Activated Carbon (AC) Supported Nickel-Nanoparticles Prepared By Solid-Phase Method For Dry Reforming of Methane—Effect of Different Activated Carbons (ACs)

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Abstract

In order to inhibit the apparent metal agglomeration and carbon deposition of the catalysts during the dry reforming of methane (DRM), the nickel nanoparticles supported over different types of activated carbon (AC) are synthesized by the solid-phase method. The main purpose of the work is to reveal the correlation of the support properties on the catalyst activity, and explore the effect of the support properties on the enhancement of catalyst performance in the reforming process. The results show that the catalyst using AC$_1$ as the support has the more uniform metal dispersion and form the least nickel nanoparticles of 4.11 nm, due to higher carbon content and the more developed surface area of AC$_1$. It is also found that the catalyst prepared using AC$_1$ shows high catalytic activity and long-term stability. Moreover, the catalyst of Ni/AC$_1$ presents a self-enhancement of catalytic activity in the reforming process and promotes the conversion rates of CH$_4$ and CO$_2$ to 94.1% and 96.5%, respectively over 12 h. No obvious metal agglomeration is existed on the catalyst of Ni/AC$_1$ after the reforming testing of 12 h. Meanwhile, the carbon deposit has little effect on catalytic performance, and metal agglomeration is the main affecting catalytic performance. In addition, the syngas generated using Ni/AC$_1$ has a favorable H$_2$/CO ratio of 1.

Introduction

The global temperature has been rising for decades due to the continuous increase in the emission of greenhouse gases (GHGs) into the atmosphere. The reduction and utilization of GHGs had attracted more attention as an effective way to avoid their impact on the environment (Vakili et al., 2020). It was reported that CO$_2$ and CH$_4$ account for 76% and 14% of the global man-made emissions, respectively (Vakili et al., 2020). The reforming of CH$_4$ with CO$_2$, also designated as the dry reforming of methane (DRM), was regarded as an attractive pathway for the conversion of GHGs into syngas (i.e., H$_2$ + CO). Syngas is an important intermediate for the synthesis of various chemicals and fuels, such as ammonia, methanol, and dimethyl ether (DME) (Bouchoul et al., 2020; Cao et al., 2018; Vakili et al., 2020). Despite the optimization of reforming conditions, such as temperature, the composition of the reactant gas, space velocity, and pressure, there had been great efforts to reduce the energy consumption associated with DRM due to the high endothermicity of the reaction. The catalytic DRM was an efficient way to resolve the problem. Thus, numerous catalysts with high activity and stability were developed. The catalysts for DRM are classified into metal-supported and carbon-supported catalysts. The former is further divided into noble metal and transition metal catalysts (Pakhare et al., 2014; Zhang et al., 2018). However, metal-based catalysts possessed a series of limitations, such as limited availability, low cost-efficiency of noble metals, and rapid deactivation of transition metals caused by severe coke deposition. Thus, the use of carbon-based catalysts for DRM is a promising method, which is also advantageous for industrial processes (Li et al., 2016; He et al., 2015; Xu et al., 2014). Carbon-based catalysts are classified into two categories: one is carbonaceous materials are directly served as the catalysts in the reforming process, and the other is metallic components are supported over the carbonaceous materials. Commonly, the latter shows the better catalytic activities (Li et al., 2016; He et al., 2015; Xu et al., 2014; Zhang et al.,
In particular, carbon-based catalysts using nickel as the active component have been widely used in the reforming process, mainly due to their low cost and relatively high activity.

The most common carbonaceous materials for the synthesis of carbon-based catalysts include activated carbon (AC), biomass-derived char, coal-derived char, metallurgical coke, and carbon nanofibers (CNF) (Cao et al., 2018; Chinthaginjala et al., 2007; Fidalgo et al., 2010; He et al., 2015; Li et al., 2016; Xu et al., 2014). Due to high surface porosity, large surface area, and cost-efficiency, AC has been extensively studied. AC was also found to have the potential to be the most cost-effective and environment-friendly catalyst for DRM (Xu et al., 2014). It has been reported in the literature that the catalytic activity of AC mainly depends on the concentration of alkaline and alkaline earth metals present in the ash as well as the oxygen-containing functional groups attached to the surface (Xu et al., 2014). Zhang et al. found that the oxygen-containing functional groups on the AC surface, such as carbonyl, carboxyl, and lactone, were the primary active sites for DRM (Zhang et al., 2017a). Xu et al. used AC treated with HNO$_3$ for DRM and reported that the hydroxyl group had a significant role in DRM (Xu et al., 2014). Moreover, AC could serve as a catalyst as well as a microwave absorber in the microwave-assisted DRM process (Fidalgo et al., 2008; Fidalgo et al., 2011; Fidalgo et al., 2012). Despite the high initial catalytic ability, AC can be quickly deactivated (Xu et al., 2014). Conversely, metal-supported carbon-based carriers have better resistance to carbon deposition, thereby prolonging the catalytic activity for the DRM process (Cao et al., 2018; Fidalgo et al., 2011; Li et al., 2017; Li et al., 2019; Zhang et al., 2015). The metallic components, such as Ni, Fe, Co, alkaline and alkaline earth metal, are incorporated onto the carbonaceous carrier through mechanical mixing or impregnation method (Cao et al., 2018; Fidalgo et al., 2011; Li et al., 2017; Li et al., 2019; Zhang et al., 2015). The catalyst developed via mechanical mixing has a combined catalytic effect of the mixed metallic substances, which limits the enhancement of catalytic activity. On the other hand, the catalysts constructed by the impregnation method completely exploit the catalytic effects of the metallic component and carbon-based carrier. The main threats to the catalysts prepared by the impregnation method were the agglomeration of metals and carbon deposition. The catalysts synthesized by the impregnation method often requires a great deal of energy consumption in the calcination process. In addition, the unavoidable carbon deposition and consumption of the carbon existed in the carbon-based catalysts can speed up deactivation of the carbon-based catalysts (Li et al., 2016; Li et al., 2017). Therefore, developing a highly active and stable catalyst with low cost and energy consumption is of significance towards the dry reforming of methane, by searching for appropriate carbonaceous supports and preparation methods of the catalysts.

