



Article The Effect of Preparation Method of Ni-Supported SiO₂ Catalysts for Carbon Dioxide Reforming of Methane

Hua-Ping Ren, Si-Yi Ding, Qiang Ma, Wen-Qi Song, Yu-Zhen Zhao, Jiao Liu, Ye-Ming He and Shao-Peng Tian *

Xi'an Key Laboratory of Advanced Photo-Electronics Materials and Energy Conversion Device, School of Science, Xijing University, Xi'an 710123, China; hpren2034@163.com (H.-P.R.); dingsiyi@xijing.edu.cn (S.-Y.D.); maqiang@xijing.edu.cn (Q.M.); songwenqi@xijing.edu.cn (W.-Q.S.); zhaoyuzhen@xijing.edu.cn (Y.-Z.Z.); liujiao@xijing.edu.cn (J.L.); heyeming@xijing.edu.cn (Y.-M.H.) * Correspondence: tenviiing@163.com

* Correspondence: tspxijing@163.com

Abstract: Reforming methane to produce syngas is a subject that generates considerable interest. The process requires catalysts that possess high-performance active sites to activate stable C–H bonds. Herein, we report a facile synthetic strategy to prepare Ni-based catalysts by complexation–impregnation (Ni-G/SiO₂-C) and precipitation–impregnation (Ni-G/SiO₂-P) methods using glycine as a complexing agent. The particle size of Ni in both types of catalysts is decreased by adding glycine in the preparation process. Nevertheless, the preparation methods and amount of glycine play a significant role in the particle size and distribution of Ni over the Ni-based catalysts. The smaller particle size and narrower distribution of Ni were obtained in the Ni-G/SiO₂-P catalyst. The catalysts were comparatively tested for carbon-dioxide reforming of methane (CDR). Ni-G/SiO₂-P showed better CDR performance than Ni-G/SiO₂-C and Ni/SiO₂ and increased stability because of the smaller particle size and narrower distribution of Ni. Moreover, a high-performance Ni-based catalyst was prepared by optimizing the amount of glycine added. An unobservable deactivation was obtained over Ni-G-2/SiO₂-P and Ni-G-3/SiO₂-P for CDR during TOS = 20 h. Thus, a new promising method is described for the preparation of Ni-based catalysts for CDR.

Keywords: reforming of methane; carbon dioxide; nickel; glycine; SiO₂

1. Introduction

With the rapid development of technology and social economy in recent years, the greenhouse effect caused by the burning of fossil fuels has become progressively serious [1,2]. CO_2 is one of the main greenhouse gases. In this connection, the reduction and effective use of CO_2 has attracted significant attention. Carbon dioxide reforming of methane (CDR) technology has also been substantially examined [2–4]. Except for the simultaneous use of the two major greenhouse gases, CO_2 and CH_4 , the H_2/CO ratio of the produced syngas is close to 1, which can be used to synthesize carbonyls, organic oxygenates, and liquid fuel by Fischer–Tropsch synthesis [2,4–6]. More importantly, CDR technology can directly convert CH_4 and CO_2 of flue gas into synthesis gas without pre-separation of CO_2 and CH_4 [3,7–9] Therefore, accelerating the industrialization process of CDR reaction is very important for CO_2 emission reduction and efficient utilization.

The catalysts applied in CDR are mainly noble metal (Rh, Ru, Pt, and Pd) and transition metal (Ni, Co, and Fe) catalysts [10,11]. Although noble metal catalysts have excellent catalytic activity and stability, their high cost limits their industrial application. Ni-based catalysts are the most promising catalysts for CDR because of their high catalytic activity and low cost [12–15]. However, the sintering at high temperatures and the serious coking of the Ni-based catalysts lead to rapid deactivation, limiting its industrial application development [16]. Therefore, reasonably designed Ni-based catalysts with high antisintering and anti-coking capacities are very urgent.



Citation: Ren, H.-P.; Ding, S.-Y.; Ma, Q.; Song, W.-Q.; Zhao, Y.-Z.; Liu, J.; He, Y.-M.; Tian, S.-P. The Effect of Preparation Method of Ni-Supported SiO₂ Catalysts for Carbon Dioxide Reforming of Methane. *Catalysts* **2021**, *11*, 1221. https://doi.org/10.3390/ catal11101221

Academic Editor: Paraskevi Panagiotopoulou

Received: 22 September 2021 Accepted: 5 October 2021 Published: 10 October 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). A comprehensive analysis of related literature reports indicates that the particle size of Ni is an essential factor affecting the formation of carbon deposits. Small Ni particles can inhibit the formation of coking deposits and affect CH₄ decomposition [10,11,14,15]. Moreover, the sintering of the active component Ni at high-temperature reduction and reaction conditions facilitates the formation of carbon deposits, which can cover the active site of Ni, resulting in the deactivation of catalysts. Therefore, the key to improving the catalytic performance of the Ni-based catalysts for the CDR is to decrease the Ni particle size and prevent the sintering of Ni at higher temperatures [10,14,15].

On the basis of the above-mentioned key factors, many new strategies were proposed to improve the anti-sintering and anti-coking features of Ni-based catalysts, such as (1) choosing suitable support—smaller Ni particles size and anti-sintering of Ni was obtained by loading Ni on ordered mesoporous materials [17–21]; (2) changing the preparation method—techniques such as low-temperature combustion synthesis method [22], evaporation induced self-assembly method (EISA) [19,23], plasma-assisted processing method [15,24–26], etc. were also employed by some researchers; (3) adding promoters—Ni-based catalysts were prepared by adding rare earth [27–29] and non-noble metals (Co, Cu, Sn, and Fe) [30–33].

