO₂ methanation mechanism on the Ni/ZrO₂ catalyst by in-situ FTIR and DFT methods, and found that c-ZrO₂ could improve the electron mobility, the reducibility of Ni, and thus increase the catalytic activity of the catalysts. Martínez et al. [36] found that Ni/ZrO₂ had a higher catalytic activity due to the strong interaction between Ni and ZrO₂ by comparing the catalytic performance of Ni/ZrO₂, Ni/SiO₂, and Ni/MgAl₂O₄ catalysts. Hu et al. [37] also used ZrO₂ as support, due to its good synergetic function, to explore the effect of La on the CO₂ methanation reaction. Jia et al. [38] found that the structure of the catalyst had a significant influence on the catalytic performance. In addition, 71.9% CO₂ conversion and 69.5% CH₄ yield at 300 °C could be obtained on the Ni/ZrO₂ catalyst prepared by the DBD plasma decomposition of nickel nitrate, while the CO₂ conversion and CH₄ yield were only 32.9% and 30.3% on the catalyst prepared thermally. Many researchers also reported that Ni/CeZrO₂ catalysts exhibited an excellent low temperature catalytic performance for CO₂ methanation due to the oxygen vacancies and high oxygen storage capacity of CeZrO₂ [40–42].

In addition, promoters could further improve the catalytic activity. Therefore, the addition of a second element into nickel-based catalysts is considered as an effective method to improve the catalytic activity and stability at low temperature [14,21,43]. There are many types of promoters, including alkaline earth metals (Mg, Ca) [44,45], noble metals (Pt, Pd, Rh) [43], rare earth metals (La, Ce, Sm) [46], etc. The activation of CO₂ can be enhanced by changing the surface basicity of the catalyst and the metal-support interaction [30,44,46]. Guilera et al. [30] studied the metal-oxide promoted Ni/Al₂O₃ catalyst, which exhibited a higher catalytic performance compared with the Ni/Al₂O₃ catalyst, due to the increase in basic sites and nickel dispersion. Xu et al. [46] found that the surface basicity and the intensity of CO₂ chemisorption on Ni-based catalysts promoted by rare earth metals greatly increased, which could enhance the low-temperature catalytic activity of the catalysts. Wang et al. [47] found that the Ni-Si/ZrO₂ catalyst (Si as promoter) had a better catalytic performance on the DRM reaction than the Ni-Zr/SiO₂ catalyst (Zr as promoter). The Si on the Ni-Si/ZrO₂ catalyst could promote the dispersion of Ni and improve the stability of metal Ni in the DRM reaction process. The highly dispersed Ni species on Ni-Si/ZrO₂ increased the activation of CH₄ and CO₂, thus increasing the catalytic activity.

Since CO₂ adsorption and activation were the key steps in both the DRM reaction and CO₂ methanation, and CO₂, CH₄, and H₂ co-existed in both the two systems. This study tried to apply the Ni-Si/ZrO₂ catalyst to CO₂ methanation to improve the activation of CO₂ and promote CO₂ methanation. Therefore, Ni-xSi/ZrO₂ (Ni is 10 wt%, x = 0, 0.1, 0.5, 1 wt%) catalysts with different contents of Si were prepared by the co-impregnation method. The catalysts were characterized by different methods, including BET, H₂-TPR, H₂-TPD, H₂-chemisorption, CO₂-TPD, XRD, TEM, XPS, and TG-DSC, to explore the influence of Si.

