Experimental Study on Dry Reforming of Biogas for Syngas Production over Ni-Based Catalysts

Reiyu Chein* and Zengwei Yang

Department of Mechanical Engineering, National Chung Hsing University, Taichung 40227, Taiwan

Supporting Information

ABSTRACT: Syngas production from dry reforming of biogas (DRB) is studied experimentally in this work. Ni/Al₂O₃, Pt/Al₂O₃, and Pt-Ni/Al₂O₃ are used as catalysts to examine the effect of CO₂ content in biogas and H₂O addition on DRB performance for reaction temperatures in the 600−800 °C range. It is found that the bimetallic Pt−Ni catalyst exhibits the best activity and thermal stability among the three types of catalysts studied due to better carbon deposition resistance. Because CO₂ functions as the oxidant in combustion, CH₄ conversion is enhanced when the biogas contains more CO₂. One hundred percent CO₂ conversion can be reached for biogas containing a less amount of CO₂ at high temperatures. With H₂O addition in DRB, the steam reforming of methane (SRM) reaction is the dominant reaction, resulting in higher H₂ and CO yields with biogas containing lesser amounts of CO₂. However, lower CH₄ conversion and negative CO₂ conversion do result. With higher CO₂ content in the biogas, higher CH₄ and CO₂ conversions can be obtained. Lower yields of H₂ and CO are obtained due to less SRM dominance. With H₂O addition in biogas, the H₂/CO ratio with a value greater than 1 can be obtained from DRB. It is also found that the H₂/CO ratio with a value of 2.1 can be obtained for reactant composition with a molar ratio of CH₄/CO₂/H₂O = 1:0.25:1 and reaction temperature of 800 °C.

1. INTRODUCTION

Due to continuous increase in energy demand and impact of fossil fuel on the environment, search for new energy resources becomes an important issue. Biogas has been recognized to be a versatile renewable energy source and is receiving increased interest because it can be used to replace fossil fuels. It is formed by the anaerobic digestion or bacterial fermentation of biomass. Biogas is composed mainly of methane (CH₄), carbon dioxide (CO₂) with minor species such as hydrogen sulfide (H₂S), and ammonia (NH₃). Biogas can be utilized in various applications such as heat, mechanical power, and electricity generation.

Biogas can also serve as feedstock for the catalytic dry reforming process for syngas production because the main species are CH₄ and CO₂. Similar to conventional methane dry reforming, the chemical reactions involved in the dry reforming biogas (DRB) reactions are dry reforming of methane (DRM) and reverse water-gas shift (RWGS) reactions:

DRM: CH₄ + CO₂ ⇌ 2H₂ + 2CO, ΔH₂⁹⁸K = 247 kJ/mol (1)

RWGS: CO₂ + H₂ ⇌ CO + H₂O, ΔH₂⁹⁸K = 41 kJ/mol (2)

Syngas, consisting mainly of H₂ and CO, is an important raw material in Fischer−Tropsch synthesis for high-chained hydrocarbon fuels or to produce oxygenated compounds. However, there are two serious problems involved in DRB. It is a highly endothermic reaction according to eq 1, which consumes much energy and deactivates catalysts due to catalyst carbon deposition. DRB is usually operated at high temperatures because of high energy requirement. This results in catalyst support collapse or metal sintering. In DRB, carbon is formed mainly by methane decomposition (MD) and the Boudouard reaction (BR):

MD: CH₄ ⇌ C + 2H₂, ΔH₂⁹⁸K = 75 kJ/mol (3)

BR: 2CO ⇌ CO₂ + C, ΔH₂⁹⁸K = −171 kJ/mol (4)

The endothermic MD reaction is favored at higher temperatures and lower pressures. The exothermic Boudouard reaction is favored at lower temperatures and higher pressures. For enhancing catalyst stability and carbon deposition resistance ability, the process parameters such as reaction temperature, reactant flow rate, and catalyst support and active phase can be adjusted.