Among the above methods, the co-impregnation method of nickel nitrate and a chelating agent has been proven to be an effective method to reduce the Ni particle size. Zhao et al. successfully prepared Ni/ZrO₂ catalysts with smaller Ni particle sizes by using L-arginine as a complexing agent, which showed excellent anti-sintering and anti-coking performance, resulting in higher catalytic activity and stability for CDR [34]. Moreover, many organic ligands, such as ammonia [35,36], citric acid [37–39], glucose [40], and glycine [41–43], etc., have been used as complexing agents to prepare Ni-based catalysts. The basis of these methods is to replace the H₂O ligand in the metal complex with an organic ligand, resulting in the complex of metal ions with the chelating agent. The structure and coordination characteristics of the complexes complicate during impregnation and are influenced by the ratio of the chelating agent and metal ion and the pH of the solution [42,44].

Glycine is the smallest amino acid, which is inexpensive and readily available, making it a promising chelating agent for synthesizing highly dispersed metal-supported catalysts [36,38,42]. Glycine molecule contains both amino and carboxyl coordination groups. Metal nitrates or chloride salts are generally not chosen as the metal precursor to synthesize the complex because they would release H⁺ in the aqueous solution, generating protonated forms of the amino acid in significant quantity. In this work, nickel hydroxide was used as the precursor to avoid the pH change when added to the aqueous solution [42]. Although the solid nickel hydroxide is insoluble in the impregnating solution, it can be dissolved by complexing with the amino acid to form a complex. Thus, the complex synthesized by glycine and nickel hydroxide was used as the impregnating solution to prepare the SiO₂-supported Ni-based catalyst. For comparison, supported Ni catalysts were also prepared by the traditional impregnation method and the co-impregnation of nickel nitrate and glycine. The effects of the preparation method, coordination characteristics, and coordination number on the Ni particle size and dispersion were investigated. The CDR performance of the prepared Ni-based catalysts was evaluated under 1.0 atm pressure, 750 °C temperature, CO₂/CH₄ ratio of 1.0, and GHSV of 120,000 mL·g⁻¹·h⁻¹. Regardless of the preparation method, the smaller Ni particle size and higher dispersion of Ni were obtained after complex impregnation with glycine, compared with the traditional impregnation method. However, the preparation method significantly influenced Ni particle size and particle distribution. The catalyst prepared by glycine and nickel hydroxide exhibited the smallest Ni particle size and narrower size distribution, resulting in higher activity and stability in the CDR reaction. Thus, a new preparation method of Ni-based catalysts for CDR is presented, which has more industrial application prospects.

2. Results and Discussion

2.1. Textural Properties of Ni-Based Catalysts

Table 1 lists the textural properties of all catalysts, including SiO₂, such as specific surface area (S_{BET}), pore volume (V_p), and pore diameter (d_p), tested by the N₂ adsorption– desorption isotherms. SiO₂ exhibits the highest BET surface area (231.3 m² · g⁻¹). After the loading of Ni, the BET surface area, pore volume, and pore diameter of all catalysts significantly decreased due to the deposition of NiO on the pore walls of the support Q-50. Careful comparison of the above properties of the prepared catalysts shows a negligible difference in the pore volume and pore diameter, i.e., 0.89-0.93 cm³·g⁻¹ of pore volumes and 20.6–21.0 nm of pore diameter. In contrast, an observable difference of S_{BET} was obtained for all Ni-supported catalysts. Compared with Ni/SiO₂ (176.9 m²·g⁻¹), larger S_{BET} was obtained for Ni-G/SiO₂-C (188.3 $m^2 \cdot g^{-1}$) and Ni-G/SiO₂-P (193.6–201.8 $m^2 \cdot g^{-1}$). Some of the new pores are formed by the decomposition of the frame of Ni-glycine complexes of Ni-G/SiO₂-P and Ni-G/SiO₂-C. In addition, the smaller NiO particle size in Ni-G/SiO₂-P and Ni-G/SiO₂-C contributes to the larger surface area, which is consistent with the results of XRD (Figure 1). For Ni-G/SiO₂-P catalysts, with an increasing molar ratio of glycine to nickel, the S_{BET} slightly increased, which shows that the amount of glycine used for complexation plays an unimportant role in the S_{BET} of Ni-G/SiO₂-P.

Table 1. Textural properties of support and catalysts.

Samples	$S_{BET}~(m^2 \cdot g^{-1})$ a	Pore Volumes (cm 3 ·g $^{-1}$) ^b	Pore Diameter (nm) ^c
SiO ₂	231.3	1.28	23.6
Ni/SiO ₂	176.9	0.91	20.8
Ni-G-2/SiO ₂ -C	188.3	0.91	20.7
Ni-G-1/SiO ₂ -P	193.6	0.93	21.0
Ni-G-2/SiO ₂ -P	199.5	0.89	20.7
Ni-G-3/SiO ₂ -P	201.8	0.90	20.6

^a: BET surface area; ^b: total pore volumes calculated by the BJH method with adsorption curves; ^c: average pore diameter determined by the BJH method.



Figure 1. X-ray diffraction patterns of the as-prepared Ni/SiO₂ (**a**), Ni-G-2/SiO₂-C (**b**), Ni-G-1/SiO₂-P (**c**), Ni-G-2/SiO₂-P (**d**), and Ni-G-3/SiO₂-P (**e**) catalysts.