2. Results and Discussion
2.1. The Catalytic Performance of Ni-xSi/ZrO₂ Catalysts

The catalytic performance of Ni-xSi/ZrO₂ catalysts was investigated over the temperature range from 200 to 400 °C under atmospheric pressure. The results of the catalytic test were presented in Figure 1, including the conversion of H₂ and CO₂, and the selectivity and yield of CH₄. The catalytic activity increased as the temperature increased until it was...
thermodynamically limited by the equilibrium. Among all catalysts, the Ni-0.1Si/ZrO$_2$ catalyst was the most active over the whole temperature range, followed by the Ni/ZrO$_2$ catalyst, which exhibited an excellent catalytic activity at 250 °C. On the unpromoted Ni/ZrO$_2$ catalyst, the CO$_2$ conversion and CH$_4$ yield were 66.6% and 66.2%, respectively with the 99.4% CH$_4$ selectivity. Si-promoted Ni/ZrO$_2$ catalysts exhibited a different catalytic activity, which changed with the amount of Si. The Ni-0.1Si/ZrO$_2$ catalyst exhibited the highest CO$_2$ conversion of 72.5% and H$_2$ conversion of 73.4% among the studied catalysts. Simultaneously, it showed the highest CH$_4$ selectivity of 99.6% and the highest CH$_4$ yield of 72.2%, whose catalytic activity was about 6% higher than the Ni/ZrO$_2$ catalyst. However, the Ni-0.5Si/ZrO$_2$ catalyst showed a rather low activity, with 10% H$_2$ conversion and 9.8% CO$_2$ conversion. The lowest catalytic activity was obtained on the Ni-1Si/ZrO$_2$ catalyst, with only 1% CH$_4$ yield. In general, adding the appropriate Si was beneficial to CO$_2$ methanation.

Figure 1. The conversion of H$_2$ (A) and CO$_2$ (B), the selectivity of CH$_4$ (C), and the yield of CH$_4$ (D) on Ni-xSi/ZrO$_2$ catalysts over the temperature range from 200 to 400 °C.

Then, the catalytic stability of Ni-xSi/ZrO$_2$ catalysts was investigated at 250 °C where the catalyst exhibited a high activity. The results of the catalytic test were presented in Figure 2. All the catalysts exhibited the high stability with 10 h on stream. TG-DSC analysis results showed that the weight of all spent catalysts did not decrease during the heating process (Figure S1), which illustrated that there was no carbon deposition on the catalysts after reaction.
The conversion of H$_2$ (A) and CO$_2$ (B), the selectivity of CH$_4$ (C), and the yield of CH$_4$ (D) on Ni-xSi/ZrO$_2$ catalysts at 250 °C with a time on stream (H$_2$/CO$_2$ = 4/1, F = 150 mL/min).

2.2. The Textural Properties of Ni-xSi/ZrO$_2$ Catalysts

The physical properties of Ni-xSi/ZrO$_2$ catalysts were characterized by N$_2$ adsorption-desorption experiments. Figure 3 showed the N$_2$ adsorption-desorption isotherms, pore volume, and size distribution of the catalysts. All isotherms of the catalysts were assigned to the type IV isotherm and the P/P$_0$ for the hysteresis loop was 0.7~0.9, which indicated that all the catalysts were with the mesoporous structure, and that also could be proved by the pore size distribution in Figure 2B [48-50]. The textural properties of catalysts were summarized in Table 1. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method and the pore size and volume were calculated by the Barrett-Joyner-Halenda (BJH) method. Obviously, it could be seen that the BET results of catalysts with a different Si content had no significant differences, which suggested that the different loading of Si did not damage the pore structure of the Ni/ZrO$_2$ catalyst.

Figure 2. The conversion of H$_2$ (A) and CO$_2$ (B), the selectivity of CH$_4$ (C), and the yield of CH$_4$ (D) on Ni-xSi/ZrO$_2$ catalysts at 250 °C with a time on stream (H$_2$/CO$_2$ = 4/1, F = 150 mL/min).

Figure 3. N$_2$ adsorption-desorption isotherms (A) and pore volume and size distribution (B) of Ni-xSi/ZrO$_2$ catalysts.
Table 1. Textural properties and element contents of Ni-xSi/ZrO$_2$ catalysts.

| Catalyst       | $S_{\text{BET}}$ $^{a}$ (m$^2$·g$^{-1}$) | $V_{\text{BJH}}$ $^{b}$ (m$^3$·g$^{-1}$) | $D_p$ $^{c}$ (nm) | Ni (%) $^{d}$ | Si (%) $^{d}$ |
|----------------|----------------------------------------|----------------------------------------|-----------------|----------------|----------------|
| Ni/ZrO$_2$     | 42.5                                   | 0.15                                   | 13.5            | 6.74           | -              |
| Ni-0.1Si/ZrO$_2$ | 46.0                                   | 0.16                                   | 12.8            | 6.66           | 0.11           |
| Ni-0.5Si/ZrO$_2$ | 44.6                                   | 0.15                                   | 13.2            | 6.51           | 0.34           |
| Ni-1Si/ZrO$_2$  | 44.4                                   | 0.15                                   | 13.2            | 5.79           | 0.58           |

$^{a}$: Surface area ($S_{\text{BET}}$) determined by the BET method; $^{b}$: BJH adsorption cumulative volume of pores; $^{c}$: BJH adsorption average pore diameter; $^{d}$: Obtained by XRF.