Nano-sized metallic components supported over AC are of great interest as nanosizing increases specific surface areas by highly dispersing metals on the support and thus exposes more active centers and potentially improves the catalyst performance (Pegios et al., 2018; Shang et al., 2017; Xie et al., 2013). Besides, the resistance of the catalyst to carbon deposition is enhanced by controlling the metallic particles at nanometer. Many types of preparation method have been studied for the fabrication of nanoparticles (Zhao et al., 2018). The solid-phase method of grinding is labeled as a green approach for the development of catalysts, and possesses a series of advantages, such as in-situ synthesis, improved
synthetic efficiency, less energy consumption, and enhanced reactivity (Lu et al., 2016; Zhang et al., 2017b). The preparation of the catalyst using this method reduces the particle size of the metallic component to the nanometer scale. Wang et al. developed a catalyst based on the commercial carbon substrate using this method and found the corresponding particle size of the metallic component to be around 2 nm (Wang et al., 2006). In this paper, the increase in the interaction between the metallic component and carrier for catalysts developed using the solid-phase method, relative to the impregnation method, has also been demonstrated (Wang et al., 2006). Q.L. Zhang et al. developed a nickel-based catalyst on the SBA-15 substrate by the solid-phase method of grinding. The results indicated a carbon deposition of 6.3% on testing the DRM for 100 h at 700°C (Zhang et al., 2017b). In contrast, the catalysts synthesized by the impregnation method experienced a serious carbon deposition as high as 38.3% under the same conditions (Zhang et al., 2017b).

In the related literature, it is found that the catalysts synthesized using solid-phase method have the metal nanoparticles and exhibit the desirable catalytic effect on the process of DRM (Lu et al., 2016; Zhang et al., 2017b). These studies pay extensive attention to the effect of main preparation parameters on the catalyst activity. To the best our knowledge, the properties of the support are important to ensure the dispersion of metal particles and enhance the catalyst performance. Nevertheless, the connection of the support properties, for instance the surface chemical properties and porous structure with its catalytic activity remains to be further explored, when the catalyst is prepared via solid-phase method and using AC as the support. In our previous paper, we prepared the nickel-supported catalysts over AC by the solid-phase method, and the results show that the catalytic activity of the used catalyst can be strengthened after a certain time in the process of DRM. However, there is no in-depth research on the effect of different supports on the self-reinforced catalytic activity. Herein, a series of nickel nanoparticles supported over different activated carbons is obtained using the solid-phase method in the paper. The prime purpose of this work is to investigate the effect of different activated carbons (ACs) on the catalytic performance of AC supported nickel nanoparticles for dry reforming of methane (DRM). The paper also concerns about the in-depth effect of the support properties on the self-enhancement of catalyst activity in the reforming process. The work will provide valuable information on the synthesis of a highly active and stable catalyst by the solid-phase method.

**Experimental Section**

### 2.1 Synthesis and characterization of catalysts

The AC carriers in this study, designated as AC$_1$, AC$_2$, and AC$_3$, respectively, were composed of coconut shell activated carbon, commercial activated carbon, and coal-made activated carbon. The activated carbons were purchased from Suzhou Charcoal Whirlwind Activated Carbon Company. The Ni/AC catalyst was synthesized by the solid-phase method, which has grinding and reduction as the key steps. The detailed process of catalyst preparation is presented in Figure S1, which is described as follows: The AC and polyvinylpyrrolidone (PVP, K-30) were dissolved in deionized water to achieve a mass ratio of 6:1.
The mixture was stirred at 40°C for 6 h using a magnetic stirrer under a rotational speed of 550 rpm. Next, the treated AC was centrifugally washed thrice and placed in a vacuum-drying oven until dry. Later, the mixture of AC and nickel salt (NiCl₂·6H₂O) was ground for 15 min. Sodium borohydride (molar ratio of Ni²⁺:BH₄⁻=1:6) was added to the mixture and further ground for 30 min. N₂ was continuously fed during the grinding process under a flow rate of 200 mL/min. The remaining residue was washed thrice with deionized water and dried for subsequent utilization. After a series of treatments, the Ni/AC with the nickel loading concentration of 5 wt% was formed. Based on the different types of ACs used for the synthetic process, the catalysts were labeled as Ni/AC₁, Ni/AC₂, and Ni/AC₃, respectively. The concentration of the solution required for immersion and grinding time of the precursor was optimized prior to the synthetic process. Accordingly, the synthetic parameters adopted in the process were also optimized.

The first solid-phase reduction of each catalyst was performed at room temperature, using sodium borohydride (NaBH₄) as the reducing agent. However, a minor concentration of nickel gets oxidized in the reduction process due to the nanometer size of the metal particles. The oxidized nickel was further reduced using an in-situ reduction process implemented at 600°C under the nitrogen atmosphere. The oxidized nickel was partially reduced by activated carbon during the second reduction process. Thus, nickel was effectively dispersed in the form of deoxidized metal on the support. It was reported in the literature that the reduction of the catalysts synthesized using the solid-phase method was commonly achieved by performing a calcinated process in the temperature range of 400–800°C (Lu et al., 2016; Wang et al., 2006; Zhang et al., 2017b). In this work, the moderate temperature of 600°C was chosen to conduct the second reduction process. The reduction temperature of 600°C was in accordance with the initial temperature used for testing the catalytic performance. The subsequent testing experiment was performed instantly by utilizing the heat energy from the reduction process stabilized at 600°C. This is a beneficial method for energy conversion.

