

Dry Reforming of Methane (DRM) by Highly Active and Stable Ni Nanoparticles on Renewable Porous Carbons

Yinming Li ¹, Zhaojia Wang ¹, Bo Zhang ², Zhengang Liu ^{3,4,*} and Tianxue Yang ^{5,*}

¹ State Key Laboratory of Solid Waste Reuse for Building Materials, Beijing Building Materials Academy of Sciences Research, Beijing 100041, China; liyinming1986@163.com (Y.L.); zhaojiaw@bbma.com.cn (Z.W.)

² Shandong Province Environmental Technology Service Center, Jinan 250102, China; zhbhky@163.com

³ Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

⁴ University of Chinese Academy of Sciences, Beijing 100049, China

⁵ State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

* Correspondence: zgliu@rcees.ac.cn (Z.L.); ytx13@126.com (T.Y.); Tel.: +86-10-62915966 (Z.L.); +86-10-84913805 (T.Y.)

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Abstract: In this study, Ni nanoparticles supported on renewable porous carbon were prepared using hydrochar as a carbon precursor via *in situ* formation and self-reduction. The structure properties of the prepared nanocatalysts were characterized by multiple techniques, including XRD, SEM, and HR-TEM, and the dry reforming of methane (DRM) performance of the nanocatalysts in terms of conversion efficiency and reactivity stability was evaluated. The results revealed that the Ni²⁺ was uniformly anchored on the surface of the hydrochar, and subsequently the Ni nanoparticles were well dispersed in the composite with a diameter of less than 8 nm and had a narrow particle size distribution at a temperature lower than 800 °C. With an increased temperature from 800 to 900 °C, the significant sintering and agglomeration of nickel particles and the transformation from amorphous carbon to graphitic structure were observed in the composite. The nanocatalysts prepared at a temperature of 700 °C (Ni@C-700) and 800 °C (Ni@C-800) exhibited a high reforming conversion rate and catalytic stability of CH₄ by CO₂ (around 52% for Ni@C-700 and 70% for Ni@C-800 after 800 min of run-time, respectively). As for the composite obtained at 900 °C (Ni@C-900), the highly graphitic degree was coupled with the significantly increased nickel particle size, and this resulted in a remarkably decreased conversion efficiency. The present study offers a valuable application of the hydrochar and a facile and green approach to prepare highly active and cost-efficient Ni nanoparticles on porous carbons towards the dry reforming of methane.

Keywords: biomass; carbon material; carbon dioxide reforming; syngas; renewable energy

1. Introduction

Production of fuel from renewable biomass is of increasing importance owing to the growing energy demand and climate change caused by excessive use of fossil fuel. The biogas is mainly composed of CH₄ and CO₂ and is one of the important renewable biofuel carriers generated from the anaerobic digestion of biomass feedstocks [1]. However, CH₄ and CO₂ are the main greenhouse gas, especially for CH₄. In addition, CH₄ is also not the ideal raw material for the production of valuable chemicals and high quality fuels based on the existing chemical industry.

The dry reforming of methane (DRM) with CO₂ is getting attractive because the biogas can be converted into syngas (CO and H₂) by DRM, and CO and H₂ are the most promising platform compounds to produce many value-added chemicals [2,3]. Noble metals such as Pt and Ru have been extensively investigated for catalytic DRM, and despite high activity and resistance towards carbon deposition, their high cost and limited availability restrict their large-scale application industrially [4–6]. By contrast, Ni-based catalysts provide an alternative and have the highest potential for the widespread application in practical industry because they are active, cheap, and abundant. Compared to conventional microscale nickel particles, nanoscaled Ni generally offers a high surface-area-to-volume ratio and high surface area, showing a high catalytic activity. However, nanoscaled Ni is subject to aggregate into microscale particles because of high surface energy and intrinsic magnetic interaction. Thus, many materials have been employed to serve as a support to achieve a better nanoscale Ni distribution [7–9]. Porous carbons as a catalyst support have received increasing attention because of their tunable properties and high chemical stability, as well as the significant synergetic or complementary effect between the active center and the carbonaceous support. For instance, nano Ni supported on carbon material (Ni@C) exhibited excellent catalytic performance in hydrogen production and tar reduction during biomass conversion [10]. Conventional preparation of Ni@C composite is a time-consuming procedure, and toxic agents (strong acid), costly reductant (hydrogen or NaHB₄), and commercial porous carbon are necessarily used. In addition, due to the microspore's condensation, Ni particles are usually randomly distributed in a carbon matrix, which is unfavorable for their catalytic reactivity. Therefore, it is crucial to seek a cheap, green, and simple approach for the preparation of these Ni@C composites.