In the past, great efforts have been devoted to develop a variety of noble and transition-metal-supported catalysts for DRM or DRB. Among all the metals, Ni-based catalysts are more attractive for DRM or DRB due to their high activity and low cost. However, sintering of Ni nanoparticles and...
deposition of carbon on Ni-based catalyst surfaces cause rapid catalyst deactivation.14,15 There are large amounts of efforts have also been made to improve the capability of Ni-based catalysts.16 In the study by Li et al.,17,18 they pointed out that catalyst design with a core/yolk-shell structure is one of the most effective ways for resisting the sintering and carbon of catalysts in the application of syngas production from hydrocarbon reforming reactions. In the studies by Das et al.19 and Tang et al.,20 various catalyst supports were developed for improving the catalyst capability. In addition to catalyst developments, reactor design also plays an important role in enhancing the DRM performance. As compared with the traditional fixed-bed reactor, DRM performance can be enhanced using a membrane reactor21 and fluidized bed reactors.22 As noted above, biogas contains various impurities. Effects of these impurities on catalyst capability for DRM were also reported in the literature.23–25

According to the studies by Bian et al.26 and De et al.27 bimetallic catalysts may exhibit superior activity, selectivity, and deactivation resistance compared to the corresponding monometallic catalysts. Ni-based catalyst modification using a very small amount of noble metal can result in an inexpensive bimetallic catalyst that assures both high activity and carbon deposition resistance.28–31 In the study by Garcia-Diequez et al.28 Pt–Ni/Al2O3 catalysts were prepared and used for the DRM reaction. They reported that Pt addition inhibited global carbon formation and avoided Ni sintering at 700 °C reaction temperature. Gould et al.29 found that Pt-Ni/Al2O3 activity prepared using atomic layer deposition can be doubled compared with that prepared using conventional incipient wetness impregnation. Li et al.30 reported that surface modification by adding Pt atoms can effectively enhance catalytic activity and carbon deposition resistance for impregnating Pt onto reduced Ni/Al2O3. In the study by Özkar-Aydınoglu and Aksoy,31 kinetics and the surface reaction mechanism of DRM were studied over Pt-Ni/Al2O3 catalysts with various Ni/Pt loading ratios. They pointed out that the CO inhibition effect is stronger and CO2 utilization is suppressed on the catalyst with high Ni/Pt loading ratios.

In addition to catalyst development, carbon deposition can be significantly inhibited by adding steam in the dry reforming process.32,33 With steam addition, the DRB or DRM is coupled with steam reforming of methane (SRM) described as

\[
\text{SRM: } \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2, \quad \Delta H_{298K} = 167 \text{ kJ/mol}
\]

(5)

The combined DRM and SRM are also known as the bireforming of methane (SRM) described as

\[
\text{BRM: } 3\text{CH}_4 + 2\text{H}_2\text{O} + \text{CO}_2 \leftrightarrow 4\text{CO} + 8\text{H}_2, \quad \Delta H_{298K} = 220 \text{ kJ/mol}
\]

(6)

As pointed out in the study by Kumar et al.,34 BRM has benefits such as H2/CO ratio flexibility for the produced syngas, carbon formation reduction, high methane conversion, and high selectivity to H2 and CO. In the study by Olah et al.,35 BRM was carried out for syngas with an H2/CO ratio of 2 for methanol synthesis using metal oxide-supported catalysts at elevated pressures. Choudhary and Rajput36 reported on the complete methane conversion toward syngas using combined dry steam reforming of methane at 850 °C. Koo et al.37 investigated the combination of DRM and SRM and found that an H2/CO ratio of 2 could be achieved using a feed ratio of CH4/CO2/H2O = 1:0.4:0.8. In the study by Karemore et al.,38 the influence of reaction variables over dry and mixed reforming of methane for syngas production using the Ni/Al2O3 catalyst in a fixed bed reactor was studied. Their results showed that reactant conversion and product yield increased with the increase in space time. In the study by Ashok et al.,39 the Ni-SiO2–MgO catalyst was prepared for the BRM reaction. At 750 °C, the CH4 conversion of 80%, CO2 conversion of 60%, and H2/CO ratio of 2 can be reached with negligible carbon deposition.

Although bimetallic Ni-based catalysts for DRM have been studied extensively in the past, its ability in DRB having a lesser amount of CO2 is unclear. Similarly, combined DRM and SRM were also studied extensively in the literature. The CO2 amount effect in the feedstock on syngas production performance is also not clear. Biogas was used as the feedstock for syngas production via the dry reforming process in this study. The CO2 amount contained in the biogas, catalyst type, and H2O addition effects on the syngas production performance are addressed.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterization. Three kinds of catalysts were prepared and tested in this study. As indicated in Table S1, the weight percentage is based on the weight of the support. From Table S1, it can be seen that the chemical composition determined by XRF is close to the designed values. Table 1 shows the textural properties of the catalyst and support based on the N2 physisorption test. Using Al2O3 support surface area as a reference, the specific catalyst surface area decreases due to the metal impregnation onto the Al2O3 pore surface. Table 1 shows the average pore diameters ranged from 20 to 40 Å. This indicates that the catalysts are mesoporous solids.