The BET analysis was performed using the 3H-2000PS2 instrument to obtain the specific surface area and pore diameter of the catalyst. The adsorption and desorption isotherms were tested using the volumetric method under relative pressure and liquid nitrogen saturation temperature of 77.3 K. The scanning electron microscope (SEM) images were obtained using the HITACHI SU8010 instrument with an acceleration voltage of 0.1–30 kV and a resolution of 1.0nm(15 kV)/1.3nm(1 kV). The transmission electron microscopy (TEM) analysis of each catalyst was performed using the FEI Tecnai G2 F20 electron microscope (working voltage: 200 kV, magnification: 100000x). The elemental analysis and atomic percentage of samples were tested by energy dispersion spectrometry. The X-ray electron spectrometer (XPS) analysis was performed using a Japanese Keatos Axis Ultra HAS spectrometer to determine the elemental composition and atomic percentage of the samples. The Fourier transform infrared (FTIR) analysis was performed using the Bruker VERTEX70 instrument. The Raman scattering of the catalysts was performed using the HR800 (HORIBA Jobin Yvon) Confocal Raman spectrometer (532 nm He-Ne laser, measuring band 300–3000 cm⁻¹).

2.2 Reforming experiment
The DRM was tested using an electrical heating device in the temperature range of 600 °C to 900 °C. In each trial, 1 g of the catalyst was placed at the center of the horizontal quartz tube (I.D = 50 mm) reactor using quartz wool. Prior to the experiment, the catalyst was reduced at 600°C for 1 h under the nitrogen atmosphere. During the reforming process, the total flow rate of the feeding gases was maintained at 100 mL/min. The detailed volume fraction of N₂, CH₄, and CO₂ was 3:1:1. Thus, the gas hourly space velocity (GHSV) in this paper is calculated to be 6000 mL/h·g-cat. Under such GHSV, the effects of internal and external diffusion on the intrinsic reaction is less significant (Song et al., 2008). Despite the low flow rate of feed gas and nanometer-scaled metal particle size of the catalysts prepared by the solid-phase method, the volume of the catalyst bed was still relatively small for the horizontal reactor. Therefore, the pressure drop within the reactor was ignored to perform the experiments at an approximate atmospheric pressure. The reforming test was performed at different temperatures for a limited period of 20 min, while the stability test was prolonged for 12 h. The gases generated from the reforming reaction were collected periodically and detected using gas chromatography (Glarus 500GC). The gas analyzer was equipped with two detectors (TCD and FID), whose temperatures were maintained at 200 °C and 250 °C, respectively. The schematic diagram of the methane reforming experimental setup is shown in Figure S2.

The catalytic performance of different catalysts on the DRM was evaluated from the conversion rates of CH₄ and CO₂, as well as the product selectivity (H₂/CO ratio). Meanwhile, the H₂ selectivity, and carbon balance were calculated to evaluate the strength of the reverse water-gas reaction and carbon deposit. The detailed expressions for the above indicators were given below.

\[
X_{CH_4} = \frac{\left(F_{CH_4,in} - F_{CH_4,out}\right)}{F_{CH_4,in}} \times 100\% \tag{1}
\]

\[
X_{CO_2} = \frac{\left(F_{CO_2,in} - F_{CO_2,out}\right)}{F_{CO_2,in}} \times 100\% \tag{2}
\]

\[
R_{(H_2/CO)} = \frac{F_{H_2,out}}{F_{CO,out}} \tag{3}
\]

\[
\text{H}_2 \text{ selectivity (\%) = } \frac{F_{H_2}}{2 \times (F_{CH_4,in} - F_{CH_4,out})} \times 100\% \tag{4}
\]

\[
\text{Carbon balance (\%) = } \frac{F_{CH_4,out} + F_{CO_2,out} + F_{CO}}{F_{CH_4,in} + F_{CO_2,in}} \times 100\% \tag{5}
\]

Where “X” (%) was the conversion of CH₄ and CO₂; “F” (mL/min) meant gas flow rate. In order to ensure the accuracy of experimental data, each group of experiments was repeated three times and the average value was taken.

**Results And Discussion**

**3.1 Characterization of the used AC**
The proximate and ultimate analysis results of three types of AC were summarized in Table S1. The proximate analysis results revealed that AC$_1$ had the least concentrations of volatile compounds and ash. Moreover, AC$_1$ had the highest concentration of fixed carbon among the selected ACs. Thus, the incorporation of AC$_1$ favors better thermal stability. On the contrary, the concentrations of volatile compounds and ash in AC$_3$ were evidently higher than those in AC$_1$ and AC$_2$, thereby resulting in poor thermal stability for the corresponding catalyst. Additionally, the release of volatile compounds from AC$_3$ at high temperatures might cause metal agglomeration on the corresponding catalysts. According to the ultimate analysis results of the three types of AC, it was found AC$_1$ had the highest concentration of carbon and the least concentrations of nitrogen and sulfur. This is in consistent with the fact that AC$_1$ is a biomass-derived activated carbon. The nitrogen adsorption and desorption isotherms, as well as the pore size of ACs, are exhibited in Figure S3. The fitting results showed that the isotherms of the three activated carbons were in accordance with the type I isotherm. AC$_1$ was found to have a highly microporous structure compared to the other activated carbons. The pore sizes of AC$_1$ and AC$_3$ were mainly distributed around 3 nm, while that of AC$_2$ was evenly distributed within a range of 2–8 nm. The average pore sizes of AC$_1$, AC$_2$, and AC$_3$ were calculated to be 2.15 nm, 4.13 nm, and 3.89 nm, respectively. The highly microporous structure of the used AC favors the metal dispersion and the penetration of metal particles into the pore of AC.