The development of carbon materials from renewable biomass has been drawing interest as a low-cost, environmentally friendly, and nontoxic solution to environmental remediation. Hydrothermal carbonization is one of the principal approaches for carbon material production from waste biomass, and the resultant hydrochar features substantial amounts of polar functional groups on its surface (mainly oxygen-containing groups) [11,12]. With this unique property, the hydrochar has shown potential application in many fields, including as bioadsorbent and catalyst support. In our previous reports, the hydrochar showed high adsorption capacity and removal efficiency for the metals from an aqueous solution, and a strong metal–carbon support interaction was achieved [11–13].

Here, we report a novel straightforward method for the synthesis of Ni/C nanocatalysts using hydrochar as a carbon precursor and nickel nitrate as a Ni source via *in situ* formation and self-reduction. The prepared Ni@C catalysts possessed both high activity during the DRM and excellent catalytic stability towards deactivation.

2. Results and Discussions

2.1. The Properties of Prepared Catalysts

Figure 1 shows X-ray diffraction patterns of three nanocatalysts, Ni@C-700, Ni@C-800 and Ni@C-900, and C-900. As shown in Figure 1, there is no peak detected in the XRD pattern of the C-900, implying that no crystal phase was present in C-900. As for the deviation of the baseline at low angles, it was caused by the amorphous carbon in the C-900. For the composites Ni@C-700, Ni@C-800 and Ni@C-900, the clear peaks around 44.5, 51.9, and 76.2 corresponded to the body-centered cubic structure of zerovalent nickel, and these three peaks became narrow as the temperature was increased, indicating the enlarged size of the nickel particles with the increasing temperature. The nickel particles' sizes were calculated using Scherrer's equation, and they were 4.6, 7.9, and 102 nm in Ni@C-700, Ni@C-800, and Ni@C-900, respectively. The increase of the nickel particle size resulted from the enhanced agglomeration from 700 to 900 °C. It should be noted that in the pattern of Ni@C-900, the peak at 26.30 was clearly observed, and it corresponded to the 100 face of graphitic carbon [14]. This peak revealed that a substantial amount of well-developed graphitic structure was present in Ni@C-900, indicating that the amorphous carbon was transformed to graphitic structure when the temperature was increased from 800 to 900 °C.

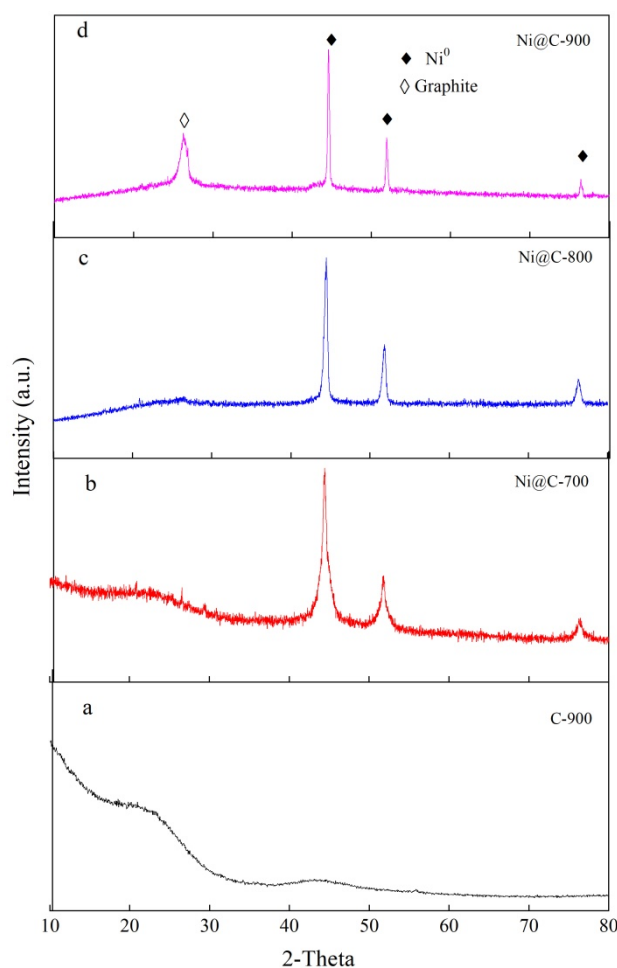


Figure 1. XRD patterns of (a) C-900 and the nanocatalysts (b) Ni@C-700, (c) Ni@C-800, and (d) Ni@C-900.