The XRD patterns for the Ni/Al2O3 catalyst before and after reduction are shown in Figure 1a. No characteristic crystalline peaks corresponding to metallic Ni or NiO species were found for the case before reduction. This indicates that the Ni is highly dispersed and has a small particle size. However, nickel aluminate spinels (NiAl2O4) were present and cannot be ignored. The spinel crystalline peaks overlap with those of γ-Al2O3 at 37.5°, 48.5°, and 66.8°. As reported by Penkova et al.,41 the Ni loading is critical to spinel formation. In this study, the Ni loading is 10 wt %. According to the study by Penkova et al.,41 Ni loading should be higher than 33% for transforming all of γ-Al2O3 into NiAl2O4. Therefore, NiAl2O4 spinels should coexist with γ-Al2O3 support (JCPDS 00-004-0880).41 Ni crystalline corresponding to the diffraction peaks appeared at 44.5°, 51.7°, and 76.4° (JCPDS 87-0712) was found and is shown in Figure 2a after reduction in a H2 atmosphere. This indicates that metallic Ni is the predominant active phase for the reaction. The XRD patterns for the Pt–Ni/Al2O3 catalyst are shown in Figure 1b. The XRD pattern of Ni–Pt/Al2O3...
before the reduction case is similar to that of Ni/Al2O3 except that a peak appeared at 39° for PtO (JCPDS 43-1100). Peaks for Pt appeared at 39.8°, 46.3°, and 67.6° (JCPDS 65-2868) can be found after reduction. As pointed out in the study by García-Diéguez et al.,28 Pt−Ni alloy can be detected from the XRD pattern of Pt−Ni catalysts. The peaks of Pt−Ni alloy appear at 41.5° and 48.4°. The appearance of Pt−Ni alloy depends on the load ratio of Pt/Ni. The Pt−Ni alloy can only be detected as the Pt/Ni ratio is high enough. Due to the low Pt/Ni ratio, the Pt−Ni alloy peaks are not detected in the XRD pattern shown in Figure 1b. From the XRD pattern for the Ni−Pt/CeO2/Al2O3 catalyst reported in the study by le Saché et al.,42 peaks of Pt and Ni can still be found in the XRD pattern of the Pt−Ni catalyst before and after the reaction. According to the study by Larimi and Khorash,43 the XRD pattern of the Pt−Ni catalyst showed no evidence of Ni or Pt peaks. They argued that this is because of the formation of Ni−Pt alloy. An increase in the Pt content resulted in a decrease in the diffraction angle related to the Ni−Pt alloy. Based on these studies, the XRD pattern shown in Figure 1b agrees with those obtained by García-Diéguez et al.28 and by le Saché et al.42

![Figure 1. XRD patterns of before and after reduced catalysts. (a) Ni/Al2O3 and (b) Pt−Ni/Al2O3.](image)

Figure 2 shows the H2-TPR profiles for Ni/Al2O3, Pt/Al2O3, and Pt−Ni/Al2O3 catalysts. By measuring the H2 consumption, it is seen that the peak temperature is observed in the 780−800 °C range for the Ni/Al2O3 catalyst. The high reduction temperature indicates strong interaction between NiO and Al2O3 support. It can also be attributed to the reduction of surface spinel species NiAl2O4 formed by the diffusion of NiO into Al2O3. Similar type TPR behavior was also observed by Chen et al.44 and le Saché et al.42 For the Pt/Al2O3 catalyst, a broad peak can be observed, which extends over the 250−400 °C range. The shape of the peak indicates that various reducible platinum species are present. For Pt-Ni/Al2O3 catalysts, two peaks appeared in the TPR curve. By comparing Pt/Al2O3 with Ni/Al2O3, these two peaks correspond to the reductions of Pt and Ni, respectively. Based on the results shown in Figure 3, the in situ reduction temperature of the catalyst is chosen as 900 °C.

2.2. Effect of Catalyst Types on DRB. We first examined the catalyst type effect on DRB performance. Figure 3 is the time-on-stream measured DRB performance for CH4/CO2/H2O = 1:1:0 (case 1 in Table S2) and various catalyst types for reaction temperatures ranging from 600 to 800 °C with an increment of 50 °C. The performance of DRB is characterized using CH4 conversion, CO2 conversion, H2 yield, CO yield, and H2/CO ratio determined according to the following equations

\[ X_{\text{CH}_4} = \frac{F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}}{F_{\text{CH}_4,\text{in}}} \times 100\% \] (7)

\[ X_{\text{CO}_2} = \frac{F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}}}{F_{\text{CO}_2,\text{in}}} \times 100\% \] (8)

\[ Y_{\text{H}_2} = \frac{F_{\text{H}_2,\text{out}}}{F_{\text{CH}_4,\text{in}}} \] (9)

\[ Y_{\text{CO}} = \frac{F_{\text{CO},\text{out}}}{F_{\text{CH}_4,\text{in}}} \] (10)

\[ H_2/CO\text{ ratio} = \frac{Y_{\text{H}_2}}{Y_{\text{CO}}} \] (11)

