Influence of Ni on Fe and Co-Fe Based Catalysts for High-Calorific Synthetic Natural Gas

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Abstract: Fe-Ni and Co-Fe-Ni catalysts were prepared by the wet impregnation method for the production of high-calorific synthetic natural gas. The influence of Ni addition to Fe and Co-Fe catalyst structure and catalytic performance was investigated. The results show that the increasing of Ni amount in Fe-Ni and Co-Fe-Ni catalysts increased the formation of Ni-Fe alloy. In addition, the addition of nickel to the Fe and Co-Fe catalysts could promote the dispersion of metal and decrease the reduction temperature. Consequently, the Fe-Ni and Co-Fe-Ni catalysts exhibited higher CO conversion compared to Fe and Co-Fe catalysts. A higher Ni amount in the catalysts could increase C1−C4 hydrocarbon production and reduce the byproducts (C4+ and CO2). Among the catalysts, the 5Co-15Fe-5Ni/γ-Al2O3 catalyst affords a high light hydrocarbon yield (51.7% CH4 and 21.8% C2−C4) with a low byproduct yield (14.1% C5+ and 12.1% CO2).

Keywords: high-calorific synthetic natural gas (HC-SNG); iron-based catalyst; nickel promoter; Ni-Fe alloy

1. Introduction

In the past decades, energy consumption has grown rapidly because of population growth. Fossil fuels such as coal, petroleum, and natural gas are the main energy sources. However, the increasing consumption of fossil fuels leads to the emission of greenhouse gases, particularly carbon dioxide (CO2), which contribute to global warming. Synthetic natural gas (SNG; CO + 3H2 = CH4 + H2O) production from biomass has been considered a substitute for fossil fuels, due to its high energy density and low greenhouse gas emission. In addition, it can be transported efficiently using existing and widely distributed gas pipelines [1–5]. The conventional SNG process mainly produces CH4, which has a heating value of 9520 kcal/Nm3. This has a problem that the heating value is lower than the standard heating value (10,400 kcal/Nm3) for power generation in South Korea and Japan. Therefore, new pathways for high-calorific synthetic natural gas (HC-SNG) production have been intensively studied, and C2−C4 as well as CH4 have been produced using the Fischer−Tropsch (FT) reaction [6–15]. Generally, for CO methanation reactions, Ni-based catalysts are attractive due to their low cost and high activity [3–5]. However, Ni-based catalysts are not suitable for producing C2−C4 due to high selectivity to CH4. Inui et al. published the paper on the conversion of coke oven gas into HC-SNG using Co-based catalysts. The Co-Mn-Ru/Al2O3 catalysts showed high CO conversion (98.8%) and C2−C4...
selectivity (19.1%) [6]. Lee et al. studied the effect of each component in the Co-Mn-Ru/Al2O3 catalyst, the optimum composition of catalysts was proposed [7]. Despite its C2–C4 selectivity, Co-based catalysts have limitations when it comes to the standard heating value.