The actual loadings of Ni and Si were determined by the X-ray fluorescence (XRF) test. The content of Ni on Ni/ZrO$_2$, Ni-0.1Si/ZrO$_2$, Ni-0.5Si/ZrO$_2$, and Ni-1Si/ZrO$_2$ were 6.74%, 6.66%, 6.51%, and 5.79%, respectively. The actual contents of Ni on these catalysts were very close, indicating the successful loading of Ni onto ZrO$_2$. The content of Si on Ni-0.1Si/ZrO$_2$, Ni-0.5Si/ZrO$_2$, and Ni-1Si/ZrO$_2$ were 0.11%, 0.34%, and 0.58%, respectively.

2.3. The Reducibility of Ni-xSi/ZrO$_2$ Catalysts

The TPR profiles of calcined Ni-xSi/ZrO$_2$ catalysts and support ZrO$_2$ were presented in Figure 4. There was a broad peak at around 500 $^\circ$C on the ZrO$_2$. Three main different reduction peaks ($\alpha$, $\beta$, and $\gamma$) could be observed on the Ni-xSi/ZrO$_2$ catalysts, which suggested that there were three kinds of nickel oxide species. The $\alpha$ peak (317–327 $^\circ$C) was attributed to the reduction of the bulk NiO species on the surface of the catalysts. The $\beta$ peak (340–366 $^\circ$C) and $\gamma$ peak (419–428 $^\circ$C) were assigned to the reduction of NiO species that interacted weakly and strongly with support, respectively. The amount of each NiO species was summarized in Table 2. The minimum amount of bulk NiO species could be observed, indicating that a little bulk NiO species existed on all catalysts. The amount of $\beta$ peak was over 60% on both Ni-0.5Si/ZrO$_2$ and Ni-1Si/ZrO$_2$ catalysts. Associated with the catalytic activity, the NiO species that interacted with ZrO$_2$ weakly was not good for the CO$_2$ methanation reaction after reduction, resulting in a lower catalytic activity. While Ni-0.1Si/ZrO$_2$ and Ni/ZrO$_2$ catalysts showed the higher amount of the $\gamma$ peak contributing to a higher catalytic activity, suggesting that the strong interaction between the nickel and the support could promote the dispersion of Ni on the support [51]. Furthermore, the $\beta$ and $\gamma$ peaks of promoted Ni/ZrO$_2$ catalysts shifted to a lower temperature compared with that of the Ni/ZrO$_2$ catalyst, suggesting that the appropriate Si (0.1 wt%) promoted the dispersion of Ni [50,51]. The peaks of the Ni-0.1Si/ZrO$_2$ catalyst shifted to the lowest temperature (the $\beta$ at 340 $^\circ$C and the $\gamma$ at 419 $^\circ$C), indicating the highest Ni dispersion, which could increase the catalytic activity of catalysts. Therefore, the strong nickel-support interaction promoted the dispersion of Ni on the support, which was beneficial to the catalytic performance [1,50].

![Figure 4. H$_2$-TPR profiles of Ni-xSi/ZrO$_2$ catalysts and ZrO$_2$.](image_url)
Table 2. The amount of each nickel oxide species on the Ni-xSi/ZrO$_2$ catalysts.