### 3.2 Characterization of the prepared catalysts

#### 3.2.1 TEM analysis

The TEM analysis of the prepared catalysts was performed to determine the dispersion and particle size of nickel over AC, as shown in Fig. 1. It was observed that the metal-supported AC-based catalyst had notable metal lattice fringes of 0.21 nm, revealing the penetration of nickel into the carrier. From Fig. 1, it is seen that the metal particles exhibited a desirable dispersion over the carrier for Ni/AC$_1$ and Ni/AC$_2$ catalysts. This indicated the absence of metal migration and agglomeration on the catalysts containing AC$_1$ or AC$_2$ as the carrier. On the other hand, the nickel particles were relatively intense in some regions of the Ni/AC$_3$ catalyst, as shown by the red line in Fig. 1a$_3$. This signified metal agglomeration was prone to occur on the Ni/AC$_3$ catalyst. This difference is primarily attributed to the larger specific surface area of AC$_1$ and AC$_2$ compared to AC$_3$, thereby providing sufficient space for supporting the nickel particles. This might also be related to the embedding depth of the nickel particles into the pore channels of AC$_1$ and AC$_2$. The adequate penetration of metallic particles into AC enhances the combination between the active component and carrier, which is favorable for the improvement of catalytic activity and stability.

Meanwhile, a statistical analysis of the particle size of each catalyst was performed. The average particle size of Ni/AC$_1$ was found to be 4.11 nm, while that of Ni/AC$_2$ was found to be 4.69 nm. Furthermore, the average particle size of Ni/AC$_3$ was calculated to be 5.15 nm. Although the particle size of nickel metal on the surface of different supported catalysts was not the same, the metal size did not produce a large gap. The nanometer size of the Ni/AC$_1$, Ni/AC$_2$, and Ni/AC$_3$ catalysts reinforced the absence of the
generation of large particles during the synthesis of the catalyst containing appropriate carriers using the solid-phase method. It was worth noting that the particle size distribution of Ni/AC$_2$ had a narrower distribution than that of Ni/AC$_1$ and Ni/AC$_3$, as well as the Ni/AC$_1$ had the broadest. This might due to the pore size of the three activated carbons. The average pore size of AC$_2$ were 1.98nm and 0.24nm larger than that of AC$_1$ and AC$_3$. From the above observation, it was concluded that the metal agglomeration is the main cause of the uneven metal dispersion over the carrier for the catalysts prepared using the solid-phase method. The uneven metal dispersion reduces the catalytic performance. The excellent metal dispersion on the Ni/AC$_1$ catalyst is also evident from the results of the STEM-EDX analysis (Fig. 1e). This indicated great similarities between nickel and carbon present in the Ni/AC$_1$ catalyst. The graph indicated that the concentration of chlorine was less significant, merely accounting for 0.21% of the surface atoms. This illustrated the removal of chlorine element from the surface during the pretreatment process. Therefore, the metal dispersion and metal particle size of the catalyst is affected by the specific surface area of AC. Among the prepared catalysts, the Ni/AC$_1$ catalyst had the least average metal particle size of 4.11 nm, accompanied by uniform nickel dispersion over AC$_1$.

### 3.2.2 XPS analysis

The XPS analysis of the prepared catalysts (Fig. 2 and Figure S4) was conducted to find the constituent elements and the elemental form of nickel present on the catalyst surface. It was noting that the three catalysts had the same constituent elements, mainly containing C, O, and Ni elements, as well as a trace amount of Cl element. Meanwhile, the three catalysts contained the same element form, which was manifested as the peaks in each element near the same binding energy. Thereby, the Ni/AC$_1$ was taken into consideration. The X-ray photoelectron spectroscopy (Fig. 2a) showed that the main elements present on the catalyst (Ni/AC$_1$) surface were C, O, and Ni. The calibrated spectrum in Fig. 3b indicated that the C element was present in the form of oxygen-containing functional groups, such as COOH, C-O, and C = O, originating from the AC surface on the addition of PVP. The nickel was mainly found to exist in the form of Ni$^0$ (854.7 eV) and Ni$^{2+}$ (856.6 eV), which was consistent with the adjoint peak of nickel shown in Fig. 2c. It should be noted that the relative binding energy position mentioned in this manuscript was quite different from the standard binding energy position. This was attributed to the strong bonding between the metallic component and support for the catalysts synthesized using the solid-phase method, thereby leading to a deviation in the nickel binding energy position (Cao et al., 2018; Lu et al., 2016).

During the synthetic process, the catalyst exposed to air was found to undergo both reduction and oxidation, leading to the formation of Ni$^0$ and Ni$^{2+}$, respectively. The formation of nickel oxide indicated the strong redox capacity of the nanometer-sized nickel particles, which increased the catalytic activity of Ni-supported catalysts. The fitting result showed that Ni$^0$ had a much higher peak value than Ni$^{2+}$. This indicated that the nickel on the surface of the catalyst mainly existed in the form of Ni$^0$ (Frattini et al., 2017). This was attributed to the self-reduction of most of the oxidized nickel (Ni$^{2+}$) to Ni$^0$ at 600°C, which was recorded in the XPS spectra. The oxygen was present in the form of Ni-O moieties on the catalyst surface, whose bonding energy was found to be 531.4 eV. Besides, the high elemental composition of oxygen was attributed to the presence of oxygen-containing functional groups, as evident
from Fig. 2d. This was further confirmed by the detection of hydroxyl (C-OH) and a carbon-oxygen double bond (O = C-O) on the catalyst surface. The existing oxygen-containing groups were beneficial for the formation of nanometer-scaled metal particles, as mentioned in the literature (Liu et al., 2017; Zhang et al., 2018). The Cl element (Fig. 2e) mainly existed as NaCl substance at a binding energy of 197.9 eV. The reason for this was that NaCl was formed during the reduction of NiCl$_2·6$H$_2$O by NaBH$_4$.