Currently, among VIII metals, Fe-based catalysts in the production of HC-SNG produced higher selectivity of light hydrocarbon (C2–C4), compared with Co-based catalysts [8–13]. However, the monometallic Fe catalysts have low activity of CO hydrogenation and production of hydrocarbons with low paraffin-to-olefin ratio due to low hydrogenation ability. The carburized Fe-Zn catalysts have been reported to exhibit high CO conversion with higher C2–C4 hydrocarbon selectivities [8]. Zn has been reported to possess hydrogen spillover ability, which increases CO hydrogenation. Iron carbides showed a stronger interaction with CO than iron oxide, which enhanced the CO conversion. In our previous report, we studied bimetallic Co-Fe catalysts with different Co/Fe ratios to compare the activity of CO hydrogenation and hydrocarbon selectivity [11]. We found that the monometallic Fe catalyst displayed lower CO conversion and higher C2–C4 selectivity, compared with the Co catalyst, whereas the 5Co-15Fe catalyst showed a relatively higher CO conversion and similar selectivity compared to the Fe catalyst. This is because the presence of cobalt enhanced the reducibility of the iron phase, leading to improved catalytic activity. In addition, the effect of reaction conditions such as H2/CO ratio, temperature, pressure, and space velocity on catalytic behavior was investigated [13]. At H2/CO of 3.0, the space velocity of 4000 mL/g/h, 20 bar, and 300 °C, the bimetallic Co-Fe catalyst affords a high light hydrocarbon yield (31.2% CH4, and 36.1% C2–C4) with a high paraffin ratio (0.90). Despite the high C2–C4 yield, C1–C4 hydrocarbon production decreased due to a considerable amount of byproducts (C5+, hydrocarbons and CO2). In our previous publication, hybrid catalysts (FT + cracking) in a double-layered bed reactor system were examined to reduce C5+ and CO2 [12]. The cracking catalysts (SAPO-34 zeolite and Ni catalysts) were loaded below the FT catalyst layer. It could be seen that SAPO-34 and Ni affect the cracking of C5+ hydrocarbons into light hydrocarbons (C1–C4). In addition, the Ni catalyst improved CO conversion and reduced CO2 selectivity via methanation. However, further research is needed to apply a double-layered bed system at a pilot scale.

In this study, Fe-Ni and Co-Fe-Ni catalysts were applied to the production of HC-SNG with low byproduct formation (C5+, and CO2). The catalysts were prepared by the impregnation of alumina with iron, cobalt, and nickel nitrate. The objective of this work is to investigate the influence of nickel on the Fe and Co-Fe catalysts. Particular attention is focused on the influence of nickel on the textural properties, reduction, and metal phase of the catalysts at different Ni amounts. The catalysts were characterized by inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray diffraction (XRD), and H2-temperature-programmed reduction (H2-TPR), and catalytic performance was discussed based on characterization results.

2. Results and Discussion
2.1. Influence of Ni on Fe Catalyst

The XRD patterns of the (a) calcined and (b) reduced monometallic and bimetallic catalysts are presented in Figure 1. The XRD patterns of calcined 20Fe/γ-Al2O3 and 20Ni/γ-Al2O3 catalysts confirm that Fe is present as Fe2O3 phase (JCPDS 52–1449) and Ni as NiO phase (JCPDS 65–6920), respectively. For the 20Fe/γ-Al2O3 catalyst, the XRD peaks of Fe2O3 were too broad due to the high dispersion of iron over the support [16,17]. With an increase in Ni in Fe catalysts, peaks of NiO gradually increased and an additional peak was observed at 43.7° corresponding to the formation of NiFe2O4 (JCPDS 89–4927). However, no peaks of Fe2O3 were observed in Fe-Ni/γ-Al2O3 catalysts. For the 15Fe-5Ni/γ-Al2O3 catalyst, low intensity of both Fe and Ni oxide was observed compared to the 20Fe/γ-Al2O3 catalyst, indicating better dispersion of Ni over the Fe catalyst [18–24]. Alternatively, for the 10Fe-10Ni/γ-Al2O3 catalyst, peaks of NiFe2O4 were observed, suggesting that a higher Ni ratio increases the interaction between Fe and Ni [18,20]. For reduced catalysts,
the 20Fe/γ-Al2O3 showed the Fe3O4 and Fe metal phases, whereas the 20Ni/γ-Al2O3 showed the NiO and Ni metal phases, indicating that both catalysts cannot be completely reduced under reduction conditions. With an increase in Ni in Fe catalysts, peaks of Fe metal gradually decreased and the peaks of NiFe2O4 and Ni3Fe2 alloy were observed. The 15Fe-5Ni/γ-Al2O3 catalyst showed the coexistence of the Fe and Ni3Fe2 phase. Then, the 10Fe-10Ni/γ-Al2O3 catalyst showed no peaks of Fe metal. It can be concluded that the increase of Ni/Fe ratio in the Fe-Ni/γ-Al2O3 catalyst leads to the formation of the alloyed metallic phase. The crystallite sizes of Fe, Ni, or Ni-Fe alloy of reduced catalysts were calculated using the Scherrer equation and the results are listed in Table 1. The crystallite sizes for Ni, Fe, or Ni-Fe alloy in catalysts changed with the composition of the Ni/Fe. Interestingly, the crystallite sizes of the metal in bimetallic catalysts exhibit a smaller size than monometallic catalysts. In particular, the 20Ni/γ-Al2O3 catalyst showed a larger particle size after reduction due to weak interaction with Ni-Al, whereas Ni-Fe catalysts showed a small particle size [25]. It is known that metal dispersion was higher and the synergy effects between Ni and Fe by forming NiFe2O4 were stronger on γ-Al2O3 [20]. Thus, the addition of Ni to the Fe/γ-Al2O3 catalyst seems to increase the metal dispersion.