| Catalyst    | $\alpha$ |         | $\beta$ |         | $\gamma$ |         |
|-------------|----------|---------|---------|---------|----------|---------|
|             | Position ($^\circ$C) | Content (%) | Position ($^\circ$C) | Content (%) | Position ($^\circ$C) | Content (%) |
| Ni/ZrO$_2$  | 321      | 13.9    | 366     | 20.5    | 428      | 65.6    |
| Ni-0.1Si/ZrO$_2$ | 317 | 5.0     | 340     | 17.5    | 419      | 77.5    |
| Ni-0.5Si/ZrO$_2$ | 319 | 14.2    | 365     | 60.1    | 426      | 25.7    |
| Ni-1Si/ZrO$_2$ | 327 | 7.8     | 366     | 62.1    | 422      | 30.1    |

2.4. The H$_2$-TPD and H$_2$-Chemisorption of Ni-xSi/ZrO$_2$ Catalysts

The amounts of active sites of reduced Ni-xSi/ZrO$_2$ catalysts were measured by H$_2$-TPD and H$_2$-chemisorption. Two peaks could be clearly observed in the patterns of reduced catalysts depicted in Figure 5. The first peak appeared at around 92–111 $^\circ$C, which was assigned to the weak active site, and a broad peak around at 500 $^\circ$C could be found over the catalysts, corresponding to the strong active site with the strong H$_2$ adsorption [51,52]. The temperature of two H$_2$ desorption peaks was different with different contents of Si. The highest temperature with 111 and 517 $^\circ$C of H$_2$ desorption peaks on the Ni-0.1Si/ZrO$_2$ catalyst suggested the strong H$_2$ adsorption to the active sites, which could be assigned to the high dispersion of Ni and the increasing number of active sites [51–53]. Considering the possible spill over in TPD over the catalysts, the pulse chemisorption of H$_2$ was also carried out. The dispersion of Ni obtained by H$_2$-chemisorption was shown in Table 3. The Ni dispersion of Ni/ZrO$_2$, Ni-0.1Si/ZrO$_2$, Ni-0.5Si/ZrO$_2$, and Ni-1Si/ZrO$_2$ were 0.65%, 0.67%, 0.34%, and 0.28%, respectively. The Ni-0.1Si/ZrO$_2$ catalyst showed the highest dispersion of Ni, which was slightly higher than the Ni/ZrO$_2$ catalyst. The amounts of adsorbed H$_2$ decreased significantly on Ni-0.5Si/ZrO$_2$ and Ni-1Si/ZrO$_2$ catalysts, suggesting that the amounts of Ni decreased, which corresponded to their lower catalytic activity.

Figure 5. H$_2$-TPD patterns of Ni-xSi/ZrO$_2$ catalysts.
Table 3. The H\textsubscript{2} uptake and Ni dispersion of Ni-xSi/ZrO\textsubscript{2} catalysts.

| Catalyst        | Peak 1          | Peak 2          | Total H\textsubscript{2} Uptake (µmol/g) | Ni Dispersion (%) |
|-----------------|-----------------|-----------------|----------------------------------------|-------------------|
|                 | T (°C)          | H\textsubscript{2} Uptake (µmol/g) | T (°C)          | H\textsubscript{2} Uptake (µmol/g) |                          |                          |
| Ni/ZrO\textsubscript{2} | 102             | 4.64            | 512                          | 5.02              | 9.66                          | 0.65                      |
| Ni-0.1Si/ZrO\textsubscript{2} | 111             | 4.64            | 517                          | 4.95              | 9.59                          | 0.67                      |
| Ni-0.5Si/ZrO\textsubscript{2} | 103             | 4.28            | 505                          | 2.59              | 6.87                          | 0.34                      |
| Ni-1Si/ZrO\textsubscript{2}   | 92              | 4.06            | 503                          | 2.51              | 6.57                          | 0.28                      |

\textsuperscript{a}: Obtained by H\textsubscript{2}-TPD; \textsuperscript{b}: Obtained by H\textsubscript{2} chemisorption.