The micrograph of the composite was determined by an SEM, and the results are shown in Figure 2. The C-900 has a relatively smooth surface, and no clear porous structure was observed (Figure 2a). By contrast, pores of different sizes and shapes were present on the irregular external surface of Ni@C-700, Ni@C-800, and Ni@C-900 (Figure 2b–d), implying that the added nickel served as the activation agent of the hydrochar during thermal treatment. This observation was well in agreement with a previous report in which the transition metals, including Fe, Co, and Ni, activated biomass during a pyrolysis process [15]. To examine the distribution of nickel within the composites, a two-dimensional X-ray mapping of Ni@C-700, Ni@C-800, and Ni@C-900 was further conducted in a selected region, and the results show that the nickel nanoparticles were nearly uniformly dispersed through these composites. The TEM images of the composite provided the evidence of the well-dispersed morphology of the nickel particles and their evolution with the increasing temperature. As shown in Figure 3, the nickel particles were well dispersed within the composites, especially for Ni@C-700 and Ni@C-800. The particle size was increased with the increasing temperature, and they were 4.3, 7.6, and 92 nm in Ni@C-700, Ni@C-800, and Ni@C-900, respectively, which were well in agreement with the calculated values by Scherrer's equation. In addition, it was confirmed that besides the significant increase of the particle size, the crystalline graphitic carbon was clearly present in Ni@C-900, which is well consistent with the XRD analysis. The size of the Ni particles had a vital effect on its catalytic performance, and the sintering was undesirable during practical application. Commercial supported Ni catalysts are usually synthesized by incipient wetness impregnation of the support materials with an aqueous solution of Ni-containing salt and then followed by drying, calcination, and reduction at a high temperature [16–18], and the resultant

Ni nanoparticles were relatively large even at a low Ni loading rate, typically tens of nanometers [19–21].

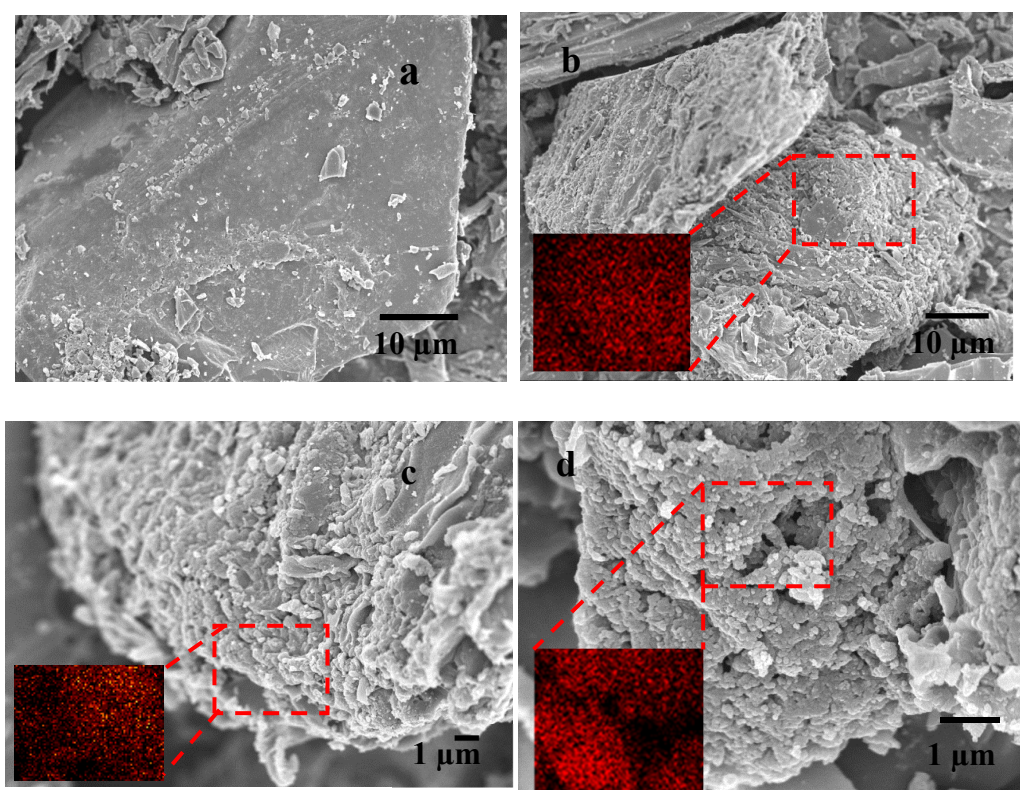


Figure 2. SEM images of (a) C-900, (b) Ni@C-700, (c) Ni@C-800, (d) Ni@C-900 (insets are the distribution of nickel particles within the catalysts).