2.2. Structural Properties of Ni-Based Catalysts

The structural properties of all catalysts were characterized by X-ray diffraction and TEM, and the respective XRD patterns and TEM images are shown in Figures 1–3. All catalysts exhibited a broad diffraction peak at the 2 θ of about 23° (Figure 1), the characteristic diffraction peak of amorphous silica [21], implying that the utilized preparation methods of supported Ni catalysts do not affect the structure of the support. Moreover,

clear diffraction peaks at 20 values of 37° , 43° , 62° , and 74.5° were obtained for Ni/SiO₂ and Ni-G-2/SiO₂-C (Figure 1a,b), attributed to the (111), (200), (220), and (311) cubic NiO planes, respectively [34,39]. The diffraction peaks of Ni-G-2/SiO₂-C were significantly weaker than Ni/SiO₂, indicating that relatively smaller-sized NiO nanoparticles were formed on the Ni-G-2/SiO₂-C catalyst because the Ni²⁺ complexed with glycine during the impregnation process. Catalyst Ni-G-1/SiO₂-P showed even weaker peaks of cubic NiO diffraction, at 20 values of 37° , 43° , and 63° , whereas no observable peaks of Ni species were obtained for Ni-G-2/SiO₂-P and Ni-G-3/SiO₂-P. These observations indicate that Ni species were dispersed well in Ni-G/SiO₂-P than Ni-G/SiO₂-C and Ni/SiO₂. The better dispersion occurs due to the increased viscosity of the impregnating solution caused by the addition of glycine that suppresses the outward flow of the solution, leading to a more uniform distribution of Ni species inside the pores of the support [36,41,42]. Moreover, the formation of the Ni complex prevents the aggregation of Ni particles during the hightemperature calcination process, affording smaller NiO particles [41], and therefore, no obvious diffraction peaks were observed in XRD.



Figure 2. X-ray diffraction patterns of the reduced Ni/SiO₂ (**a**), Ni-G-2/SiO₂-C (**b**), Ni-G-1/SiO₂-P (**c**), Ni-G-2/SiO₂-P (**d**), and Ni-G-3/SiO₂-P (**e**) catalysts.

Since metallic Ni is the active species for the CDR, the Ni particle size was also characterized by X-ray diffraction after reducing the catalysts at 700 °C for 2.5 h, and the results are shown in Figure 2. All the reduced catalysts exhibited the diffraction peaks of amorphous silica, suggesting that the SiO₂ support did not change by the reduction conditions. In addition, the characteristic diffraction peaks of metallic Ni with different intensities were obtained at 20 values of 44°, 52°, and 76° for Ni/SiO₂, Ni-G-2/SiO₂-C, and Ni-G-1/SiO₂-P, indicating that the NiO reduced to Ni at the reduction conditions [39]. However, no diffraction peaks of Ni species were observed for Ni-G-2/SiO₂-P and Ni-G-3/SiO₂-P, suggesting that particle sizes were too small to be detected by XRD. These results demonstrate that the Ni particle size was significantly influenced by the preparation method and the amount of glycine used.

In order to verify the particle size and distribution of metallic Ni in the catalysts, the reduced Ni/SiO₂, Ni-G-2/SiO₂-C, and Ni-G-2/SiO₂-P were subjected to TEM characterization. The obtained TEM images and particle size distribution of Ni are shown in Figure 3. Relatively larger Ni particle size, about 19.63 nm average particle size, and broad distribution of Ni particles of about 0–70 nm were obtained for Ni/SiO₂, while smaller Ni particle sizes and narrower distribution were observed for Ni-G-2/SiO₂-C and Ni-G-2/SiO₂-P. The Ni particle distribution and the average particle sizes were about 3–12 nm and 6.95 nm for Ni-G-2/SiO₂-C, and 1–6 nm and 2.96 nm for Ni-G-2/SiO₂-C, respectively, suggesting that



Figure 3. TEM images and particle size distribution of the reduced Ni/SiO₂ (a), Ni-G-2/SiO₂-C (b), and Ni-G-2/SiO₂-P (c) catalysts.

2.3. Reduction Ability of Ni-Based Catalysts

with the XRD results shown in Figure 2.

The reduction ability of Ni-based catalysts is characterized by H2-TPR, and the results are illustrated in Figure 4. Only Ni/SiO₂ shows a significant reduction peak at about 370 °C, while Ni-G-2/SiO₂-C and all Ni-G/SiO₂-P display two broad reduction peaks at about 370 °C and 530 °C. Generally, the reduction ability of the larger NiO particles should be lower than that of the smaller NiO particles. The reduction occurs below 400 °C for larger NiO particles and at higher temperatures for smaller NiO particle sizes and NiO with strong interaction and support [38,39]. Thus, reduction peaks at lower temperatures are attributable to NiO species with bigger particle sizes, whereas the reduction peaks at higher temperatures could be attributed to the smaller NiO particle sizes or NiO species having strong interaction with supports. Furthermore, the ratio of higher temperature to lower temperature reduction peaks in Ni-G-2/SiO₂-C is lower than all Ni-G/SiO₂-P catalysts, suggesting larger NiO particle sizes for Ni-G- $2/SiO_2$ -C. These results are in agreement with the previous XRD and TEM results.



Figure 4. H₂-TPR profiles of the as-prepared Ni/SiO₂ (**a**), Ni-G-2/SiO₂-C (**b**), Ni-G-1/SiO₂-P (**c**), Ni-G-2/SiO₂-P (**d**), and Ni-G-3/SiO₂-P (**e**) catalysts.

2.4. Catalytic Activity and Stability Tests

The CH₄ and CO₂ conversions, H_2/CO , and H_2 yield for all catalysts toward CDR at 750 °C using CH₄ to CO₂ molar ratio of 1 are presented in Figure 5. The results demonstrate that the CH₄ and CO₂ conversions significantly improved with the preparation method and the addition of glycine. The Ni/SiO₂ catalyst exhibited initial CH₄ and CO₂ conversion of 62.7% and 75.1%, respectively. As expected, Ni-G/SiO₂-C and Ni-G/SiO₂-P catalysts showed higher conversions of CH₄ and CO₂, which were about 83% and 90%, respectively. The higher activity of these catalysts can be attributed to the synergistic effect of high surface area and smaller Ni particle size that substantially improved the accessibility of active sites.