![XRD patterns](image)

Figure 1. XRD patterns of the (a) calcined and (b) reduced Ni, Fe, and Fe-Ni catalysts; (γ) γ-Al2O3, (∧) Fe2O3, (■) Fe3O4, (□) Fe metal, (●) NiO, (○) Ni metal, (▲) NiFe2O4, and (△) Ni-Fe alloy.

| Catalyst    | Metal Content (wt.%) | Crystallite Size (nm) |
|-------------|----------------------|-----------------------|
|             | Co  | Fe  | Ni  | Co  | Fe  | Ni3Fe2 | Ni  |
| 20Fe        | -   | 20.2| -   | -   | 34.5| -      | -   |
| 15Fe-5Ni    | -   | 14.7| 4.8 | -   | 22.6| 7.8    | -   |
| 10Fe-10Ni   | -   | 10.2| 9.9 | -   | -   | 9.6    | -   |
| 20Ni        | -   | -   | 19.8| -   | -   | -      | -   |
| 5Co-15Fe    | 5.2 | 14.1| -   | N/A | 20.2| -      | -   |
| 5Co-15Fe-2Ni| 5.1 | 14.8| 2.2 | N/A | 20.3| -      | -   |
| 5Co-15Fe-5Ni| 4.9 | 14.6| 5.1 | N/A | 8   | 6.3    | -   |

1 Metal content was determined by ICP-OES. 2 Determined from Scherrer’s equation from the reduced catalyst in XRD patterns.

H2-temperature-programmed reduction (H2-TPR) was conducted to investigate the reducibility of monometallic and bimetallic catalysts. Figure 2 showed the TPR profiles of 20 wt.% monometallic catalysts and the 20 wt.% bimetallic catalysts. The 20Fe/γ-Al2O3
exhibited a broad peak of two contributions (~400 °C and ~650 °C), representing the presence of different iron species. The peak at 400 °C can be assigned to the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$, and the reduction peak at 650 °C corresponds to the reduction of Fe$_3$O$_4$ to Fe metal. The 20Ni/γ-Al$_2$O$_3$ showed two peaks; the low-temperature peaks at 300 °C–380 °C were attributed to the reduction of NiO, high-temperature peaks at 480 °C–600 °C were attributed to the reduction of NiO species, corresponding to the interaction between NiO and Al$_2$O$_3$. The bimetallic Fe-Ni catalysts showed three reduction peaks. The first temperature at 340 °C may be attributed to the reduction of Fe$_3$O$_4$ to Fe and NiFe$_2$O$_4$ to Fe and Ni [20,21]. In addition, the reduction peaks of the bimetallic catalysts shift to lower temperature with increasing nickel-to-iron ratio, compared with Fe catalyst. This suggests that the addition of Ni improves the reducibility.

Table 1. Characterization of the catalysts.

| Catalyst | Metal | Crystallite Size (nm) | Intensity (a.u.) | Theta 20 | Theta 25 | Theta 28 |
|----------|-------|-----------------------|------------------|----------|----------|----------|
| 20Fe     |       |                       |                  |          |          |          |
| 15Fe-5Ni |       |                       |                  |          |          |          |
| 10Fe-10Ni|       |                       |                  |          |          |          |
| 20Ni     |       |                       |                  |          |          |          |

Figure 2. H$_2$-TPR profiles of Ni, Fe, and Fe-Ni catalysts.