In these equations, \( F_{i,\text{in}} \) and \( F_{i,\text{out}} \) are the molar flow rates of species i at the reactor inlet and outlet, respectively. Based on

![Figure 2. TPR profiles of the Ni/Al2O3, Pt/Al2O3, and Pt−Ni/Al2O3 catalysts calcined at 800 °C.](image)
eqs 7–11, the CH₄ conversion, CO₂ conversion, H₂ and CO yields, and H₂/CO ratio are shown in Figure 3a–e. Because DRB is an endothermic reaction, all of these performance parameters increase with increased reaction temperatures, as shown in Figure 3a–e. From the data shown in Figure 3, fairly stable variation with respect to time for each reaction temperature was obtained for Ni and Pt–Ni catalysts. For the Pt catalyst, unstable data resulted for low temperatures, but stable data were obtained for the high temperatures. Poor DRB
performance from the Pt catalyst at low temperatures was obtained compared with the Ni and Pt–Ni catalysts. In Figure 4, the averaged DRB performance as functions of reaction temperature and catalyst type is shown based on the

Figure 4. Averaged DRM performance as a function of the reaction temperature for various types of catalysts. CH₄/CO₂/H₂O = 1:1:0. (a) CH₄ conversion, (b) CO₂ conversion, (c) H₂ yield, (d) CO yield, and (e) H₂/CO ratio.
results obtained in Figure 3. As shown in Figure 4, the experimental results are also compared with the equilibrium results predicted by Aspen Plus (v.10.1) under the same operating conditions. From Figure 4, it can be seen that the difference between experimental and equilibrium results at lower temperatures is much greater than that at higher temperatures. This is attributed to the reason that DRM is more pronounced at higher temperatures. At lower temperatures, the experimental results are kinetically limited while the equilibrium results are obtained by assuming infinite residence time. From Figure 4a, it is clearly seen that higher CH₄ conversion can be obtained using bimetallic Pt–Ni catalysts. Low CH₄ conversion results from the Pt/Al₂O₃ catalyst for low reaction temperatures and CH₄ conversion comparable with other catalysts can only be obtained at high reaction temperatures. This indicates that the Pt/Al₂O₃ catalyst can only be activated at high reaction temperatures. Figure 4b shows the CO₂ conversion as a function of the reaction temperature. The variation trend is similar to the CH₄ conversion. Note also that high CO₂ conversion from the Pt/Al₂O₃ catalyst can be obtained for temperatures higher than 750 °C. By comparing Figure 4a,b, CO₂ conversion is higher than CH₄ conversion. This indicates the RWGS occurrence as described in eq 2. Figure 4c,d shows the H₂ and CO yields, respectively. Because of higher CH₄ conversion, higher H₂ and CO yields can also be obtained from the 3wt%Pt-10wt%Ni/Al₂O₃ catalyst. Based on the results shown in Figure 4c,d, the H₂/CO ratio is shown in Figure 4e. Due to RWGS, the H₂/CO ratio is lower than 1. As the reaction temperature increases, more H₂ results from CH₄ decomposition and the H₂/CO ratio approaches one for all catalysts studied. The H₂/CO ratio obtained from the 3wt%Pt-10wt%Ni/Al₂O₃ catalyst is slightly higher than that of other catalysts.

As shown in Figure 4b,d, the CO₂ conversion and CO yield from the Pt–Ni catalyst are higher than the equilibrium case. This is because carbon formation leading to less CO₂ formation is included in the equilibrium model. In addition, the difference can also be attributed to side reactions taking place at higher temperatures, which would be difficult to be included in any theoretical model. Moreover, the mass and heat transfers in the catalytic fixed beds may be more pronounced at higher temperatures and enhance the chemical reactions. Similar results were also reported by Charisiou et al. and Rahemi et al.