Figure 5. CH₄ conversion (**a**), CO₂ conversion (**b**), H₂/CO (**c**) and H₂ yield (**d**) over Ni/SiO₂, Ni-G-2/SiO₂-C, Ni-G-1/SiO₂-P, Ni-G-2/SiO₂-P and Ni-G-3/SiO₂-P catalysts at the conditions of P = 0.1 MPa, T = 750 °C, CH₄/CO₂ = 1, and GHSV = 120,000 mL·g⁻¹·h⁻¹.

Moreover, the CH₄ and CO₂ conversions over all the catalysts varied upon extending the reaction time, as shown in Figure 5a,b. The conversions of CH₄ and CO₂ over Ni/SiO₂ catalyst linearly decreased after 20 h to 24% and 28% from the initial 62.5% and 75.1%, respectively. Interestingly, the stability of Ni/SiO₂ prepared by the addition of glycine significantly improved. The stability of Ni-G-2/SiO₂-C decreased during the 20 h CDR reaction, accompanied by the reduction in CH₄ and CO₂ conversions from 82.5% and 87.5% to 65.4% and 70.3%, respectively. However, the stability of Ni-G-1/SiO₂-P decreased slightly, and the CH₄ and CO₂ conversions dropped marginally from 83.1% and 90.2% to 78.5% and 83.3%. With the increasing glycine content, no decrease in CH₄ and CO₂ conversions was observed for Ni-G-2/SiO₂-P and Ni-G-3/SiO₂-P catalyzed CDR, indicating their higher stability and no inactivation. This behavior might be due to the smaller Ni particle sizes and stronger interaction between Ni and SiO₂ support, in compliance with the previously described results of XRD, TEM, and H₂-TPR.

As shown in Figure 5c, H_2/CO ratio was always less than 1 due to unavoidable RWGS reaction in CDR, i.e., H_2 yield was lower than CO for all the catalysts. Interestingly, H_2/CO ratio for Ni/SiO₂ was far less than the Ni-G/SiO₂-C and Ni-G/SiO₂-P catalysts. Simultaneously, the H_2 yield exhibited the same trend with CH₄ conversion for all catalysts, while it was slightly lower than the CH₄ conversion shown in Figure 5d, which was also caused by the RWGS reaction in CDR. All these results signify the importance of Ni particle size play in RWGS in CDR reaction, which is regulated by the preparation method and glycine amount employed for the synthesis.

2.5. Characterization of Used Catalysts

After the stability tests at the reaction conditions of P = 1.0 atm, T = 750 °C, $CH_4/CO_2 = 1.0$, and gas hourly space velocity (GHSV) = 120,000 mL·g⁻¹·h⁻¹ for 20 h, the used catalysts were subjected to XRD and TG characterizations to investigate the coking and sintering of Ni.

XRD patterns of the used catalysts are displayed in Figure 6. The characteristic diffraction peaks of metallic Ni and amorphous silica were obtained for all the used Nibased catalysts, similar to the XRD patterns of the reduced catalysts shown in Figure 2, implying the same crystal structure of Ni-based catalysts after CDR. Moreover, Ni/SiO₂ displayed a prominent shoulder peak at 20 of approximately 26°, a typical diffraction peak of graphitic carbon. Although a small graphitic carbon diffraction peak was obtained for used Ni-G-2/SiO₂-C and Ni-G-1/SiO₂-P catalysts, no such peak was found in the XRD patterns of used Ni-G-2/SiO₂-P and Ni-G-3/SiO₂-P. Thus, the XRD data infer that relatively more coke was deposited on Ni/SiO₂, causing the linear inactivation for CDR, which was attributed to larger Ni particle size [10,15]. Large Ni particle sizes are prone to the formation of carbon deposits on the surface of the catalyst, which can cover the active components, thereby deactivating the catalyst [14].



Figure 6. X-ray diffraction patterns of the used Ni/SiO₂ (**a**), Ni-G-2/SiO₂-C (**b**), Ni-G-1/SiO₂-P (**c**), Ni-G-2/SiO₂-P (**d**), and Ni-G-3/SiO₂-P (**e**) catalysts.

The sintering of Ni after CDR is the primary reason for the deactivation of Ni-based catalysts. Therefore, Ni particle sizes of the used and reduced catalysts were carefully compared. The peak intensities of the used Ni/SiO₂, Ni-G-2/SiO₂-C, and Ni-G-1/SiO₂-P were more than those of the corresponding reduced catalysts, indicating Ni sintering after CDR [39], while Ni-G-2/SiO₂-P and Ni-G-3/SiO₂-P did not exhibit any diffraction peak of the metallic nickel, suggesting a smaller Ni particle size and superior anti-sintering property. Combined with the front results of TPR (Figure 4), Ni-G/SiO₂-C and Ni-G/SiO₂-P exhibited better interaction between the Ni particles and the support, as compared with Ni/SiO₂. Likewise, the strongest interaction between the Ni particles and SiO₂ existed in Ni-G-2/SiO₂-P and Ni-G-3/SiO₂-P catalysts, resulting in good CDR performance because of superior anti-sintering characteristics [10,18].

Coke deposition of the used catalysts after the CDR reaction was studied by TGA, and the results are shown in Figure 7. All the catalysts showed a distinct weight gain around 200–400 °C, during the oxidation of Ni to NiO in the air atmosphere [37,45]. Further, a weight loss from 300 °C was observed for all the catalysts utilized in 20 h CDR due to the gasification of the coke deposited. The amount of the deposited coke on used catalysts decreased in the order of Ni/SiO₂ << Ni-G-2/SiO₂-C < Ni-G-1/SiO₂-P \approx Ni-G-2/SiO₂-P \approx Ni-G-3/SiO₂-P, i.e., 3.2% for Ni/SiO₂, 2.2% for Ni-G-2/SiO₂-C, and about 1.7–1.5% for Ni-G/SiO₂-P. The amount of deposited coke is affected by the smaller Ni particle size of Ni-G/SiO₂-P (Figures 2 and 3), leading to its stable performance after 20 h CDR testing (Figure 4). The highest weight loss of about 3.2% was obtained for used Ni/SiO₂, consistent with the literature that the large Ni particle sizes of the catalyst are susceptible to the coke deposition during the CDR, which can deteriorate the activity of the catalyst [14,39]. Thus, adding glycine and changing preparation methods significantly decrease coke deposition due to smaller Ni particle formation, leading to the high stability of the catalysts for CDR.