The Ni supported multiwalled carbon nanotube was prepared under a hydrogen atmosphere, and its size was found to around 15–35 nm, whereas Ni loadings were 10%–30% [21]. The size of Ni supported by La_2O_3 was characterized to be 33 nm at a Ni loading of 17% [22]. In CeO_2 supported Ni, the size was determined to be 36.3 nm at a loading of 10% [23]. In this study, the Ni loadings were 19.2% in Ni@C-700 and 20.3% in Ni@C-800, respectively. At such a high Ni loading, the Ni was still confined to be a very tiny size by *in situ* formation and self-reduction, and no clear aggregation occurred at a temperature lower than 800 °C. This was mainly ascribed to the unique property of the hydrochar, such as the functional groups on the surface and the reduced atmosphere generated during thermal treatment. During impregnation, the functional groups on the hydrochar's surface coordinated with the nickel ions and the coordination of well-anchored nickel ions, and they avoided the growing of the nickel particles during subsequent treatment, i.e., the functional groups acted as the removable templates by imposing a steric hindrance to inhibit agglomeration of the nickel precursor [24,25]. Meanwhile, the decomposition of the functional groups of the hydrochar offered a reducing atmosphere, which served as a reductant for the formation of zerovalent nickel particles [13]. Thus, the highly dispersed nickel particles were formed and confined to be a very tiny size at temperatures lower than 800 °C. In this study, the hydrogen or NaBH_4 were not necessary for the reduction of nickel ions, and renewable hydrochar was used as the precursor of carbon support as a reductant source, which led to a completely green and sustainable catalyst synthesis route.

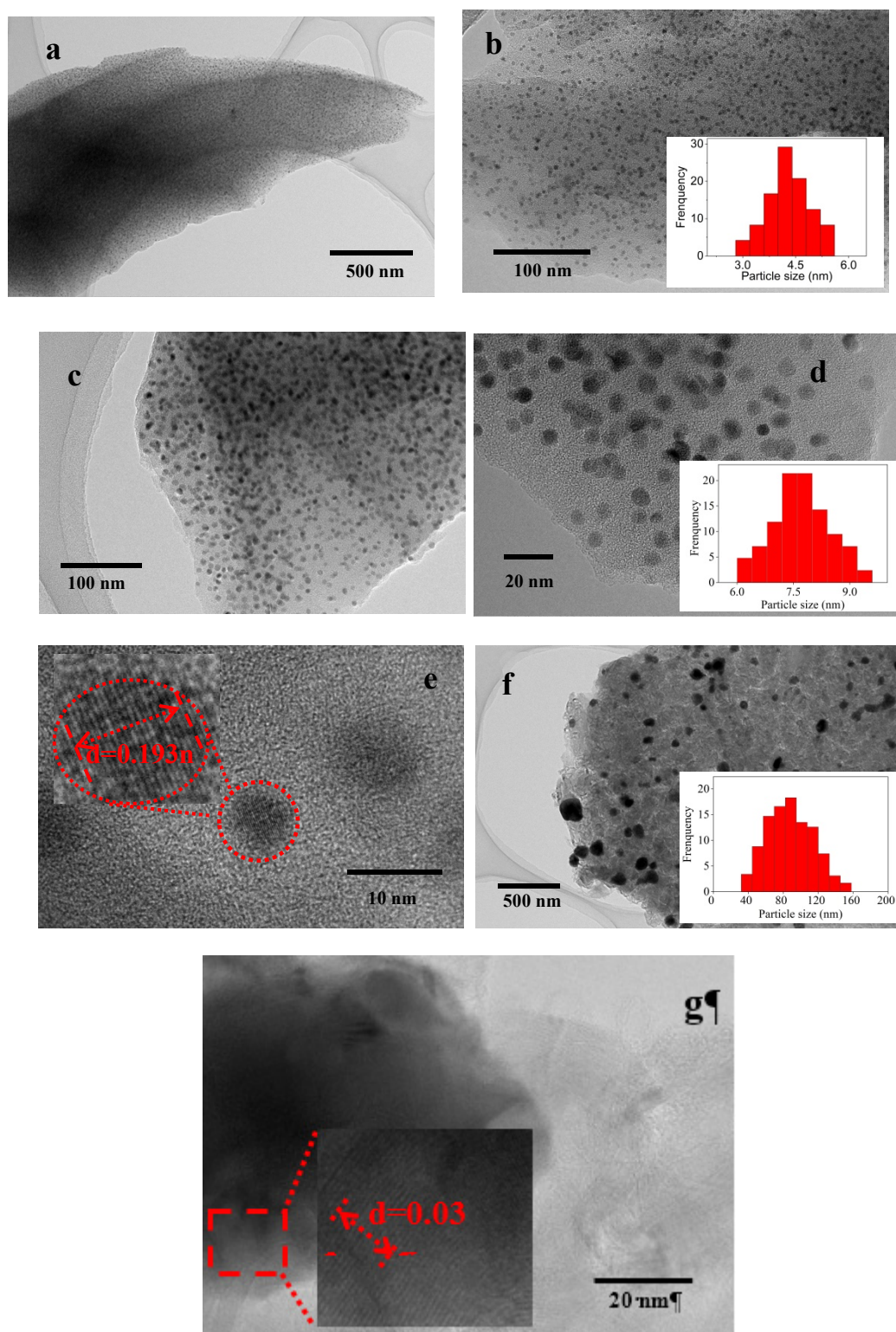


Figure 3. TEM of (a,b) Ni@C-700, (c–e) Ni@C-800, (f,g) Ni@C-900 (insets are the size distribution of nickel particles (b,d,f) and the HR-TEM micrographs of the nickel particles(e)).