The TGA/DTA test (STA6000, PerkinElmer, USA) was performed to examine the carbon deposition onto the catalyst surface. The spent catalysts for obtaining the results shown in Figure 4 are used as the samples in the TGA test and the results are shown in Figure 5. From Figure 5, there are two weight loss ranges presented in TGA curves. The weight loss observed below 400 °C may attribute to the oxidation of volatile organic compounds and desorption of adsorbed water. The weight loss observed over 600 °C may be attributed to the oxidation of carbon. For the Ni catalyst, there is about 15% of weight loss. For the Pt–Ni catalyst, about 29% of weight loss is observed. For the Pt–Ni catalyst, there is about 15% of weight loss. Because the weight loss is due to carbon oxidation, the test results described above indicate that the Pt–Ni catalyst has better carbon deposition resistance ability as compared with the monometallic Pt or Ni catalyst.

From Figures 3, 4, and 5, the bimetallic Pt–Ni catalyst exhibits superior activity and deactivation resistance compared to those from corresponding monometallic catalysts. Bian et al. pointed out that the surface modification from adding Pt atoms can effectively enhance the catalytic activities and carbon resistance. It is also pointed out by Garcia-Dieguez et al. that the addition of Pt in Ni-based catalysts can inhibit global carbon formation, promote the relative content of active species, and avoid metal sintering, as well as improve considerably the stability of the catalysts. According to the CO₂-TPD study reported by Larimi and Khorash, Pt can be more evenly distributed on the catalyst surface due to the interaction between Pt and Ni. The interaction between Pt and Ni not only increases the type and number of surface adsorption site of the catalyst but also promotes uniform distribution of the catalyst surface.

2.3. Effect of CH₄/CO₂ Ratio on DRB Performance without H₂O Addition. Based on the results shown in Figures 3, 4, and 5, the 3wt%Pt-10wt%Ni/Al₂O₃ catalyst has the best performance among the catalysts studied. In the following, the 3wt%Pt-10wt%Ni/Al₂O₃ catalyst was used for further study on DRB performance. Since the CO₂ contained in biogas is usually less than CH₄, gas composition cases 1, 2, and 3 listed in Table S2 are used as the feedstock for DRB and the performance is shown in Figure 6. Similar to Figure 4, the results shown in Figure 6 are based on the data from time-on-stream measurement. Since CO₂ plays a role similar to an oxidant in the combustion reaction, more CO₂ in the feedstock favors the conversion of CH₄ in the DRB. This is clearly demonstrated in Figure 6a in which CH₄ conversion decreases with a decreased CO₂ amount contained in the biogas. For the CH₄/CO₂/H₂O = 1:0.25:0 case, it is seen that CH₄ conversion becomes independent of the reaction temperature when the reaction temperature is high. Because less CO₂ is involved in the reaction, Figure 6b shows that higher CO₂ conversion is obtained as the CO₂ amount is decreased. One hundred percent CO₂ conversion can be obtained for the CH₄/CO₂/H₂O = 1:0.5:0 and 1:0.25:0 cases at high temperatures. The H₂ and CO yields shown in Figure 6c,d are basically similar to the CH₄ conversion shown in Figure 6a. Although a higher H₂/CO ratio results from the CH₄/CO₂/H₂O = 1:0.25:0 case as shown in Figure 6e, the H₂ and CO yields are lower compared with the CH₄/CO₂/H₂O = 1:10:5.0 and 1:1:0 cases as shown in Figure 6c,d.
2.4. \textit{H}_2\text{O} Addition Effect on DRB Performance. The test results of the \textit{H}_2\text{O} addition effect on DRB performance are shown in Figure 7. The gas composition with cases 4, 5, and 6 listed in Table S2 is used as the feedstock. Note that the amount of \textit{H}_2\text{O} added is equal to that of \textit{CH}_4. Compared with Figure 6a in the case without \textit{H}_2\text{O} addition, Figure 7a shows

![Figure 7](image-url)
that CH$_4$ conversion can be enhanced by H$_2$O addition. This is due to the SRM reaction as indicated in eq 5. For the CH$_4$/CO$_2$/H$_2$O = 1:1:1 case, 100% CH$_4$ conversion can be reached at 800 °C. Compared with Figure 6b in the case without H$_2$O.
addition, H2O addition results in lower CO2 conversion, as shown in Figure 7b. With H2O added in the reaction system, SRM is involved in the reaction. Along with SRM, the two other reactions involved are the water-gas shift (WGS) and reverse CO2 methanation (RCM) reactions\textsuperscript{52}

\[
\text{WGS: } \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2, \quad \Delta H_{298K} = -41 \text{ kJ/mol}
\]

\[
\text{RCM: } \text{CH}_4 + 2\text{H}_2\text{O} \\
\leftrightarrow 4\text{H}_2 + \text{CO}_2, \quad \Delta H_{298K} = 165 \text{ kJ/mol}
\]  