2.5. The Results of CO\textsubscript{2}-TPD on Ni-xSi/ZrO\textsubscript{2} Catalysts

The CO\textsubscript{2} desorption capability was explored by the CO\textsubscript{2}-TPD measurement and the profiles were shown in Figure 6, which was used to describe the basicity of catalysts usually. Two main CO\textsubscript{2} desorption peaks could be observed over each catalyst, which were classified as the adsorbed CO\textsubscript{2} at weak basic sites (361–410 °C) and strong basic sites (577–604 °C), respectively. Based on the pioneer studies, the CO\textsubscript{2} adsorbed on the weak basic sites could be desorbed at a low temperature and that absorbed on the strong basic sites could be desorbed at a high temperature [44]. The contents of weak and strong basic sites were calculated by the area of the peaks (Table 4). It could be seen that the content of strong basic sites on Ni-0.1Si/ZrO\textsubscript{2} was the highest (71%) among all the catalysts studied, which could inhibit carbon formation effectively [54,55]. Le et al. [56] found that the stronger CO\textsubscript{2} desorption peak around 500 °C on the Ni-CeO\textsubscript{2} catalyst suggested the strong CO\textsubscript{2} adsorption ability, which had a positive effect on the catalytic performance. In addition, the CO\textsubscript{2} adsorption peak of strong basic sites slightly shifted to a higher temperature with the increasing of Si, suggesting that the addition of Si promoted the adsorption of CO\textsubscript{2}. The intensified surface basicity of the Ni-0.1Si/ZrO\textsubscript{2} catalyst could promote the adsorption of CO\textsubscript{2} thus promoting the CO\textsubscript{2} methanation reaction [42,44,46].

Figure 6. CO\textsubscript{2}-TPD profiles of Ni-xSi/ZrO\textsubscript{2} catalysts.

Table 4. Peak position and basic sites of Ni-xSi/ZrO\textsubscript{2} catalysts obtained by CO\textsubscript{2}-TPD.

| Catalyst         | Peak 1            | Peak 2            | Total Basicity (µmol/g) |
|------------------|-------------------|-------------------|------------------------|
|                  | Position (°C)     | Content (%)        | Position (°C)          | Content (%)        |                          |
| Ni/ZrO\textsubscript{2} | 372               | 44                | 577                    | 56                | 123                      |
| Ni-0.1Si/ZrO\textsubscript{2} | 402               | 29                | 588                    | 71                | 124                      |
| Ni-0.5Si/ZrO\textsubscript{2} | 361               | 49                | 595                    | 51                | 127                      |
| Ni-1Si/ZrO\textsubscript{2}   | 410               | 46                | 604                    | 54                | 124                      |
2.6. Crystallite Structure of Ni-xSi/ZrO$_2$ Catalysts

The XRD patterns of catalysts could be seen in Figure 7. Before reduction, the diffraction peaks at 37.2, 43.3, and 62.9° were attributed to NiO (PDF no. 47-1049), as shown in Figure 7a [1,26]. The diffraction peaks at 44.5, 51.8, and 76.4° corresponded to the Ni metal (PDF no. 04-0850) over reduced catalysts, as shown in Figure 7b, and there was no diffraction peak of NiO [57]. In addition, no obvious diffraction peak of Si species was detected on Ni-xSi/ZrO$_2$ catalysts, suggesting that Si was in a high dispersion or amorphous state [51]. The crystallite sizes of NiO and Ni metal were calculated by the Scherrer equation at 2θ = 43.3° and 2θ = 44.5°, respectively, and the results were listed in Table 5. It could be seen that the particle sizes of NiO had no significant changes and the crystallite sizes of NiO were all around 25 nm on Ni-xSi/ZrO$_2$ catalysts before reduction. The grain sizes of the Ni metal were around 22 nm on reduced Ni-xSi/ZrO$_2$ catalysts, which also showed no obvious variation.

![XRD patterns of Ni-xSi/ZrO$_2$ catalysts](image)

**Figure 7.** XRD patterns of Ni-xSi/ZrO$_2$ catalysts (a) before reduction, (b) after reduction.

| Catalyst         | Before Reduction | After Reduction |
|------------------|------------------|-----------------|
| Ni/ZrO$_2$       | 24 nm            | 22 nm           |
| Ni-0.1Si/ZrO$_2$ | 26 nm            | 23 nm           |
| Ni-0.5Si/ZrO$_2$ | 26 nm            | 23 nm           |
| Ni-1Si/ZrO$_2$   | 25 nm            | 21 nm           |

2.7. The TEM Images of Ni-xSi/ZrO$_2$ Catalysts

The TEM images of reduced Ni-xSi/ZrO$_2$ catalysts were presented in Figure 8. It can be seen that all the catalysts exhibited a similar morphology, and the particle sizes were distributed between 10 and 30 nm. From Figure 8B, Ni was more evenly distributed with particle sizes of 18–20 nm on the Ni-0.1Si/ZrO$_2$ catalyst. However, on the Ni-1Si/ZrO$_2$ catalyst, the size distribution of nickel particles was uneven, and there were big nickel particles. From Figure 8D, bulk particles were found on the Ni-1Si/ZrO$_2$ catalyst, which might be bulk Ni particles or the mixture of Ni and Si.