### 3.2.3 FTIR and BET analysis

The FTIR analysis of the prepared catalysts showed that the major oxygen-containing groups present on the catalysts were OH (3430 cm$^{-1}$), C = O (1685 cm$^{-1}$), and R-OH (1105 cm$^{-1}$) groups, as shown in Fig. 3. This was consistent with the measurement results reported in earlier studies (Hulsey et al., 2018; Lua et al., 2005). Additionally, minor peaks were predominantly observed within the range of 1105–1685 cm$^{-1}$ for the prepared catalysts. This implied the presence of trace amounts of other oxygen-based groups on the catalysts. These results were in agreement with the analytical results obtained from the measurement of XPS spectra. Compared to Ni/AC$_2$ and Ni/AC$_3$, the transition intensity of Ni/AC$_1$ was lower, resulting from the larger surface area of AC$_1$. This was ascribed to the availability of sufficient sites for the adsorption of oxygen-containing groups on the catalysts possessing ample surface area. Consequently, there was a relatively even dispersion of oxygen groups on the Ni/AC$_1$ catalyst. Moreover, the abundant oxygen-containing groups favor the combination of the metallic component with the carrier in order to achieve a uniform dispersion of the metal particles on the carrier. Therefore, the dispersion of nickel particles on the Ni/AC$_1$ catalyst was relatively uniform compared to the other catalysts. The nitrogen adsorption and desorption isotherms, as well as the pore size of the prepared catalysts, are exhibited in Figure S5. The specific surface area values of the prepared catalysts and corresponding ACs were obtained through the BET analysis, as listed in Table 1. There was an evident shrink in the specific surface area on the addition of AC for the development of catalysts via the solid-phase method. This is mainly due to the penetration of metal particles into the pore channel of the used ACs. The specific surface area of Ni/AC$_1$ was lowered drastically from 904.3 cm$^3$/g to 734.1 cm$^3$/g compared to the other catalysts. The Ni/AC$_3$ catalyst showed a minor reduction of 38.3 cm$^3$/g. The embedded nickel particles within the pore could be effectively resistant to the deposition of carbon during the DRM. Therefore, a larger decline in the surface area corresponds to an increase in the concentration of nickel particles distributed on the catalyst, which results in a uniform metal dispersion.
### Table 1
Specific surface area of the prepared catalysts and the used activated carbons

| Specific surface area | Values (cm$^3$/g) |
|-----------------------|-------------------|
| AC$_1$                | 904.3             |
| Ni/AC$_1$             | 734.1             |
| AC$_2$                | 591.4             |
| Ni/AC$_2$             | 487.9             |
| AC$_3$                | 252.1             |
| Ni/AC$_3$             | 213.8             |

#### 3.2.4 XRD analysis

The XRD analysis of the activated carbon and prepared catalysts were performed, as shown in Fig. 4. The activated carbon and corresponding carbon-based catalysts were found to show similar peaks at 23.3° and 26.7°. The former peak represents the characteristic peak of carbon present in the activated carbon. The latter might be related to some constituent elements in the catalysts (Cao et al., 2017; Wang et al., 2018). However, the characteristic peaks of nickel theoretically positioned at 44.8°, 52.4°, and 76.3° were not detected by XRD analysis. This does not indicate the absence of nickel over the activated carbon. By contrast, this observation further confirmed the nanometer particle size and good dispersion of the metal loaded over the carrier, which weakens the signal for nickel in the XRD analysis. Therefore, the absence of nickel diffraction peaks in Fig. 4 was attributed to the small particle size and high metal dispersion of the prepared catalyst. The absence of diffraction peaks in the XRD analysis for the catalysts with small particle size and high metal dispersion had been reported in the literature as well (Wang et al., 2018).

#### 3.3 Catalytic activity

##### 3.3.1 Catalytic activity

In this study, the DRM was initiated within the temperature range of 600°C to 900°C for 20 min. The catalytic activities of different catalysts were examined within the same temperature range, as plotted in Fig. 5. Meanwhile, the H$_2$ selectivity curves and the carbon balance curves (Figure S6) of the three catalysts were calculated. Ni/AC$_2$ and Ni/AC$_3$ catalysts showed the similar CH$_4$ conversions that increased with temperature from less than 20% at 600°C to about 75% at 900°C. The Ni/AC$_1$ catalyst were obviously better than those obtained using the Ni/AC$_2$ and Ni/AC$_3$ catalysts, being 41% at 600°C to about 87% at 900°C. This indicated the good catalytic performance of Ni/AC$_1$ on DRM, which is likely related to the uniform metallic nickel nanoparticles dispersion and oxygen-containing groups on the catalyst. The conversion rate of CO$_2$ was basically greater than that of CH$_4$ in the presence of the
synthesized catalysts under the same temperature, except for the presence of Ni/AC\textsubscript{1} at 600°C and 700°C. The larger CO\textsubscript{2} conversion confirmed the occurrence of reverse water-gas shift reaction and carbon consumption during the DRM process. The stronger degree of CH\textsubscript{4} conversion indicated the enhanced catalytic activity of Ni/AC\textsubscript{1} on the decomposition reaction of methane at 600°C and 700°C. Consequently, the generation and consumption of carbon were significant to ensure catalytic stability. In the reforming process, the generation of carbon were mainly attributed to the decomposition of methane at a high temperature and the Boudouard reaction at a low temperature, while the carbon consumption was attributed to the removal of the deposited as well as constituent carbon present in the catalysts. The H\textsubscript{2}/CO ratio obtained in the presence of Ni/AC\textsubscript{1} decreased initially and then increased with temperature until the stable value of 1 was obtained, as shown in Fig. 5c. By contrast, the H\textsubscript{2}/CO ratio achieved in the presence of Ni/AC\textsubscript{2} or Ni/AC\textsubscript{3} increased continuously with temperature. This indicated that the formation of H\textsubscript{2} was more sensitive to the temperature conditions. Thus, there was an enhancement in the production of H\textsubscript{2}, compared to that of CO with the increase in temperature. Nonetheless, the H\textsubscript{2}/CO ratio achieved in the presence of Ni/AC\textsubscript{3} was found to be 0.9 as the temperature rose to 900°C. The side reactions contributing to the formation of CO were highly significant compared to those for the production of H\textsubscript{2}, as the H\textsubscript{2}/CO ratio was lower than 1. Similarly, the H\textsubscript{2}/CO ratio achieved in the presence of Ni/AC\textsubscript{2} was below 1 for temperatures lower than 750°C and reached 1.15 at 900°C. This is possibly attributed to the enhancement of CH\textsubscript{4} cracking at high temperatures.