As shown from eqs 12 and 13, more CO2 and H2 are produced from SRM, WGS, and RCM. The CO2 production from WGS and RCM reactions causes a decrease in CO2 conversion. As shown in Figure 7b, the CO2 conversion depends on the CO2 amount in the feedstock. For CH4/CO2/H2O = 1:0.5:1 and 1:0.25:1 cases, negative CO2 conversion results from the low reaction temperature regime. In these cases, methane steam reforming reactions (eqs 5, 12, and 13) are dominant and more CO2 is produced with more H2O and less CO2 in the feedstock. Although CO2 can be consumed in DRM, the reaction rate is low because of low temperatures. As a result, negative CO2 conversion results due to more CO2 produced and less CO2 consumed. A similar result was also reported from both thermodynamic analysis\textsuperscript{34,35} and numerical modeling.\textsuperscript{53}

Figure 7c,d shows the H2 and CO yields for DRB with H2O addition. From Figure 7c,d, higher H2 and CO yields can be obtained from biogas having less CO2 amount. The reason for this result may be attributed to the dominance of methane steam reforming reactions stated above (eqs 5, 12, and 13). With less CO2 amount involved in the DRB and with H2O addition, the methane steam reforming reaction is more dominant than the dry reforming reaction. As shown in eqs 5, 12, and 13, more H2 can be produced from steam reforming as compared with dry reforming. That is, a higher H2 yield can be obtained with less CO2 as shown in Figure 7c. Although CO is consumed in the WGS reaction, the overall CO production is higher in the SRM-dominated reaction system, resulting in a higher CO yield, as shown in Figure 7d. For biogas containing more CO2, a higher CO2 amount is not favored for the SRM reaction, leading to lower H2 and CO yields, as shown in Figure 7c,d. Because of a higher H2 yield, Figure 7e shows that a higher H2/CO ratio than 1 can be obtained. For the CH4/CO2/H2O = 1:0.25:1, a H2/CO ratio with a value close to three results at 600 °C and to 2.1 at 800 °C. This indicates the
dominance of SRM in the reaction as discussed above. As temperature increases, the H2/CO ratio decreases due to the RWGS that consuming H2 and producing CO.

2.5. Thermal Stability Test. Time-on-stream tests with longer times were carried out to realize the thermal stability of catalysts. In Figure 8a,b, the CH4 and CO2 conversions using 10wt%Ni/Al2O3 and 3wt%Pt-10wt%Ni/Al2O3 catalysts and gas composition of CH4/CO2/H2O = 1:0.5:0 at 700 °C are shown. As shown in Figure 8, the Pt−Ni/Al2O3 catalyst has better thermal stability than the Ni/Al2O3 catalyst. In Figure 9, thermal stability was carried out under the same conditions used in Figure 8 except that the reaction temperature was 800 °C and the test time was longer. The test time of 72 h for the results shown in Figure 9 is comparable to that reported in the literature.40,54 From the results shown in Figure 8a,b, it is also indicated that the Pt−Ni/Al2O3 catalyst is more stable than the Ni/Al2O3 catalyst. The results shown in Figures 8 and 9 indicate that Pt addition improved the catalyst stability.

3. CONCLUSIONS

Syngas production via the dry reforming process using simulated biogas as the feedstock was experimentally studied. The monometallic Ni and Pt and bimetallic Pt−Ni catalysts supported by Al2O3 were used as the catalysts. The CO2 amount contained in biogas and H2O addition effects on the syngas production performance were investigated. The following conclusions can be made based on the measured results presented:

1. The bimetallic Pt−Ni catalyst has better activity compared with monometallic Ni or Pt catalysts. Low activity from the Pt catalyst was found when the reaction temperature is low.
2. In the case without H2O addition, CH4 conversion decreased with the decreased CO2 amount contained in the biogas. Higher CO2 conversion can be obtained because of less CO2 amount involved. The yileds of H2 and CO are found to increase with an increased CO2 amount because of higher CH4 conversion.
3. For the H2O addition case, methane steam reforming is the dominant reaction when less CO2 amount is contained in the biogas. This results in higher H2 and CO yields and negative CO2 conversion. With a higher CO2 amount contained in the biogas, lower H2 and CO yields resulted, indicating that methane steam reforming is less dominant because of higher CO2 content.
4. Long time-on-stream test results show that better thermal stability can be obtained from the bimetallic Pt−Ni/Al2O3 catalyst.