Figure 7. TG analysis of the used Ni/SiO₂, Ni-G-2/SiO₂-C, Ni-G-1/SiO₂-P, Ni-G-2/SiO₂-P and Ni-G-3/SiO₂-P catalysts.

3. Materials and Methods

3.1. Preparation of Catalysts

 $Ni(NO_3)_2 \cdot 6H_2O$ (98.5%), glycine (99%), and sodium hydroxide (NaOH, 96%) were purchased (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and used without further purification. Commercial SiO₂ (Q-15 was purchased (Fuji, Fujisilysia Chemical Ltd., Kyoto, Japan) was used as support for the catalysts. Before use, SiO₂ was calcined at 750 °C for 4 h to remove moisture and impurities. The SiO₂-supported Ni catalysts were prepared by the precipitation–impregnation method using Ni complex as the precursor, prepared by Ni(OH)₂ and glycine. The Ni loading for all of the catalysts was 10 wt.%. The detailed preparation of catalysts is as follows: The Ni(NO₃)₂ solution was added to the NaOH solution, where the molar ratio of NaOH to Ni(NO₃)₂ of 2.0 was used to form Ni(OH)₂ precipitate. The Ni(OH)₂ precipitate was filtered and washed with deionized water, and the light green solid Ni(OH)₂ was dried at 80 °C for 12 h. In order to prepare three different Ni(II)-glycine complexes, the Ni(OH)₂ powder was slowly added to three 0.2 mol/L aqueous glycine solutions at 80 °C while stirring for 2 h with final glycine to Ni(OH)₂ ratio of 1, 2, and 3. Then, the SiO₂ powder was impregnated with the obtained solutions. Finally, all the samples were dried at 100 °C for 12 h and calcined at 500 °C for 4 h. The obtained catalysts were denoted as Ni-G-x/SiO₂-P, where x = molar ratio of glycine to Ni(OH)₂. For comparative studies, a SiO₂-supported Ni catalyst was also prepared by the complexation–impregnation method using a mixed solution of Ni(NO₃)₂ and glycine with a glycine-to-Ni molar ratio of 2, listed as Ni-G-2/SiO₂-C. Moreover, the Ni/Q-50 catalyst was prepared following the same procedure with the same preparation parameters (conventional incipient impregnation method) but without the addition of citric acid.

3.2. Characterization Techniques

Specific BET surface areas of the prepared catalysts were measured by a surface area analyzer (Bel, BelSorp-Max, Osaka, Japan) at liquid nitrogen temperature (-196 °C). Before measurements, samples were heated to 300 °C for 12 h under vacuum (10^{-2} kPa) to remove contaminants and water. The BET surface areas were acquired by the BET method, while pore volumes were obtained from the nitrogen adsorption data at the relative pressure (P/P0) = 0.99.

X-ray powder diffraction (XRD) patterns of the catalysts were recorded by X-ray diffractor (D8 advanced, Bruker, Germany) using CuK α (λ = 1.5406 Å) radiation. The measurement was conditioned at 40 kV and 40 mA. The crystalline size of NiO was calculated according to the (200) diffraction peak according to the formula of Scherrer (D = K λ /Bcos θ).

Transmission electron microscopy (TEM) images of the reduced catalysts were taken by a transmission electron microscope (JEM-2100, JEOL, Tokey, Japan). Specimens were prepared by dispersing samples in ethanol by ultrasonication for 2 min, and droplets of the suspension were deposited on a copper grid, which was dried in air.

 H_2 temperature-programmed reduction (H_2 -TPR) was performed on a chemisorption apparatus (Micromeritics Autochem 2920, GA, USA) with a thermal conductivity detector to test the reduction behaviors of the catalysts. Prior to the experiments, approximately 0.0500 g sample was pretreated at 300 °C for 2 h under flowing Ar (30 mL/min) to remove impurities. After cooling to 100 °C, a 10% H_2 /Ar (30 mL/min) mixture was introduced to obtain a stable baseline. Then, the H_2 -TPR profile was recorded from 100 °C to 1000 °C at the heating rate of 10 °C min⁻¹.

Thermogravimetric (TG) analysis was carried out on a thermoanalyzer system (TA Instruments, Q1000DSC + LNCS + FACS Q600SDT, DE, USA) to analyze the coke deposited on used catalysts, which was performed from 100 to 900 °C at a heating rate of 10 °C min⁻¹ under air atmosphere.

3.3. Activity Evaluation of the Catalysts

Catalytic activity measurements of the prepared Ni-based catalysts for CDR were carried out in a fixed-bed reactor with a quartz reaction tube (8 mm internal diameter). About 0.1 g catalyst (40–60 mesh) mixed with quartz sand (5 times of catalysts weight) was loaded in the reactor and in situ reduced by 10% H_2/N_2 (50 mL/min) at 700 °C for 150 min. The reactor was then heated to 750 °C by purging N₂ (40 mL/min) with a heating rate of 5 °C min⁻¹. After reaching 750 °C temperature, an equimolar CH₄/CO₂ mixture was passed through the catalyst (100 mL/min). The product gases in the outlet were separated by molecular sieve 5A and Porapak Q capillary column and then analyzed by an online gas chromatography (GC9720 II, Zhejiang Fuli chromatographic analysis Co., Ltd., Zhejiang, China) equipped with a TCD. Conversions of CH₄ and CO₂, H₂ yield, and the molar ratio of H₂/CO were determined from corresponding flow rates in the inlet and outlet.