The catalytic behavior of Fe-Ni/γ-Al$_2$O$_3$ catalysts with different Ni/Fe ratios was observed under the conditions of 300 °C, 10 bar, H$_2$/CO = 3.0, and 6000 mL/g/h (Figure 3 and Table S1). The CO conversion was much lower with 20Fe/γ-Al$_2$O$_3$ compared with the value obtained for 20Ni/γ-Al$_2$O$_3$. Ni shows high catalytic activity for CO hydrogenation among transition metals. With increasing Ni in Fe catalysts, the bimetallic catalysts present a higher CO conversion (99.9%) compared to Fe catalysts. It was reported that Fe-Ni bimetallic catalysts not only showed a high metal dispersion but also improved reducibility [18–24]. This confirms that the addition of Ni to Fe catalysts could facilitate higher dispersion and enhance the reducibility (Table 1 and Figure 2). In addition, the 20Ni/γ-Al$_2$O$_3$ catalyst showed lower CO conversion (91.5%) compared to Fe-Ni catalysts. This drawback of the CO conversion may be in agreement with the low Ni dispersion. The selectivity to hydrocarbon and CO$_2$ is affected by the Ni/Fe ratio. Generally, Ni catalysts exhibited high CH$_4$ selectivity (>90%) with low selectivity of C$_2$ when CO$_2$ under methanation conditions (H$_2$/CO ratio = 3.0 °C and 300 °C). However, the 20Ni/γ-Al$_2$O$_3$ catalyst showed selectivity of CH$_4$ (77.1%), C$_2$–C$_4$ (8.6%), C$_5$+ (9.4%), and CO$_2$ (4.9%) due to the lower Ni dispersion. It has been reported that high dispersion of Ni exhibited the highest CH$_4$ selectivity, whereas low dispersion of Ni showed selectivity of C$_2$–C$_4$ [26,27]. The 20Fe/γ-Al$_2$O$_3$ catalyst, by contrast, showed high selectivity of C$_2$–C$_4$, C$_5$+, and CO$_2$. Fe metal has more of a long-chain growth ability than Ni metal due to the stronger adsorption of CO in Fe. Moreover, Fe-based catalysts have significant activity in the water gas shift reaction. With increasing Ni in Fe catalysts, there was a remarkable change in selectivity. For the 15Fe-5Ni/γ-Al$_2$O$_3$, the selectivity to CH$_4$ significantly increased from 21.8% to
65.1%, whereas the selectivity to C₂–C₄, C₅₊, and CO₂ significantly reduced from 26.6% to 15.4%, from 26.2% to 4.8%, and 25.4% to 14.7%, respectively, compared to the 20Fe/γ-Al₂O₃ catalyst. Interestingly, the 10Fe-10Ni/γ-Al₂O₃ catalyst almost showed selectivity to CH₄ (96.6%). It might be due to the defect in the Fe metal phase with increasing Ni, resulting in XRD of 10Fe-10Ni/γ-Al₂O₃ showed Ni-Fe alloy phase, which has a much higher methanation reaction than Fe metal [22]. Thus, it could be concluded that the addition of Ni to Fe catalysts changes the metal phase, which not only enhances the CO hydrogenation but also significantly affects selectivity to hydrocarbon and CO₂. Among the catalysts, the 15Fe-5Ni/γ-Al₂O₃ catalyst displayed a high CO conversion and low byproduct formation (C₅₊ and CO₂), but the addition of Ni also decreased the selectivity of C₂–C₄, indicating that is not enough for HC-SNG. In our previous work, 5Co-15Fe/γ-Al₂O₃ catalysts showed high C₂–C₄ selectivity at high CO conversions, but this led to substantial byproducts (C₅₊ and CO₂). Therefore, the effect of Ni on the suppression of byproducts for the 5Co-15Fe/γ-Al₂O₃ catalyst needs to be investigated further.