The H\textsubscript{2} selectivity curves (Figure S6a) showed that the ratio of the three catalysts were always lower than 1 and the ratio became smaller as the temperature increased. It was showed that the reverse water-gas shift reaction occurred throughout the process, as well as the higher the temperature, the stronger the reverse water-gas shift reaction occurred. The H\textsubscript{2} selectivity of Ni/AC\textsubscript{2} and Ni/AC\textsubscript{3} were higher than that of Ni/AC\textsubscript{1}, indicating that the reverse water-gas shift reaction of Ni/AC\textsubscript{2} and Ni/AC\textsubscript{3} was weaker than that of Ni/AC\textsubscript{1}. This can also prove the previous conclusion that the formation of H\textsubscript{2} was more sensitive to the temperature conditions of Ni/AC\textsubscript{2} and Ni/AC\textsubscript{3}. The carbon balance curves (Figure S6b) represented the same trends, which was showed that carbon deposition happened. When then temperature arrived at 600°C, the value of carbon balance of Ni/AC\textsubscript{1} and Ni/AC\textsubscript{3} were close to 1. While the Ni/AC\textsubscript{2} at 600°C had already lower than 1, and it was always lower than Ni/AC\textsubscript{1} and Ni/AC\textsubscript{3} in the entire temperature range. It showed that Ni/AC\textsubscript{2} was easier to produce carbon deposit. As the temperature arrived to 900°C, the carbon depositions were the most. The reason for this was that the decomposition of methane became more violent as the temperature rose.

### 3.3.2 Catalytic stability

The catalytic stabilities of the three catalysts were tested at 900°C for 12 h, and the results were shown in Fig. 6. At the same time, the Figure S7 showed the H\textsubscript{2} selectivity and carbon balance of the catalysts at 900°C for 12 h. In the presence of Ni/AC\textsubscript{1} or Ni/AC\textsubscript{2}, the CH\textsubscript{4} and CO\textsubscript{2} conversions declined initially and then increased. It was emphasized that the gas conversions at the end of the test were already greater
than the initial conversions. Throughout the test, the increase in the conversion of CH\textsubscript{4} in the presence of Ni/AC\textsubscript{1} and Ni/AC\textsubscript{2} was found to be around 7% and 6%, respectively. Meanwhile, the CO\textsubscript{2} conversions in the presence of Ni/AC\textsubscript{1} and Ni/AC\textsubscript{2} showed an observable strengthen of 3% and 13%, respectively. Thus, it was concluded that the catalytic effects of Ni/AC\textsubscript{1} and Ni/AC\textsubscript{2} on the conversion of CH\textsubscript{4} and CO\textsubscript{2} enhanced in a similar trend. However, the catalytic ability of Ni/AC\textsubscript{2} for the conversion of CO\textsubscript{2} was higher than that of Ni/AC\textsubscript{1} with an increase in the duration of the test, especially after 10 h. The enhancement of CO\textsubscript{2} conversion might lead to a severe increase in the consumption of constituent carbon during the reforming reaction, which further reduces the stability of the catalyst. This contributes to the low CH\textsubscript{4} conversion obtained in the presence of Ni/AC\textsubscript{2} compared to that obtained in the presence of Ni/AC\textsubscript{1}. The declined of gas conversion during the initial stage was probably attributed to the unstable state of dissociation of the nickel particles supported over the AC surface (Li et al., 2020). The regeneration of catalytic activity after a certain time was attributed to the following factors: firstly, the dissociated nickel particles transformed into a stable state at high temperatures, thus reinforcing the interaction between the metal particles and the carrier; secondly, the nickel particles were further reduced and associated to carbon, thus forming a stable structure and effectively resisting the generation of large-sized metal particles (Sun et al., 2019); and finally, the uniform distribution of small-sized metal particles over AC\textsubscript{1} and AC\textsubscript{2} could increase the catalytic capacity. By contrast, the gas conversions in the presence of Ni/AC\textsubscript{3} reduced continuously with time, which is particularly demonstrated by a clear decline in the CH\textsubscript{4} conversion from 73–49%. This is consistent with the poor dispersion of nickel particles on the Ni/AC\textsubscript{3} catalyst. Throughout the whole process, the CO\textsubscript{2} conversion rate of the three catalysts were higher than CH\textsubscript{4} conversion rate. This can confirm the occurrence of reserve water-gas shift reaction and carbon consumption. The corresponding H\textsubscript{2}/CO ratio was relatively lower than those of the other two catalysts, as indicated in Fig. 6c. The average H\textsubscript{2}/CO ratios for Ni/AC\textsubscript{1}, Ni/AC\textsubscript{2}, and Ni/AC\textsubscript{3} catalysts were found to be 1.01, 1.57, and 0.87, respectively. According to Fig. 6, the conversion rate of CO\textsubscript{2} is higher than that of CH\textsubscript{4}, but the H\textsubscript{2}/CO ratio in the presence of Ni/AC\textsubscript{1} and Ni/AC\textsubscript{2} is found to be greater than 1. This is resulted from the existence of reverse water-gas shift reaction in the DRM process, and the ratio of H\textsubscript{2} selectivity (Figure S7a) was lower than 1 can indicate the occurrence of reverse water-gas shift reaction. Thus, the steam reforming of methane was taken place, which brought about the production of hydrogen was three times that of CO. It was further determined that the ratio obtained in the presence of Ni/AC\textsubscript{1} was more close to 1. This is consistent with the stoichiometric ratio of DRM. The industrially used syngas possessed the same ratio. Conventionally, the use of a carbon-based catalyst for DRM resulted in the formation of syngas with an H\textsubscript{2}/CO ratio of less than 1, owing to the occurrence of side reactions (Li et al., 2017; Li et al., 2019). On utilizing Ni/AC\textsubscript{3} as the catalyst in the reforming reaction, the corresponding H\textsubscript{2}/CO ratio was found to be lower than 1 during the entire test, which indicated a decrease in the formation of H\textsubscript{2} compared to that of CO. This also suggested an increase in the gasification of the constituent carbon in the presence of Ni/AC\textsubscript{3}. The carbon balance curve (Figure S7b) showed that the increase in carbon deposition over time is very small. It indicated that at 900°C, the balance of between
carbon consumption and carbon deposits. Moreover, it was noted that the Ni/AC₃ had the least carbon deposits. This showed that carbon deposit had little effect on the catalytic ability of the three catalysts.