The conversion of CH₄ and CO₂ (abbreviated as X_i), the molar ratio of H₂ to CO (H₂/CO), and H₂ yield (*Y*) were calculated as follows:

$$\begin{split} X_{\rm CH_4}(\%) &= \frac{F_{\rm CH_4,in} - F_{\rm CH_4,out}}{F_{\rm CH_4,in}} \times 100\% \\ X_{\rm CO_2}(\%) &= \frac{F_{\rm CO_2,in} - F_{\rm CO_2,out}}{F_{\rm CO_2,in}} \times 100\% \\ H_2/\rm CO &= \frac{F_{\rm H_2,out}}{F_{\rm CO,out}} \\ Y_{\rm H_2}(\%) &= \frac{F_{\rm H_2,out}}{2(F_{\rm CH_4, in} - F_{\rm CH_4, out})} \times 100\% \end{split}$$

4. Conclusions

The Ni-G/SiO₂-C and Ni-G/SiO₂-P catalysts were successfully prepared by complexationimpregnation and precipitation-impregnation methods using different amounts of glycine as the complexing agent. Compared with Ni/SiO₂, a smaller Ni particle size and a narrower Ni distribution were obtained, suggesting that sintering of Ni was significantly inhibited through the complexation of metallic Ni by glycine in the preparation process. All the catalysts were tested for CDR at P = 0.1 MPa, T = 750 $^{\circ}$ C, CH₄/CO₂ = 1, and GHSV = 120,000 mL \cdot g⁻¹·h⁻¹ for 20 h time on stream. The results demonstrated that Nisupported catalysts prepared with glycine as complexing agents possess enhanced activity (conversions of CH_4 and CO_2 above 82% and 87%, respectively) and improved stability. Moreover, the preparation methods and the amount of glycine used to prepare the Ni-based catalysts also play an important role in the CDR performance because of the Ni particle size and Ni dispersion. The Ni-G-2/SiO₂-P and Ni-G-3/SiO₂-P catalysts showed smaller Ni particle sizes and higher dispersion of Ni, resulting in high CDR activity and stability. The analyses of used catalysts showed that Ni-G-2/SiO₂-P and Ni-G-3/SiO₂-P exhibit carbon deposition and sintering of Ni, which is the reason for the deactivation of the catalysts. Thus, the results conclude that the CDR catalysts with small particle sizes and narrower Ni distribution can be easily prepared with the precipitation-impregnation method, a promising strategy for CDR.

Author Contributions: Conception and design of experiments, H.-P.R.; operation of the experiment, S.-Y.D. and W.-Q.S.; data analysis, Q.M. and Y.-M.H.; material characterization, Y.-Z.Z. and J.L.; writing—original draft preparation, H.-P.R.; writing—review and editing, S.-P.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (21908182 and 21901214), the Natural Science Foundation of Shaanxi Science and Technology Department (2020JM-643 and 2020JQ-918), the Scientific Research Foundation for Youth Innovation Team of Education Department of Shaanxi Provincial Government (21JP139 and 21JP136), and the Youth Innovation Team of Shaanxi Universities.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Moura, I.P.; Reis, A.C.; Bresciani, A.E.; Alves, R.M.B. Carbon dioxide abatement by integration of methane bi-reforming process with ammonia and urea synthesis. *Renew. Sustain. Energy Rev.* **2021**, *151*, 111619. [CrossRef]
- 2. Pérez-Fortes, M.; Schöneberger, J.C.; Boulamanti, A.; Tzimas, E. Methanol synthesis using captured CO₂ as raw material: Techno-economic and environmental assessment. *Appl. Energy* **2016**, *161*, 718–732. [CrossRef]
- Yu, Y.; Yang, J.; Zhu, K.; Sui, Z.; Chen, D.; Zhu, Y.; Zhou, X. High-throughput screening of alloy catalysts for dry methane reforming. ACS Catal. 2021, 11, 8881–8894. [CrossRef]
- 4. Akri, M.; Zhao, S.; Li, X.; Zang, K.; Lee, A.F.; Isaacs, M.A.; Xi, W.; Gangarajula, Y.; Luo, J.; Ren, Y.; et al. Atomically dispersed nickel as coke-resistant active sites for methane dry reforming. *Nat. Commun.* **2019**, *10*, 5181. [CrossRef] [PubMed]