![Figure 3. CO conversion and product selectivity in the Ni, Fe, and Fe-Ni catalysts.](image)

2.2. Influence of Ni on Co-Fe Catalyst

The XRD patterns of Co-Fe and Co-Fe-Ni catalysts in the calcined and reduced states are shown in Figure 4. The calcined Co-Fe catalyst showed very broad peaks of the Fe₂O₃ phase compared to those of the Co₃O₄ phase because of the high dispersion of the iron phase over alumina [11]. With increasing Ni in Co-Fe catalysts, the additional diffraction peaks of NiFe₂O₄ and NiCo₂O₄ were confirmed. However, for the Co-Fe-Ni catalysts, peaks of Fe₂O₃ and Co₃O₄ were difficult to distinguish. In the case of the reduced state, the Co-Fe catalyst showed XRD peaks of CoO and Fe metal, indicating the incorporation of Co into Fe [11,16,17]. With an increase in Ni in Co-Fe catalysts, additional peaks of NiFe₂O₄ and Ni-Fe alloy were observed. However, for trimetallic catalysts, distinguishing CoO from NiFe₂O₄ is difficult due to the very close resemblance in diffraction patterns. With the increasing Ni content, the diffraction peaks corresponding to Ni-Fe alloys gradually increased, while peaks of the Fe phase decreased due to the different compositions of the metal alloys. The 5Co-15Fe-2Ni catalyst showed a very broad Ni-Fe alloy peak at 43.7°. For the 5Co-15Fe-5Ni catalyst, the diffraction peaks of the Ni-Fe alloy were more clearly observed compared to the 5Co-15Fe-2Ni catalyst. In addition, for the 5Co-15Fe-
5Ni/γ-Al2O3 catalyst, smaller crystallite sites of Fe metal were observed compared with 5Co-15Fe-2Ni/γ-Al2O3, implying that the increasing Ni amount improves the dispersion (Table 1). The H2-TPR profiles of the addition of Ni to the Co-Fe catalyst (5Co-15Fe, 5Co-15Fe-2Ni, and 5Co-15Fe-5Ni) are shown in Figure S1. In our previous work, we showed that for 5Co-15Fe catalysts, the first temperature peak (at 300 °C−400 °C) was assigned to the reduction of Co3O4 to CoO and Fe2O3 to Fe3O4 and the second peak (at 400 °C−700 °C) may be ascribed to the sequential reduction of CoO to Co and Fe3O4 to Fe [11]. A comparison of the results for the Co-Fe catalyst and Co-Fe-Ni catalysts shows that, in the case of Co-Fe-Ni, the second peak was shifted to lower temperatures. This might be attributed to chemically interacting species such as NiFe2O4 and NiCo2O4 due to the strong mutual effect of metal [28].

Figure 4. XRD patterns of the (a) calcined and (b) reduced Co-Fe and Co-Fe-Ni catalysts; (γ) γ-Al2O3, (○) Fe2O3, (□) Fe metal, (●) Co3O4, (▽) CoO, (▽) NiCo2O4, (▲) NiFe2O4, and (△) Ni-Fe alloy.