A comparative study of the catalysts in this work with those reported in the literature was performed to determine the catalytic stability, which is listed in Table 2. It was observed that the stability of the catalyst constituting a single activated carbon was relatively poor. In the literature, it was reported that the concentration of CH₄ and CO₂ decreased by 15% and 23%, respectively, on performing the test at 900°C for 5 h (Song et al., 2008). The wood-derived AC was used in the reaction of DRM under microwave irradiation (Tan et al., 2019). The catalytic activity of AC was found to show a sharp reduction, which is attributed to the poor performance of AC toward anti-carbon deposition in the reforming process. Therefore, the researchers attempted to modify AC in order to utilize them for catalyzing the process of DRM. For instance, the immersion treatment of AC by HNO₃ or NaNO₃ could promote the corresponding catalytic performance, which enhances the initial gas conversions up to 90% at 1000°C (Xu et al., 2014). However, the CH₄ and CO₂ conversions over these catalysts were reported to decline considerably by about 30% (relative value) within the same duration. This indicated the unsustainable catalytic ability of the synthesized catalysts to the reforming process (Xu et al., 2014). The deactivation of these catalysts might be attributed to the loss of active sites, severe carbon deposition, and consumption of the constituent carbon present in the catalysts (Xu et al., 2014). Besides, the treatment of the commercial AC by the addition of CO₂ or oxidation in the (NH₄)₂S₂O₈/H₂SO₄ solution could maintain their stability for 2 h (Fidalgo et al., 2010). However, there was a remarkable loss in the activity of the catalysts (Fidalgo et al., 2010). Similarly, the mechanical mixing of the treated AC with some metallic oxides exhibited undesirable catalytic stability, resulting in an evident drop in the conversion of the reactant gases with time (Bermudez et al., 2011). Besides, the catalytic performance could be affected by the porous structure, surface groups, and reactivity of carbons to the CO₂ present in the used AC (Fidalgo et al., 2010). It was noticed from Table S2 that the metal-supported biomass-derived AC-based (pipe sawdust AC, palm kernel shell AC and oil palm shell AC) catalysts presented weaker stability toward DRM (Aziz et al., 2019; Izhab et al., 2017) compared to the catalysts used in this study. Moreover, the catalytic stability of Ni-supported AC-based catalysts synthesized by the solid-phase method could rival the Co-Ca/AC and metal (Co, Ce, and W) supported AC-based catalysts developed by the impregnation method (Li et al., 2020; Zhang et al., 2017a). The comparative study further verified the excellent catalytic performance of the Ni/AC₁ catalyst. This was attributed to the favorable properties of AC₁ and the technical advantages of the solid-phase method for the preparation of the catalyst. Besides, the catalysts possessed some unique advantages: firstly, the catalysts applied in this work had a single active metallic component with an average addition concentration of 5 wt%, which reduced the metal consumption in the preparation of the catalyst; and secondly, the solid-phase method reduces energy consumption for the preparation of the catalyst, as mentioned in the introduction of this paper.
| Catalyst                          | Preparation method                  | Metal loading | Catalytic performance                                                                 | Ref                        |
|----------------------------------|-------------------------------------|---------------|---------------------------------------------------------------------------------------|----------------------------|
| AC                               | --                                  | --            | The CH$_4$ and CO$_2$ conversions showed an obvious downward trend, respectively from 95–80% and from 85–62% after a test of 5 h at 900 °C. | Song et al., 2008          |
| AC                               | --                                  | --            | AC presented high catalytic activity at the beginning and a sharp loss of catalytic activity was taken place after 40 min. The decrease of CH$_4$ and CO$_2$ conversions was up to 56.6% and 36.6% after the test of 90 min at microwave power of 560 W (about 840 °C). | Li et al., 2020            |
| commercial AC (FY5 and BPL)      | Activation with CO$_2$ or oxidation in a (NH$_4$)$_2$S$_2$O$_8$/H$_2$SO$_4$ solution | --            | CH$_4$ and CO$_2$ conversions could be maintained at the relatively high level up to 2 h. Afterwards, an evident activity loss was emerged on these catalysts. | Fidalgo et al., 2010       |
| AC-HNO$_3$/NaNO$_3$              | Activation method                   | --            | The CH$_4$ and CO$_2$ conversions over these catalysts declined considerably by about 30% (relative value) within the same time period at 700 °C. The similar decreasing trend was also observed at the higher temperature. | Sun et al., 2019           |
| AC + Ni/Al$_2$O$_3$              | Physical mixing                     | 4.2 wt%       | The use of a mixed catalyst could keep CH$_4$ and CO$_2$ conversions at 89% and 94%, but the gases conversions reduced to 65% and 30% after the testing. | Tan et al., 2019           |
| Ni supported on palm kernel shell AC | --                                  | 19 wt%        | The catalysts showed a certain activity towards DRM reaction, with the initial CH$_4$ conversion of 28% and CO$_2$ conversion = 31% at 800 °C. Catalyst activity loss was over 2 h, evidenced by the reduction of CH$_4$ conversion (7%) and CO$_2$ conversion (5%). | Xu et al., 2014            |
| Co supported oil palm shell AC   | Impregnation method                 | 6 wt%         | Experimental results revealed the catalysts exhibited lower conversions of CO$_2$ and CH$_4$, with the increase in temperature from 923 K to 1023 K. | Bermudez et al., 2011      |
| Catalyst                  | Preparation method | Metal loading | Catalytic performance                                                                                                                                                                                                 | Ref                  |
|--------------------------|--------------------|---------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|
| Co-Ca/AC                 | Impregnation method| 0 ~ 14 wt%    | The stability test was carried out at 800°C for 2000 min. In the end, the conversions of CH₄ and CO₂ maintained at 85% and 91%, respectively.                                                                           | Aziz et al., 2019    |
| Co, Ce, and W supported over AC | Impregnation method |               | The optimal catalyst performance (CH₄ conversion of 90.15%, CO₂ conversion of 93.89% at 800 °C.                                                                                                                         | Izhab et al., 2017   |
| Ni/ACₓ                   | Solid-phase method | 5 wt%         | The conversions of CH₄ and CO₂ decreased in the first 2 h and then the conversions begun to rise, finally increasing to 94.1% and 96.5% after 12 h at 900 °C.                                                       | Our work             |

3.4 **Post catalyst characterization**

The SEM, and Raman analyses were performed for post catalyst characterization in order to explore the cause to the catalytic stability.