4. EXPERIMENTAL SECTION

In this study, Ni/Al2O3, Pt/Al2O3, and Pt−Ni/Al2O3 catalysts were prepared using weteness incipient impregnation. The preparation procedure and characterization of the catalyst were described in detail in the previous studies.55,56 A schematic diagram of the experimental setup is shown in Figure S1. Details regarding the reaction temperature control, flow rate regulation, and test procedure were also described in the previous studies.45,46 Before the reaction tests, the in situ catalyst reduction was carried out at a temperature determined by the H2-TPR test for 2 h in 50% H2/N2 at a flow rate of 50 mL/min. The activity test was performed from 600 to 800 °C. The total reactant volume flow was fixed at 50 sccm to focus on the catalyst and reactant composition effect. As indicated in Table S2, the CH4 flow rate is taken as the reference flow rate. The CH4/CO2 ratio is varied from 0.25 to 1 for simulating the biogas composition while N2 serves as the balance inert gas. For the H2O addition cases, the amount of H2O added is equal to that of CH4.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b01784.

Table S1, catalysts prepared and tested in this study; Table S2, reactant composition used for test; Figure S1, experimental setup (PDF)

AUTHOR INFORMATION

*E-mail: rychein@dragon.nchu.edu.tw. Tel: +886-4-22840433 ext 307. Fax: +886-4-22877170.

ORCID

Reiyu Chein: 0000-0003-3101-9970

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from Ministry of Science and Technology of Taiwan (MOST 106-2221-E-005-073-MY3) is acknowledged.

REFERENCES

(1) Scarlat, N.; Dallemagne, J.-F.; Fahl, F. Biogas: Developments and perspectives in Europe. Renewable Energy 2018, 129, 457−472.
(2) Sarker, S.; Lamb, J. J.; Hjelme, D. R.; Lien, K. M. Overview of recent progress towards in-situ biogas upgradation techniques. Fuel 2018, 226, 686−697.
(3) Chein, R. Y.; Chen, Y. C.; Yu, C. T.; Chung, J. N. Thermodynamic analysis of dry reforming of CH4 with CO2 at high pressures. J. Nat. Gas Sci. Eng. 2015, 26, 617−629.
(4) Nikoo, M. K.; Amin, N. A. S. Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation. Fuel Process. Technol. 2011, 92, 678−691.
(5) Dry, M. E. High quality diesel via the Fischer-Tropsch process - a review. J. Chem. Technol. Biotechnol. 2001, 77, 43−50.
(6) Hernández, B.; Martín, M. Optimal process operation for biogas reforming to methanol: Effects of dry reforming and biogas composition. Ind. Eng. Chem. Res. 2016, 55, 6677−6685.
(7) Amin, A. M.; Croiset, E.; Epling, W. Review of methane catalytic cracking for hydrogen production. Int. J. Hydrogen Energy 2011, 36, 2904−2935.
(8) Lahijani, P.; Zainal, Z. A.; Mohammadi, M.; Mohamed, A. R. Conversion of the greenhouse gas CO2 to the fuel gas CO via the Boudouard reaction: a review. Renewable Sustainable Energy Rev. 2015, 41, 615−632.
(9) Lavoie, J.-M. Review on dry reforming of methane, a potentially more environmentally-friendly approach to the increasing natural gas exploitation. Front. Chem. 2014, 2, 81.
(10) Usman, M.; Wan Daud, W. M. A.; Abbas, H. F. Dry reforming of methane: Influence of process parameters—A review. Renewable Sustainable Energy Rev. 2015, 45, 710−744.
(11) Aramouni, N. A. K.; Touma, J. G.; Tarbouch, B. A.; Zeaiter, J.; Ahmad, M. N. Catalyst design for dry reforming of methane: Analysis review. Renewable Sustainable Energy Rev. 2018, 82, 2570−2585.
(12) Fan, M. S.; Abdullah, A. Z.; Bhatia, S. Catalytic technology for carbon dioxide reforming of methane to synthesis gas. ChemCatChem 2009, 1, 192−208.
(13) 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, 3565–3575.

(14) Ito, M.; Tagawa, T.; Goto, S. Suppression of carbonaceous depositions on nickel catalyst for the carbon dioxide reforming of methane. Appl. Catal., A 1999, 177, 15–23.

(15) Bartholomew, C. H. Carbon deposition in steam reforming and methanation. Catal. Rev.: Sci. Eng. 2007, 49, 67–112.

(16) Abdullah, B.; Ghani, N. A. A.; Vo, D.-V. N. Recent advances in dry reforming of methane over Ni-based catalysts. J. Cleaner Prod. 2017, 162, 170–185.