To further study the effect of Ni on the Co-Fe catalysts, we tested the catalytic performance of Co-Fe and Co-Fe-Ni, and the results are shown in Figure 5. There is no drastic change during the experiment as shown in Figure S2. It was found that the addition of Ni to Co-Fe catalysts increased CO conversion from 91.5% to 99.9%. This is because the presence of Ni in catalysts not only leads to high activity for CO hydrogenation but also enhances the reducibility. With increasing nickel content, for the 5Co-15Fe-2Ni/γ-Al2O3 catalyst, the selectivity to CH4 increased from 23.5% to 38.9%, and the selectivity to C2–C4 and C5+ decreased from 28.2% to 22.3% and from 26.0% to 15.1%, respectively, compared to 5Co-15Fe/γ-Al2O3 catalyst. However, the selectivity to CO2 presents a similar value between 22.3–23.6%, indicating that a small Ni amount in Co-Fe catalysts only affects hydrocarbon selectivity. Alternatively, for the 5Co-15Fe-5Ni/γ-Al2O3 catalyst, the selectivity to CH4 significantly increased to 51.9% with a decrease of CO2 selectivity without changing the selectivity to C2–C4 and C5+. As mentioned above, increasing the Ni amount in Fe catalysts affects the interaction between Fe and Ni resulting in the Ni-Fe alloy phase, which indicates a high methanation reaction. As shown in Figure 5, it could be confirmed that the 5Co-15Fe-2Ni/γ-Al2O3 catalyst showed no significant change in metal phase compared to 5Co-15Fe/γ-Al2O3. However, 5Co-15Fe-5Ni/γ-Al2O3 showed coexistence of Fe and Ni-Fe alloy, resulting in the high selectivity of light hydrocarbon (C1–C4), and low byproduct formation (C5+ and CO2).
Figure 5. CO conversion and product selectivity in the Fe-Co and Fe-Co-Ni catalysts.

Table 2 shows the comparison of the catalytic performance of Co-Fe-Ni catalysts with that of the 5Co-15Fe/γ-Al2O3 catalyst. In a previous report, the 5Co-15Fe/γ-Al2O3 catalyst was studied for the effects of operating conditions such as space velocity, reaction pressure, and temperature. The 5Co-15Fe/γ-Al2O3 catalyst showed high CO conversion (99.7%), high light hydrocarbon yield (31.2% CH₄ and 36.1% C₂–C₄), and low byproduct yield (17.6% C₅+ and 14.9% CO₂) under certain conditions (SV: 4000 mL/g/h, T: 350 °C and P: 20 bar), compared to reaction conditions of SV: 6000 mL/g/h, T: 300 °C and P: 10 bar). In terms of C₁–C₄ yield, it increased with the increase in CO conversion under certain conditions (SV: 4000 mL/g/h, T: 350 °C and P: 20 bar), whereas C₁–C₄ hydrocarbon production rate in these conditions decreased compared to that under reaction conditions (SV: 6000 mL/g/h, T: 300 °C and P: 10 bar) due to low space velocity. On the other hand, the Co-Fe-Ni catalysts were superior to the Co-Fe catalyst under reaction conditions (SV: 6000 mL/g/h, T: 300 °C and P: 10 bar), in regard to the C₁–C₄ hydrocarbon production rate due to the fact that the increase in C₁–C₄ production with increasing CO conversion can mainly be attributed to decrease of byproducts. In particular, the 5Co-15Fe-5Ni catalyst produced the highest C₁–C₄ hydrocarbon production rate (530 mL/h) compared to other catalysts. In addition, the heating value of the product gas of 5Co-15Fe-5Ni catalyst is higher than the heating value of the product gas of 5Co-15Fe catalyst.

Table 2. Summary of catalytic performance of the Co-Fe and Co-Fe-Ni catalysts at a reaction time of 10 h.

| Catalyst | Reaction Condition | CO Conv (%) | Yield (%) | C₁–C₄ Hydrocarbon Production Rate (mL/h) | Heating Value (kcal/Nm³)¹ | Ref |
|----------|--------------------|-------------|-----------|-----------------------------------------|--------------------------|-----|
| 5Co-15Fe | SV: 4000 mL/g/h, 700 °C, 10 bar | 91.5 ± 1.0 | 21.5 ± 0.7 | 25.8 ± 0.6 | 23.8 ± 1.6 | 20.4 ± 0.4 | 341 | 15,230 | [13] |
| 5Co-15Fe | SV: 4000 mL/g/h, 350 °C, 20 bar | 99.7 ± 0.1 | 31.2 ± 0.4 | 36.1 ± 0.6 | 17.6 ± 0.4 | 14.9 ± 0.2 | 323 | 13,170 | [13] |
| 5Co-15Fe-2Ni | SV: 4000 mL/g/h, 700 °C, 10 bar | 98.5 ± 0.2 | 36.2 ± 0.2 | 21.9 ± 0.6 | 14.8 ± 0.7 | 23.2 ± 0.2 | 433 | 11,980 | This study |
| 5Co-15Fe-5Ni | SV: 4000 mL/g/h, 300 °C, 10 bar | 99.9 ± 0.1 | 51.7 ± 0.1 | 21.8 ± 0.2 | 14.1 ± 0.3 | 12.1 ± 0.2 | 530 | 11,580 | This study |