3.4.1 **SEM analysis**

It was observed from SEM images (Fig. 7) that the large Ni particles were appeared on the post-reaction catalysts, and the results of XRD can prove these particulate matters were Ni. The existence of metal agglomeration on the Ni/AC₃ catalyst was not negligible. This was attributed to the smaller surface area of AC₃, resulting in an uneven metal distribution over the AC and weaker bonding between the nickel particle and carrier. Also, the high volatile matter present in the Ni/AC₃ catalyst was higher than that of Ni/AC₁ and Ni/AC₂ catalysts, resulting in an increase in the metal content per unit area that speeds up the metal agglomeration. Thus, the metal agglomeration was the main cause of the continuous deactivation of the Ni/AC₃ catalyst. It was further concluded that the specific surface area and the amount of fixed carbon of AC, which changes the degree of metal agglomeration on the catalyst, was the factors for the catalytic stability in the process of DRM. The SEM analysis indicated that the metal particle size of the used catalyst was enlarged to a certain extent during the reforming process. This indicated a tendency of slight metal agglomeration on the used catalysts. Despite this, the conversion rates of CH₄ and CO₂ achieved using Ni/AC₁ and Ni/AC₂ increased instead, according to Fig. 6. This is due to the presence of uniform oxygen-containing functional groups on the surface and the carbon deposition of the three catalysts, which were active to catalyze the process of DRM (Lua et al., 2005; Zhang et al., 2018). In addition, the carrier of AC possesses a certain catalytic activity on the DRM reaction.

3.4.2 **Raman analysis**
It was reported that the graphitized carbon (I_D) and disordered carbon (I_G) present within the AC showed certain catalytic effects on the reforming reactions, especially in the presence of the latter component. This is attributed to the large number of active sites caused by the defects in the disordered carbon, which exploits the catalytic ability of the material toward the reactions. Thus, the I_D/I_G ratio was found to be a major factor for the catalytic activity of AC-based catalysts. The results of the Raman analysis (Fig. 8) revealed that the I_D/I_G ratio of the used catalysts was increased to a certain extent. This implied a change in the equilibrium concentrations of graphitized carbon and disordered carbon present in the catalysts synthesized by the solid-phase method. This resulted in an increase in the concentration of disordered carbon than that of graphitized carbon for the catalysts undergoing the reforming test under experimental conditions. In other words, there was a greater increase in the disordered carbon compared to that of the graphitized carbon during the reforming process. As a result, the catalysts were able to regain the catalytic activity in the process of DRM.

Conclusions

In the work, we compare the catalytic activity of nickel nanoparticles supported over different types of AC on the reaction of DRM. The main conclusions are summarized as follows:

1. The properties of AC has an apparent impact on the prepared catalysts. A biomass-derived activated carbon of AC_1 is more favorable for the formation of nickel nanoparticles and metal dispersion, due to its high carbon content and more developed surface area. The nickel particles over this AC has a nanosize of 4.11 nm. The characterization results of the prepared catalysts show that the nickel existed on the catalyst is mainly present in the form of Ni^0, and the dominant oxygen-containing groups on these catalysts are found to be OH, C = O, and R-OH. After the preparation of the catalysts using different types of AC, the oxygen-containing functional groups on the Ni/AC_1 becomes more uniform, and the penetration of nickel nanoparticles into the pore structure of AC is more sufficient. These changes are in accordance with the more uniform metal dispersion on Ni/AC_1.

2. The Ni/AC_1 shows a highly active and stable catalytic performance on DRM. Furthermore, the catalyst using AC_1 as the support exhibits a self-enhancement of catalytic activity in the testing of DRM at 900°C within 12 h. Under the use of this catalyst, the conversion rates of CH_4 and CO_2 rise to 94.1% and 96.5%, respectively, at the end of the test. Besides, the syngas produced in the presence of Ni/AC_1 has an ideal H_2/C0 ratio approaching the value of 1. Through characterization, it is found that no obvious metal agglomeration and an improvement in the intensity of disordered carbon are observed in the presence of Ni/AC_1.

Declarations

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**Figures**

**Figure 1**

TEM images and particle size: Ni/AC1 a1-c1); Ni/AC2 a2-c2); Ni/AC3 a3-c3); d) size distribution histogram of Ni/AC1; e-f) element analysis of Ni/AC1

**Figure 2**

High-resolution XPS spectra of Ni/AC1: a) Ni/AC1; b) C 1s; c) Ni 2p3/2 d) O 1s e) Cl 2p3/2
Figure 3

FTIR spectra of the prepared catalysts
Figure 4

XRD patterns of three types of AC and their corresponding catalysts: a) AC1 and Ni/AC1, b) AC2 and Ni/AC2, c) AC3 and Ni/AC3
Figure 5

Catalytic performance of Ni/AC on DRM at different temperatures: a, b), CH4 and CO2 conversations; c) H2/CO ratio
Figure 6

Catalytic stability of Ni/AC at 900 °C: a, b), CH4 and CO2 conversations; c) H2/CO ratio
Figure 7

SEM images of the prepared and post catalysts
Figure 8

Raman spectra of the prepared and post catalysts

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