2.2. Reforming Reaction of CO₂ and CH₄ Alone

Figure 4a shows the catalytic performance of the prepared catalyst Ni@C-700, Ni@C-800, Ni@C-900, and C-900 in the conversion of CO₂ to CO according to the Boudward reaction $\text{CO}_2 + \text{C} = 2\text{CO}$. For C-900, the conversion rate was sharply decreased with the time increased from 10 to 80 min, and with the further prolonged time to 120 min, the conversion kept constant. Compared to C-900, the Ni@C-700 and Ni@C-800 showed a slightly low catalytic conversion performance within

the initial 80 min. Different from Ni@C-700 and Ni@C-800, the catalysis of Ni@C-900 was very low with a conversion rate around 2% and kept constant within the entire time range of 0–120 min. The sharply decreased catalytic performance was related to the decrease of the active sites of the catalyst. As shown in Figure 1, no graphitic structure was observed in Ni@C-700 and Ni@C-800 while when the temperature was increased to 900 °C, a considerable amount of graphitized carbon was formed in Ni@C-900. Because of the conversion from active amorphous carbon to the crystallized carbon, the active sites of the carbons decreased, resulting in the decreased conversion rate of CO₂. Meanwhile, slightly lower conversion rates of Ni@C-700 and Ni@C-800 than C-900 were also ascribed to the lower content of amorphous carbon in Ni@C-700 and Ni@C-800 [15].

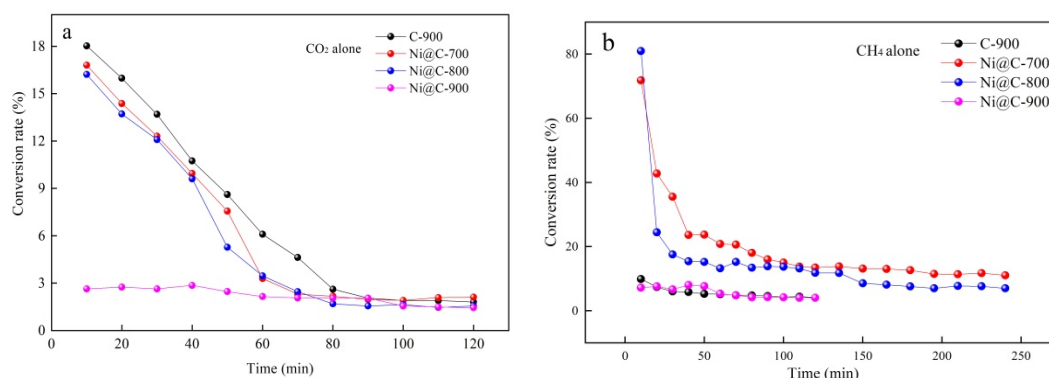


Figure 4. Variation of the (a) CO₂ and (b) CH₄ conversion over Ni@C-700, Ni@C-800, Ni@C-900, and C-900 (Conditions: 700 °C; VHSV = 0.17 Lg^{−1}h^{−1}).

When CH₄ passed through the reactor without the addition of a catalyst, no conversion of the CH₄ was observed. While the catalyst was added, a considerable amount of H₂ was detectable, and this was attributed to the conversion of CH₄ = C + 2H₂ (shown in Figure 4b). The C-900 and Ni@C-900 showed low catalysis, and within the entire time range of 0–250 min, the conversion rate was kept constant with a rate of around 3%. In comparison with C-900 and Ni@C-900, the obviously enhanced catalytic effects were observed for Ni@C-700 and Ni@C-800, especially at the initial stage. The catalytic performance decreased sharply from the initial 10 min to 40 min, and then the conversion rates were almost kept constant around 11% and 7% for Ni@C-700 and Ni@C-800, respectively. The remarkably decreased conversion rate mainly resulted from the blockage of the active sites on the catalyst surface by the carbon deposits generated from the decomposition of the CH₄. Compared to C-900, the significantly enhanced conversion rates of Ni@C-700 and Ni@C-800 were ascribed to the presence of the nickel nanoparticles in the composites. Similarly, it was reported that the nickel in the rice husk derived biochar catalytically enhanced CH₄ gasification, in which the Ni loading increased the carbon conversion at a high temperature, and with the increasing temperature, the catalytic performance was remarkably decreased [26]. As for the Ni@C-900, only a slight conversion was observed for both CH₄ and CO₂. The low conversion rate originated in its high graphitic degree and significantly increased the nickel particle size [27]. As we know, the deactivation caused by carbon deposition and particle growth is the main problem for the nickel-reforming catalysts. As shown in TEM images (shown in Figure 3f–g), most of the carbon in Ni@C-900 was graphite, and the average size of the Ni was significantly increased to around 100 nm. In addition, it was observed from Figure 3g that some of the active surface of the nickel particle was covered by the graphitic structure. The high graphitic degree and the large nickel particles led to the significantly decreased catalytic activity of Ni@C-900 compared to Ni@C-700 and Ni@C-800.