¹ The heating value of each product gas was determined from the volumetric hydrocarbon fraction by calculating the heating values of the pure gases in the C₁–C₄ hydrocarbon range in the outlet gas.
3. Materials and Methods

3.1. Catalysts Preparation

The catalysts were prepared using the wet impregnation method. The Ni-Fe/γ-Al₂O₃ and Ni-Co-Fe/γ-Al₂O₃ catalysts were prepared by impregnating γ-Al₂O₃ with an anhydrous ethanol solution of Ni(NO₃)₂·6H₂O, cobalt nitrate Co(NO₃)₂·6H₂O, and Fe(NO₃)₃·9H₂O (Sigma-Aldrich, St. Louis, MO, USA) for 24 h at room temperature. Then, the solvent was removed using a rotary evaporator at 40 °C. The samples were dried at 120 °C for 12 h and calcined at 400 °C for 8 h in air. The Ni-Fe and Ni-Co-Fe catalysts supported by γ-alumina were denoted by xFe-yNi/γ-Al₂O₃ and xCo-yFe-zNi/γ-Al₂O₃, where x, y, and z represent the weight percentage of each metal based on the catalyst.

3.2. Characterization

The metal content of the catalysts was measured with ICP-OES (PerkinElmer, Waltham, MA, USA). The crystal structures of the bimetallic and trimetallic catalysts were analyzed using a Cu Kα radiation source (λ = 1.5406 Å) in a Phillips XPERTXRD (PANalytical, Amsterdam, Netherlands) located at the Korea Basic Science Institute in Daegu. The crystallite size of the metal phase was calculated using the Scherrer equation, which is shown in Equation (1) [8].

\[
t = \frac{K \gamma}{B \cos \theta}
\]

\[t = \text{the mean size of the crystalline domains (nm)}
\]
\[K = \text{dimensionless shape factor (}= 0.9)
\]
\[k = \text{wavelength of X-ray (Cu Kα1, 0.15406 nm)}
\]
\[B = \text{full width at half maximum in radians}
\]
\[h = \text{Bragg angle}
\]

H₂-Temperature-programmed reduction (H₂-TPR) was performed by heating the reactor from 120 to 900 °C at a rate of 5 °C/min under 10% H₂/N₂ (100mL/min) after pretreating the sample (0.2 g) at 150 °C under N₂ flow for 1 h.

3.3. Activity Tests

The activity test was conducted in a fixed-bed reactor (O.D. 1/2 in). In a typical experiment, 0.5 g of catalyst (150–250 µm) was initially pre-reduced for 1 h at 500 °C under 10% H₂/N₂ (100 mL/min) flow before each test. Then, cooling down to 200 °C under N₂ gas, the gas was switched to 72% H₂, 24% CO, and 4% N₂ mixture gas with a total volumetric flow of 50 mL/min at standard temperature and pressure. The reactor was pressurized to 10 bar, using a back-pressure regulator. Subsequently, the temperature of the reactor was increased to 300 °C at a heating rate of 10 °C/min. To avoid possible condensation of the reaction products, the gas transfer lines were maintained at temperatures above 180 °C, and the heavy hydrocarbons were collected in a cold trap (4 °C) before analyzing the outlet gases online using a gas chromatograph (Agilent 6890, Santa Clara, CA, USA). The CO, H₂, N₂, and CO₂ gases were analyzed using a Carboxen 1000 column (Supelco, Bellefonte, PA, USA) with a thermal conductivity detector and a GS-GASPRO capillary column (Agilent, Santa Clara, CA, USA) connected with a flame ionization detector for analysis of the hydrocarbons. The CO conversion and selectivity for each product were calculated using Equations (2)–(4).