- Abdulrasheed, A.; Jalil, A.A.; Gambo, Y.; Ibrahim, M.; Hambali, H.U.; Hamid, M.Y.S. A review on catalyst development for dry reforming of methane to syngas: Recent advances. *Renew. Sustain. Energy Rev.* 2019, 108, 175–193. [CrossRef]
- 6. Centi, G.; Quadrelli, E.A.; Perathoner, S. Catalysis for CO₂ conversion: A key technology for rapid introduction of renewable energy in the value chain of chemical industries. *Energy Environ. Sci.* **2013**, *6*, 1711–1731. [CrossRef]
- Nahar, G.; Mote, D.; Dupont, V. Hydrogen Production from reforming of biogas: Review of technological advances and an indian perspective. *Renew. Sustain. Energy Rev.* 2017, *76*, 1032–1052. [CrossRef]
- 8. Mortensen, P.M.; Dybkjær, I. Industrial scale experience on steam reforming of CO₂-rich gas. *Appl. Catal. A Gen.* **2015**, 495, 141–151. [CrossRef]
- 9. Song, C. Global challenges and strategies for control, conversion and utilization of CO₂ for sustainable development involving energy, catalysis, adsorption and chemical processing. *Catal. Today* **2006**, *115*, 2–32. [CrossRef]
- 10. Kawi, S.; Kathiraser, Y.; Ni, J.; Oemar, U.; Li, Z.; Saw, E.T. Progress in synthesis of highly active and stable nickel-based catalysts for carbon dioxide reforming of methane. *ChemSusChem* **2015**, *8*, 3556–3575. [CrossRef]
- 11. Shang, Z.; Li, S.; Li, L.; Liu, G.; Liang, X. Highly active and stable alumina supported nickel nanoparticle catalysts for dry reforming of methane. *Appl. Catal. B Environ.* 2017, 201, 302–309. [CrossRef]
- Simonov, M.; Bespalko, Y.; Smal, E.; Valeev, K.; Fedorova, V.; Krieger, T.; Sadykov, V. Nickel-containing ceria-zirconia doped with Ti and Nb. Effect of support composition and preparation method on catalytic activity in methane dry reforming. *Nanomaterials* 2020, 10, 1281. [CrossRef]
- 13. Azancot, L.; Bobadilla, L.F.; Centeno, M.A.; Odriozola, J.A. Effect of potassium loading on basic properties of Ni/MgAl₂O₄ catalyst for CO₂ reforming of methane. *J. CO₂ Util.* **2021**, *52*, 101681. [CrossRef]
- 14. Li, S.; Gong, J. Strategies for improving the performance and stability of Ni-based catalysts for reforming reactions. *Chem. Soc. Rev.* **2014**, *43*, 7245–7256. [CrossRef] [PubMed]
- Liu, C.; Ye, J.; Jiang, J.; Pan, Y. Progresses in the preparation of coke resistant Ni-based catalyst for steam and CO₂ reforming of methane. *ChemCatChem* 2011, *3*, 529–541. [CrossRef]
- Ramantani, T.; Bampos, G.; Vavatsikos, A.; Vatskalis, G.; Kondarides, D.I. Propane steam reforming over catalysts derived from noble metal (Ru, Rh)-substituted LaNiO₃ and La_{0.8}Sr_{0.2}NiO₃ perovskite precursors. *Nanomaterials* 2021, *11*, 1931. [CrossRef] [PubMed]
- 17. Wang, C.; Qiu, Y.; Zhang, X.; Zhang, Y.; Sun, N.; Zhao, Y. Geometric design of a Ni@silica nano-capsule catalyst with superb methane dry reforming stability: Enhanced confinement effect over the nickel site anchoring inside a capsule shell with an appropriate inner cavity. *Catal. Sci. Technol.* **2018**, *19*, 4877–4890. [CrossRef]
- Zhang, C.; Zhu, W.; Li, S.; Wu, G.; Ma, X.; Wang, X.; Gong, J. Sintering-resistant Ni-based reforming catalysts obtained via the nanoconfinement effect. *Chem. Commun.* 2013, 49, 9383–9385. [CrossRef]
- 19. Wang, N.; Shen, K.; Huang, L.; Yu, X.; Qian, W.; Chu, W. Facile route for synthesizing ordered mesoporous Ni-Ce-Al oxide materials and their catalytic performance for methane dry reforming to hydrogen and syngas. *ACS Catal.* **2013**, *3*, 1638–1651. [CrossRef]
- Daoura, O.; Fornasieri, G.; Boutros, M.; Hassan, N.E.; Beaunier, P.; Thomas, C.; Selmane, M.; Miche, A.; Sassoye, C.; Ersen, O.; et al. One-pot prepared mesoporous silica SBA-15-like monoliths with embedded Ni particles as selective and stable catalysts for methane dry reforming. *Appl. Catal. B Environ.* 2021, 280, 119417. [CrossRef]
- 21. Zhang, Q.; Sun, M.; Ning, P.; Long, K.; Wang, J.; Tang, T.; Fan, J.; Sun, H.; Yin, L.; Lin, Q. Effect of thermal induction temperature on re-dispersion behavior of Ni nanoparticles over Ni/SBA-15 for dry reforming of methane. *Appl. Surf. Sci.* 2019, 469, 368–377. [CrossRef]
- 22. Danghyan, V.; Kumar, A.; Mukasyan, A.; Wolf, E.E. An active and stable NiOMgO solid solution based catalysts prepared by paper assisted combustion synthesis for the dry reforming of methane. *Appl. Catal. Environ.* **2020**, 273, 119056. [CrossRef]
- 23. Fang, X.; Peng, C.; Peng, H.; Liu, W.; Xu, X.; Wang, X.; Li, C.; Zhou, W. Methane dry reforming over coke-resistant mesoporous Ni-Al₂O₃ catalysts prepared by evaporation-induced self-assembly method. *ChemCatChem* **2015**, *7*, 3753–3762. [CrossRef]
- 24. Dai, Y.; Zou, R.; Ba, T.; Zhang, J.; Liu, C. Highly active and coke resistant Ni/CeZrO₂ catalyst prepared by cold plasma decomposition for CO₂ reforming of methane. *J. CO₂ Util.* **2021**, *51*, 101647. [CrossRef]
- Zhu, X.; Huo, P.; Zhang, Y.; Cheng, D.; Liu, C. Structure and reactivity of plasma treated Ni/Al₂O₃ catalyst for CO₂ reforming of methane. *Appl. Catal. B Environ.* 2008, *81*, 132–140. [CrossRef]
- Hu, X.; Jia, X.; Zhang, X.; Liu, Y.; Liu, C. Improvement in the activity of Ni/ZrO₂ by cold plasma decomposition for dry reforming of methane. *Catal. Commun.* 2019, 128, 105720. [CrossRef]
- 27. Li, B.; Yuan, X.; Li, L.; Li, B.; Wang, X.; Tomishige, K. Lanthanide oxide modified nickel supported on mesoporous silica catalysts for dry reforming of methane. *Int. J. Hydrogen Energy* **2021**, *46*, 31608–31622. [CrossRef]
- 28. Agueniou, F.; Vidal, H.; Yeste, M.P.; Hernández-Garrido, J.C.; Cauqui, M.A.; Rodríguez-Izquierdo, J.M.; Calvino, J.J.; Gatica, J.M. Ultrathin washcoat and very low loading monolithic catalyst with outstanding activity and stability in dry reforming of methane. *Nanomaterials* **2020**, *10*, 445. [CrossRef]
- 29. Świrk, K.; Gálvez, M.E.; Motak, M.; Grzybek, T.; Rønning, M.; Costa, P.D. Dry reforming of methane over Zr- and Y-modified Ni/Mg/Al double-layered hydroxides. *Catal. Commun.* **2018**, *117*, 26–32. [CrossRef]
- Iftikhar, S.; Jiang, Q.; Gao, Y.; Liu, J.; Gu, H.; Neal, L.; Li, F. LaNi_xFe_{1-x}O_{3-δ} as a robust redox catalyst for CO₂ splitting and methane partial oxidation. *Energy Fuels* 2021, *35*, 13921–13929. [CrossRef]
- Wang, H.; Dong, X.; Zhao, T.; Yu, H.; Li, M. Dry reforming of methane over bimetallic Ni-Co catalyst prepared from LaCo_xNi_{1-x})_{0.5}Fe_{0.5}O₃ perovskite precursor: Catalytic activity and coking resistance. *Appl. Catal. B Environ.* 2019, 245, 302–313. [CrossRef]