2.3. Dry Reforming Reaction of CH₄ by CO₂

The results of a DRM reaction over C-900, Ni@C-700, Ni@C-800, and Ni@C-900 are given in Figure 5. For C-900, the co-conversion rates of CO₂ and CH₄ were very close to those of the conversion of CO₂ and CH₄ alone. In the case of Ni@C-900, as expected, the low conversion rate was

observed because of the high graphitic degree and the large nickel particles. For Ni@C-700 and Ni@C-800, the catalytic conversions were significantly increased for both CO₂ and CH₄, especially for CO₂. The conversion rate of CO₂ was decreased with the prolonged time to around 50 min and then kept constant with rates of 80% and 82% for Ni@C-700 and Ni@C-800, respectively. A similar trend was also observed from the CH₄ conversion, in which the conversion rate was decreased with the increasing time and kept constant after 200 min with rates of 52% and 70% for Ni@C-700 and Ni@C-800, respectively. The significantly increased CO₂ conversion rate was ascribed to the quick gasification of the carbon deposits by CO₂, which not only avoided the deactivation of the nickel nanoparticles but also enhanced the CO₂ conversion by the reaction $C + CO_2 = 2CO$. The equilibrium of carbon deposition and deposit gasification was achieved after a 100 min reaction, and then the conversion rate kept almost constant [28]. In addition, the reverse water–gas shift reaction ($CO_2 + H_2 = CO + H_2O$) also contributed to the enhanced CO₂ conversion. This hypothesis is in agreement with the varied CO/H₂ ratio in the syngas. As shown in Figure 6, in general, the CO/H₂ ratio was lower than 1.0 within the time range of 0–50 min for both Ni@C-700 and Ni@C-800, indicating that the decomposition rate of CH₄ was higher than that of CO₂. By contrast, when the reaction time was longer than 50 min, the amount of CO was increased, and the CO/H₂ was almost constant with the value of 1.35 and 1.08 for Ni@C-700 and Ni@C-800, respectively. The above observation confirmed that nickel@carbon composites prepared via *in situ* formation and self-reduction had a high catalytic reforming performance of CH₄ by CO₂ in this study.

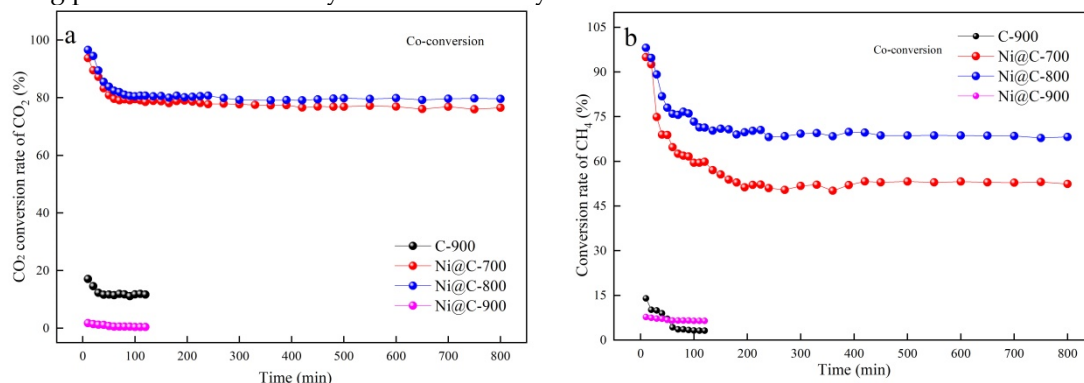


Figure 5. Variation of dry reforming of methane (DRM) conversion of (a) CO₂ and (b) CH₄ over Ni@C-700, Ni@C-800, Ni@C-900, and C-900 (Conditions: 700 °C; VHSV=0.17 Lg^{−1}h^{−1}).