(17) Li, Z.; Wang, Z.; Kawi, S. Sintering and coke resistant core–shell catalyst for hydrocarbon reforming. ChemCatChem 2018, 11, 202–224.

(18) Li, Z.; Li, M.; Bian, Z.; Kathiraser, Y.; Kawi, S. Design of highly stable and selective core–shell nanocatalysts—a review. Appl. Catal., B 2016, 188, 324–341.

(19) De, S.; Ashok, J.; Bian, Z.; Dewangan, N.; Wai, M. H.; Du, Y.; Borgna, A.; Hidajat, K.; Kawi, S. Silica-Ceria sandwiched Ni-Fe catalyst for low temperature dry reforming of biogas: coke resistance and mechanistic insights. Appl. Catal., B 2018, 230, 220–236.

(20) Tang, M.; Xu, L.; Fan, M. Effect of Ce on 5 wt% Ni/ZSM-5 structure derived Ni-SiO2-MgO catalysts for bi-reforming applications: acidity, basicity and thermal stability. Catal. Soc. Technol. 2018, 8, 1730–1742.

(21) Clo, A.; Basset, J.-M. Controlled surface segregation leads to efficient Pt/Ni catalysts synthesized by atomic layer deposition. ACS Omega 2019, 4, 20911–20922.

(22) Koo, K. Y.; Roh, H. S.; Jung, U. H.; Yoon, W. L. Combined H2O and CO2 reforming of CH4 over Ce-promoted Ni/Al2O3 catalyst for gas to liquid (GTL) process: Enhancement of Ni–CeO2 interaction. Catal. Today 2012, 185, 126–133.

(23) Foreman, A. L.; Vaidya, P. D.; Sinha, R.; Chugh, P. On the dry and mixed reforming of methane over Ni/Al2O3. Influence of reaction variables on syngas production. Int. J. Hydrogen Energy 2016, 41, 22963–22975.

(24) Ashok, J.; Bian, Z.; Wang, Z.; Kawi, S. Ni-phyllosilicate structure derived Ni-SiO2-MgO catalysts for bi-reforming applications: acidity, basicity and thermal stability. Catal. Soc. Technol. 2018, 8, 1730–1742.

(25) Ettre, L. S. IUPAC-International Union of Pure and Applied Chemistry. Pure and Applied Chemistry 1993, 65, 819.

(26) Wang, T.; Porosoff, M. D.; Chen, J. G. Effects of oxide supports on the water-gas shift reaction over Pt-Ni bimetallic catalysts. Catal. Today 2014, 233, 61–69.

(27) Chen, J.; Wang, R.; Zhang, J.; He, F.; Han, S. Effects of preparation methods on properties of Ni/Co/Al2O3 catalysts for methanol synthesis via direct reforming of CO and H2O mixture. J. Catal. 2018, 359, 335–345.

(28) García-Diéguez, M.; Pieta, I. S.; Herrera, M. C.; Larrubia, M. A.; Alemany, L. J. Improved Pt-Ni nano catalysts for dry reforming of methane over Ni/Al2O3 catalyst: Effect of Pt/Ni Ratio. Chem. Eng. J. 2013, 215–216, 542–549.

(29) Ahmed, S.; Lee, S. H. D.; Ferrandon, M. S. Catalytic steam reforming of biogas-Effects of feed composition and operating conditions. Int. J. Hydrogen Energy 2015, 40, 1005–1015.
(51) Figueredo, G. P.; Medeiros, R. L. B. A.; Macedo, H. P.; de Oliveira, A. A. S.; Braga, R. M.; Mercury, J. M. R.; Melo, M. A. F.; Melo, D. M. A. A comparative study of dry reforming of methane over nickel catalysts supported on perovskite-type LaAlO$_3$ and commercial $\alpha$-Al$_2$O$_3$. *Int. J. Hydrogen Energy* 2018, 43, 11022−11037.

(52) Xu, J.; Froment, G. F. Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics. *AIChE J.* 1989, 35, 88−96.

(53) Chein, R. Y.; Hsu, W. H.; Yu, C. T. Parametric study of catalytic dry reforming of methane for syngas production at elevated pressures. *Int. J. Hydrogen Energy* 2017, 42, 14485−14500.

(54) Li, Z.; Mo, L.; Kathiraser, Y.; Kawi, S. Yolk−Satellite−Shell Structured Ni−Yolk@Ni@SiO$_2$ Nanocomposite: Superb Catalyst toward Methane CO$_2$ Reforming Reaction. *ACS Catal.* 2014, 4, 1526−1536.