2.8. Chemical State of the Elements on Ni-xSi/ZrO$_2$ Catalysts

The surface element composition and chemical state of reduced Ni-xSi/ZrO$_2$ catalysts were obtained by the XPS experiment, which were shown in Figure 9. There were four main peaks in the Ni 2p spectra. The peak at around 852 eV was assigned to the characteristic peak of Ni$^{0}$ [7]. There were two characteristic peaks of Ni$^{2+}$, P1 (about 854 eV) was the low energy peak and belonged to the peak of NiO, while P2 (about 856 eV) corresponded to Ni(OH)$_2$ [25]. The peak at around 860 eV was the companioning peak of Ni$^{2+}$, produced by the orbital spin splitting [30]. The percentages of different elements on the surface of catalysts were summarized in Table 6. The surface content of Ni$^{0}$ was the highest on the
Ni-0.1Si/ZrO$_2$ catalyst, which was 2.15%. More Ni$^0$ could provide more active sites and facilitate CO$_2$ methanation [58]. It could be found that the surface content of Si was higher than its actual loading, suggesting that Si enriched on the catalysts surface and part of Ni might be covered by Si, especially on Ni-0.5Si/ZrO$_2$ and Ni-1Si/ZrO$_2$ catalysts. The O 1s spectrum exhibited two types of oxygen species, as shown in Figure 9B. The peak at 530–530.46 eV was attributed to the lattice oxygen (O$_\alpha$) and the peak at 528.9–529.1 eV belonged to the surface oxygen (O$_\beta$) [28,59]. Based on the areas of O$_\alpha$ and O$_\beta$, the ratios of the oxygen vacancies could be obtained by calculating the ratio of O$_\beta$ to O$_T$ (O$_T$ = O$_\alpha$ + O$_\beta$) [5,22,38]. In Table 6, the reduced Ni-0.1Si/ZrO$_2$ catalyst exhibited the highest ratio (0.589) of O$_\beta$ to O$_T$ compared with other catalysts, suggesting the highest amount of oxygen vacancies. The presence of oxygen vacancies was beneficial to the adsorption of CO$_2$, which could promote CO$_2$ activation [23,58]. Jiang et al. [17] found that the content of surface oxygen on the Mn promoted Ni/bentonite catalyst was 83.55%, which was higher than that of the unpromoted Ni/bentonite catalyst (74.85%), representing the higher amount of oxygen vacancies. The increased oxygen vacancies were helpful to the adsorption and dissociation of CO$_2$ on the catalyst. To sum up, the Ni-0.1Si/ZrO$_2$ catalyst exhibited the highest catalytic activity and stability due to the highest amount of Ni$^0$ and oxygen vacancies on the surface.

![Figure 8. TEM images of Ni-xSi/ZrO$_2$ catalysts (A) Ni/ZrO$_2$ catalyst, (B) Ni-0.1Si/ZrO$_2$ catalyst, (C) Ni-0.5Si/ZrO$_2$ catalyst, and (D) Ni-1Si/ZrO$_2$ catalyst.](image1)

![Figure 9. XPS spectra of reduced Ni-xSi/ZrO$_2$ catalysts (A) Ni 2p and (B) O 1s.](image2)
Table 6. Surface contents on reduced Ni-xSi/ZrO$_2$ catalysts.

| Catalyst         | Ni (%) | Si (%) | O$_{\beta}$/O$_T$ |
|------------------|--------|--------|-------------------|
| Ni/ZrO$_2$       | 1.88   | 0      | 0.56              |
| Ni-0.1Si/ZrO$_2$ | 2.15   | 0.45   | 0.59              |
| Ni-0.5Si/ZrO$_2$ | 1.78   | 1.91   | 0.51              |
| Ni-1Si/ZrO$_2$   | 1.27   | 3.74   | 0.50              |