It should be noted that the catalytic performances of Ni@C-700 and Ni@C-800 were equivalent or greater than those of the reported Ni-based catalysts, which were finely designed using costly chemicals [29–35]. The high activity of the Ni@C-700 and Ni@C-800 mainly originated in a small Ni size and a narrow practice size distribution. In the present study, the sizes of Ni particles (4.6 and 7.9 nm in Ni@C-700 and Ni@C-800, respectively) were smaller than the critical size of 9 nm for carbon deposition [36]. The narrow particle size distribution enhanced metal-support interactions and prevented coke formation and crystal growth. In addition, it was reported that K was the promoter of a Ni-based catalyst, and the partial coverage of a Ni surface by K enhanced deposit gasification [31,37]. Around 10% of the K originally contained in sawdust were retained in the hydrochar, and a considerable amount of K further promoted the catalytic performance of the prepared catalyst in this study [38].

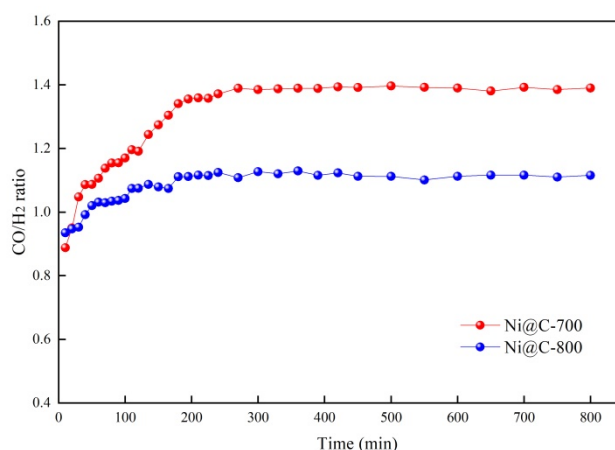


Figure 6. Variation of CO/H₂ ratio over Ni@C-700 and Ni@C-800 (Conditions: 700 °C; VHSV=0.17 Lg⁻¹h⁻¹).

Table 1. Composition and textural properties of prepared Ni@C nanocatalysts.

Sample	Ni Content (%)	Ni Particle Size (nm)		Carbon Content (%)		
		TEM ^a	XRD	Spent ^a	Fresh	Spent
Ni@C-700	19.2	4.3	4.6	4.6	80.4	80.6
Ni@C-800	20.3	7.6	7.9	7.8	79.2	79.3
Ni@C-900	25.4	92	102	-	-	-

^a Determined from the TEM graph (statistics on 100 particles randomly picked up from TEM images).

As shown in Figures 5 and 6, the CO₂ and CH₄ conversions decreased during the first 50 min and then remained stable around 80% and higher than 50%, respectively, with a CO/H₂ ratio of 1.1–1.4 after a 800 min run-time. The catalysts appeared very stable for a period of over 800 min, indicating their high reactivity and stability. In addition, the spent Ni@C catalyst (after a 500 min catalysis) was further characterized by an elemental analysis (as shown in Table 1) and TEM (shown in Figure 7). Elemental analysis results show that compared to fresh catalysts, only slightly increased carbon contents of the spent Ni@C catalysts were observed with the values of 80.6% and 79.3% for Ni@C-700 and Ni@C-800, respectively. The TEM image (Figure 7) of the spent catalysts Ni@C-700 and Ni@C-800 showed that the particles were still well dispersed within the carbon matrix after a 500 min reaction, and no significant sintering of Ni nanoparticles was observed (4.6 and 7.8 nm for spent Ni@C-700 and Ni@C-800, respectively). These were verified by a high conversion rate and stability after 500 min of the dry reforming of methane of the composites. Considering the high catalytic performance and the cost-effective, green preparation, the prepared catalysts at 700 °C and 800 °C in the present study have a high potential to implement DRM industrially.

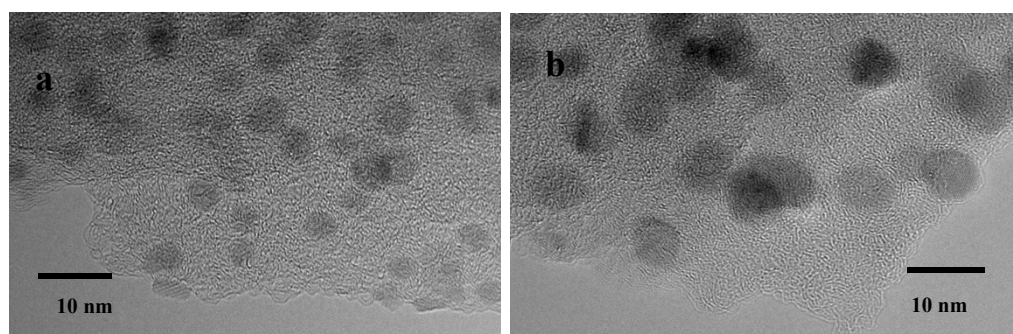


Figure 7. The TEM images of spent (a) Ni@C-700 and (b) Ni@C-800.