- 32. Han, K.; Wang, S.; Liu, Q.; Wang, F. Optimizing the Ni/Cu ratio in Ni-Cu nanoparticle catalysts for methane dry reforming. *ACS Appl. Nano Mater.* **2021**, *4*, 5340–5348. [CrossRef]
- 33. Guharoy, U.; Le Saché, E.; Cai, Q.; Reina, T.R.; Gu, S. Understanding the role of Ni-Sn interaction to design highly effective CO₂ conversion catalysts for dry reforming of methane. *J. CO*₂ *Util.* **2018**, *27*, 1–10. [CrossRef]
- Li, W.; Zhao, Z.; Ding, F.; Guo, X.; Wang, G. Syngas production via steam-CO₂ dual reforming of methane over La-Ni/ZrO₂ catalyst prepared by L-arginine ligand-assisted strategy: Enhanced activity and stability. ACS Sustain. Chem. Eng. 2015, 3, 3461–3476. [CrossRef]
- 35. Zhang, Q.; Tang, T.; Wang, J.; Sun, M.; Wang, H.; Sun, H.; Ning, P. Facile template-free synthesis of Ni-SiO₂ catalyst with excellent sintering-and coking-resistance for dry reforming of methane. *Catal. Commun.* **2019**, *131*, 105782. [CrossRef]
- Rodríguez-González, V.; Marceau, E.; Beaunier, P.; Che, M.; Train, C. Stabilization of hexagonal close-packed metallic nickel for alumina-supported systems prepared from Ni(II) glycinate. J. Solid State Chem. 2007, 180, 22–30. [CrossRef]
- Bian, Z.; Xin, Z.; Meng, X.; Tao, M.; Lv, Y.; Gu, J. Effect of citric acid on the synthesis of CO metalation catalysts with high activity and excellent stability. *Ind. Eng. Chem. Res.* 2017, 56, 2383–2392. [CrossRef]
- Zhang, Q.; Long, K.; Wang, J.; Zhang, T.; Song, Z.; Lin, Q. A novel promoting effect of chelating ligand on the dispersion of Ni species over Ni/SBA-15 catalyst for dry reforming of methane. *Int. J. Hydrogen Energy* 2017, 42, 14103–14114. [CrossRef]
- Ren, H.; Hao, Q.; Ding, S.; Zhao, Y.; Zhu, M.; Tian, S.; Ma, Q.; Song, W.; Miao, Z.; Liu, Z. A high-performance Ni/SiO₂ prepared by the complexed-impregnation method with citric acid for carbon dioxide reforming of methane. *Ind. Eng. Chem. Res.* 2018, 57, 16257–16263. [CrossRef]
- 40. Zhao, Y.; Geng, J.; Cai, Y.; Wang, C.; Zhang, Q.; Wang, H. One-step synthesis of metallic Ni-C/Al₂O₃ directly applied for CO₂ reforming of CH₄. *Int. J. Hydrogen Energy* **2014**, *44*, 21651–21658. [CrossRef]
- Ren, H.; Tian, S.; Ding, S.; Huang, G.; Zhu, M.; Ma, Q.; Song, W.; Zhao, Y.; Miao, Z.; Wang, W. Carbon dioxide reforming of methane over Ni supported SiO₂: Influence of the preparation method on the resulting structural properties. *Catalysts* 2020, 10, 795. [CrossRef]
- 42. Rodríguez-González, V.; Marceau, E.; Che, M.; Pepe, C. Influence of the morphology and impurities of Ni(OH)₂ on the synthesis of neutral Ni(II)-amino acid complexes. *J. Solid State Chem.* **2007**, *180*, 3469–3478. [CrossRef]
- 43. Gorboletova, G.G.; Metlin, A.A. Standard thermodynamic functions of Co²⁺ complexation with glycine and L-histidine in aqueous solution. *J. Phys. Chem.* **2016**, *90*, 334–338. [CrossRef]
- Sun, K.Q.; Marceau, E.; Che, M. Evolution of nickel speciation during preparation of Ni-SiO₂ catalysts: Effect of the number of chelating ligands in [Ni(en)_x(H₂O)_{6-2x}]²⁺ precursor complexes. *Phys. Chem. Chem. Phys.* 2006, *8*, 1731–1738. [CrossRef]
- Wang, F.; Xu, L.; Shi, W. Syngas production from CO₂ reforming with methane over core-shell Ni@SiO₂ catalysts. *J. CO₂ Util.* 2016, 16, 318–327. [CrossRef]