3. Materials and Methods

3.1. Catalysts Preparation

The ZrO$_2$ support was prepared by the precipitation method. A certain amount of Zr(NO$_3$)$_4$·5H$_2$O (ChengduKelong, China) was dissolved in deionized water with continuous stirring until dissolved completely. Then, NH$_3$·H$_2$O was added to the above solution to achieve a pH value of 9. After stirring for 2 h, the mixture was aged for 24 h at room temperature. After that, the mixture was filtered and washed three times with deionized water. The obtained sample was dried at 110 °C for 4 h and then calcined at 500 °C for 5 h (with the rate of 2 °C/min) to obtain the ZrO$_2$ support.

The impregnation method was used to synthesize the Ni-xSi/ZrO$_2$ catalysts (ZrO$_2$ was used as the support and Si was used as the promoter with the load of 0, 0.1, 0.5, and 1 wt%). The designed amount of Ni(NO$_3$)$_2$·6H$_2$O (ChengduKelong, Chengdu, China) and different amounts of (C$_2$H$_5$O)$_4$Si (Alfa Aesar Chemicals, Shanghai, China) were dissolved in a certain amount of absolute ethanol (Chengdu Chron Chemical, Chengdu, China). The ZrO$_2$ support was impregnated with the aforesaid ethanol solution for 24 h at room temperature. Then, these samples were dried at 80 °C for 2 h and 110 °C for 4 h. Finally, the above mixtures were heated to 500 °C (with the rate of 2 °C/min) and calcined at 500 °C for 5 h under air flow, then, the Ni-xSi/ZrO$_2$ catalysts were obtained (x = 0, 0.1, 0.5, 1 wt%).

3.2. Catalytic Activity Test

The catalytic activity test was carried out in a fixed-bed continuous flow micro-quartz-tube reactor with 10 mm in diameter at atmospheric pressure. There was a thermocouple near the reactor close to the fixed-bed, which was used to follow the temperature of the catalysts during the test. Before the activity test, 0.50 g of the catalyst was heated up to 450 °C (10 °C/min) and then reduced at a constant temperature of 450 °C for 1 h in H$_2$/Ar (F(H$_2$) = F(Ar) = 30 mL/min) mixture gas. After that, the catalyst was cooled down to the reaction temperature before the introduction of the mixture of reactants (H$_2$/CO$_2$ = 4, F = 150 mL/min) for the CO$_2$ methanation reaction. The effluent from the reactor passed through a condensing device and was analyzed online by a gas chromatograph (plot-C2000 capillary column) per hour.

$$X_{CO_2} = \frac{n_{CO_2,in} - n_{CO_2,our}}{n_{CO_2,in}} \times 100\%,$$

$$X_{H_2} = \frac{n_{H_2,in} - n_{H_2,our}}{n_{H_2,in}} \times 100\%,$$

$$S_{CH_4} = \frac{n_{CH_4,our}}{n_{CH_4,our} + n_{CO,our}} \times 100\%,$$

$$Y_{CH_4} = X_{H_2} \times S_{CH_4}$$

where $X_{CO_2}$ and $X_{H_2}$ were the conversion of CO$_2$ and H$_2$, $S_{CH_4}$ was the selectivity of CH$_4$, and $Y_{CH_4}$ was the yield of CH$_4$.

3.3. Catalysts Characterization

The physical property test was conducted in the Micromeritics Tristar II 3020 instrument by using the N$_2$ adsorption-desorption method. Before the measurements, about 0.1 g samples were outgassed at 150 °C for 2 h and then at 300 °C for 2 h under a vacuum.
The actual Ni and Si loadings of the fresh catalysts were determined by the X-ray fluorescence (XRF) test. Ni and Si were detected by the Ni Ka line and Si Ka line, respectively.