3. Experimental Section

3.1. Catalyst Preparation

Pinewood sawdust-derived hydrochar was adopted in the present study. Detailed preparation procedures of the hydrochar can be found elsewhere [38]. Briefly, around 10 g of sawdust was mixed with 100 ml de-ionized water into a 500-ml autoclave, and the reactor was heated to a final 200 °C. After maintaining at 200 °C for 20 min, the reactor was cooled down to room temperature naturally, and the hydrochar was recovered as a solid residue by vacuum filtration. The hydrochar was washed using de-ionized water and was dried at 105 °C for 24 h prior to use.

Around 4 g of the hydrochar with a diameter less than 120 mesh was immersed into 20 ml of 0.5 mol L⁻¹ nickel (II) nitrate solutions, and the resultant mixture was ultrasonicated for 40 min at room temperature. After separation through vacuum filtration, the solid residue (Ni@hydrochar) was then dried at 105 °C for 24 h. The Ni@hydrochar was charged into an alumina boat that was placed in the quartz tube and thermal treated at 700 °C, 800 °C, and 900 °C for 40 min under nitrogen atmosphere. The produced sample was denoted by the treatment temperature as Ni@C-700, Ni@C-800, and Ni@C-900, respectively. For comparison, the hydrochar without nickel (II) nitrate was also prepared under an identical procedure at 900 °C, and the product was labeled as C-900.

3.2. Catalyst Characterization

The crystalline structure of the samples was analyzed by powder X-ray diffraction (XRD) using a Bruker D8-Avance X-ray diffractometer with CuKα radiation (Bruker, Karlsruhe, Germany). The nickel content in the composite was measured by digestion in the mixture of concentrated HNO₃ and 30% H₂O₂, followed by an analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES) with a PerkinElmer 3000DV (PerkinElmer, Waltham, MA, USA). Scanning electron microscopy (SEM) images and X-ray spectroscopy (EDS) were conducted on a Hitachi SU8020 scanning electron microscope (operating at 1 kV) equipped with an IXRF 550i systems EDS detector at 15 kV (IXRF Systems, Los Alamos, NM, USA). Transmission electron microscopy (TEM) was conducted on a JEOL 2011 TEM instrument under 80 kV acceleration voltages (JEOL, Tokyo, Japan).

3.3. Catalyst Performance Test

Catalytic evaluation was carried out at atmospheric pressure (1 atm) in a vertical fixed-bed continuous flow stainless steel reactor (8mm, i.d.). The microreactor was made of a quartz tube (8 mm i.d., 1000 mm long) in which a porous platform was embedded in the middle of the tube. Some glass fiber was placed on the platform to support the catalyst (about 0.13 g every run). The reactor was heated to the desired temperature of 700 °C by an electrical furnace under an argon gas atmosphere. Then, CH₄, CO₂, or the mixture of CH₄ and CO₂ (with the molar ratio of 1:1) passed through a preheater prior to entering the reactor (in the case of the gas mixture, the gases were mixed before passing the preheater). The composition of effluent gas was analyzed by off-line gas chromatographs equipped with a thermal conductivity detector. The method for calculating the conversion of CH₄ and CO₂, as well as the selectivity of CO and H₂, was according to the following equations:

$$\text{Conversion rate CH}_4 = \frac{\text{CH}_4 \text{ inlet} - \text{CH}_4 \text{ outlet}}{\text{CH}_4 \text{ inlet}}$$

$$\text{Conversion rate CO}_2 = \frac{\text{CO}_2 \text{ inlet} - \text{CO}_2 \text{ outlet}}{\text{CO}_2 \text{ inlet}}$$

$$\text{CO/H}_2 \text{ Ratio} = \frac{\text{CO}_{\text{outlet}}}{\text{H}_2_{\text{outlet}}}$$

4. Conclusions

In this study, a simple, cost-efficient, and green approach was provided for the synthesis of Ni nanoparticles supported on renewable hydrochars, which resulted in very promising catalysts for the dry reforming of methane. The nickel ions were well anchored within the hydrochar matrix by co-coordinating with polar functional groups, and the nickel nanoparticles were *in situ* formed by self-reduction. The agglomeration was prevented during thermal treatment at the temperatures of 700 and 800 °C and resulted in a small size and a narrow size distribution of the nanoparticle in the composites. The composites obtained at 700 and 800 °C show a high catalytic reactivity and stability for the dry reforming of CH₄, and their conversion rates were higher than 52% and 70% after a 800 min reaction, respectively. Considering the simple and green preparation method as well as the high catalytic activity, this study offers a potential promising approach for the nickel supported carbons to implement DRM industrially because of the significant environmental and cost benefits.

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