The hydrogen temperature-programmed reduction (H₂-TPR) measurement was carried out with a Micromeritics AutoChem II Chemisorption Analyzer. At first, about 100 mg of the catalyst was pretreated with Ar flow at 150 °C for 30 min. Then, the TPR experiment was performed from 50 to 800 °C in the H₂/Ar (10/90 vol%) flow with the heating rate of 8 °C/min. The TCD detector was used to monitor the H₂ consumption.

The temperature-programmed desorption of H₂ (H₂-TPD) was performed on the same equipment for H₂-TPR. About 100 mg of the reduced catalyst was pretreated at 500 °C for 1 h in Ar flow. Next, H₂ was absorbed at 50 °C for 1 h in 10% H₂/Ar. After cleaning the excess unabsorbed H₂, the catalyst was heated to 800 °C with a heating rate of 10 °C/min under Ar flow. The results were detected by a TCD detector. The H₂ pulse chemisorption was also processed on the equipment. About 100 mg of the reduced catalyst was pretreated at 450 °C for 1 h in Ar flow and cooled down to 50 °C at the same atmosphere for beginning the H₂ adsorption. A gas mixture of 10% H₂ balance Ar was pulsed over the catalyst for chemisorption measurements.

Before the temperature-programmed desorption of CO₂ (CO₂-TPD), about 100 mg of the reduced catalyst (reduced at 450 °C) was pretreated at 500 °C in He flow for 1 h to remove surface impurities. Then, CO₂ was absorbed at 50 °C for 1 h in 10% CO₂/He. After cleaning the excess unabsorbed CO₂, the catalyst was heated to 900 °C with a heating rate of 10 °C/min in He flow. The observed curves were fitted into two Gaussian peaks.

The X-ray diffraction (XRD) was performed on a DX-1000 CSC diffractometer instrument, operating at 40 kV and 25 mA with a Cu Kα radiation source for the calcined and reduced catalysts. The data was recorded over the scattering angle range of 2θ from 10 to 80°, with a scan step with of 0.03°.

Transmission electron microscopy (TEM) was used to characterize the reduced catalysts on the Tecnai G2 F20 machine. The twin instrument with the 0.20 nm resolution was used, and the acceleration voltage was 200 Kv.

The analysis of X-ray photoelectron spectroscopy (XPS) was carried out on a KRATOS spectrometer with an AXIS Ultra DLD. The Al Kα monochromatized line was operated at the accelerating power of 25 W. In addition, the binding energy was calibrated with C 1s 284.6 eV.

Thermogravimetric (TG) and differential scanning calorimetry analysis (DSC) was used to characterize the deposited carbon of the spent Ni-xSi/ZrO₂ catalysts, using the NETZSCH TG209F1 instrument. Before the test, the sample was placed until a better gas equilibrium. Then, the temperature was increased from 30 to 800 °C with a 5 °C·min⁻¹ heating rate in air flow with a rate of 60 mL·min⁻¹.

4. Conclusions

Adding the appropriate amount of Si could increase the catalytic activity of Ni/ZrO₂ catalyst, and the Ni-0.1Si/ZrO₂ catalyst showed the highest catalytic activity and stability. The strong interaction between Ni and ZrO₂ could promote the dispersion of Ni on the support, and the strong basic sites on the catalyst were beneficial to the absorption of CO₂, thus to the CO₂ methanation reaction on the Ni-0.1Si/ZrO₂ catalyst. In addition, the higher amount of surface Ni⁰ could provide more active sites, and the more oxygen vacancies were beneficial to the absorption and activation of CO₂ on the 0.1Si/ZrO₂ catalyst.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4344/11/1/67/s1. Figure S1. The TG-DSC profile of the spent Ni-xSi/ZrO₂ catalysts (A) Ni/ZrO₂ catalyst, (B) Ni-0.1Si/ZrO₂ catalyst, (C)Ni-0.5Si/ZrO₂ catalyst, and (D) Ni-1Si/ZrO₂ catalyst.
Author Contributions: Conceptualization, methodology, L.L., Y.W. and C.H.; software, validation, formal analysis, investigation, resources, data curation, writing—original draft preparation, L.L. and Q.Z.; writing—review and editing, visualization, supervision, Y.W. and C.H.; project administration, funding acquisition, C.H. All authors have read and agreed to the published version of the manuscript.

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