\[
\text{CO conversion (carbon mole %)} = \left(1 - \frac{\text{CO in the product gas (mol/min)}}{\text{CO in the feed gas (mol/min)}}\right) \times 100,
\]

\[
\text{Selectivity for hydrocarbons with carbon number n (carbon mole %)} = \frac{n \times C_n \text{ hydrocarbon in the product gas (mol/min)}}{(\text{total carbon-unreacted CO}) \text{ in the product gas (mol/min)}} \times 100,
\]
Selectivity for carbon dioxide (carbon mole %) = 
\[
\frac{\text{CO}_2 \text{ in the product gas (mol/min)}}{\text{total carbon-unreacted } \text{CO}_2 \text{ in the product gas (mol/min)}}.
\]

4. Conclusions

In this study, bimetallic Fe-Ni and trimetallic Co-Fe-Ni catalysts supported by γ-alumina were developed for the production of HC-SNG with low byproduct formation (C_{5+} and CO_2). It was found that the metal dispersion and reducibility were enhanced in the presence of nickel, leading to improved catalytic activity. CH_4 selectivity increases and C_2+ and CO_2 selectivity decrease with increasing Ni amount in catalysts. In addition, high CH_4 selectivity and low CO_2 selectivity with a higher Ni amount imply that the Ni-Fe alloy is favorable for methanation reaction. The presence of Ni in catalysts diminished the byproduct yield (C_{5+} and CO_2), whereas the heating value of the product gas decreased due to higher CH_4 yield. Based on these results, the 5Co-15Fe-5Ni catalyst affords a high light hydrocarbon yield (51.7% CH_4, and 21.8% C_2–C_4) with low byproduct yield (14.1% C_{5+} and 12.1% CO_2), compared to bimetallic Fe-Ni catalysts. In addition, it exhibited the highest C_1–C_4 hydrocarbon production rate (530 mL/h) with a higher heating value than the standard heating value (10,400 kcal/Nm^3). Thus, trimetallic Co-Fe-Ni catalysts can be used for the production of HC-SNG.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11060697/s1, Table S1: CO conversion and selectivity with Fe-Ni and Co-Fe-Ni catalysts at a reaction time of 10 h., Figure S1: H_2-TPR profiles of the Co-Fe and Co-Fe-Ni catalysts. Figure S2: The CO conversion and hydrocarbon selectivity over Co-Fe and Co-Fe-Ni catalysts (a–c) as a function of time on stream.

Author Contributions: T.-Y.K. designed the experiments; S.-C.L. and J.-C.K. supervised the entire study; T.-Y.K. performed the experiments and wrote the manuscript; S.J., Y.L., S.-H.K. and J.-W.K. contributed to scientific discussions. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author. Data are contained within the article or supplementary material.

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

References
1. Davis, S.J.; Caldeira, K.; Matthews, H.D. Future CO_2 emissions and climate change from existing energy infrastructure. Science 2010, 329, 1330–1333. [CrossRef]
2. Kopycinski, J.; Schildhauer, T.J.; Biollaz, S.M. Production of synthetic natural gas (SNG) from coal and dry biomass–A technology review from 1950 to 2009. Fuel 2010, 89, 1763–1783. [CrossRef]
3. Hwang, S.; Lee, J.; Hong, U.G.; Seo, J.G.; Jung, J.C.; Koh, D.J.; Lim, H.; Byun, C.; Song, I.K. Methane production from carbon monoxide and hydrogen over nickel–alumina xerogel catalyst: Effect of nickel content. J. Ind. Eng. Chem. 2011, 17, 154–157. [CrossRef]
4. Gao, J.; Jia, C.; Li, J.; Zhang, M.; Gu, F.; Xu, G.; Zhong, Z.; Su, F. Ni/Al_2O_3 catalysts for CO methanation: Effect of Al_2O_3 supports calcined at different temperatures. J. Energy Chem. 2013, 22, 919–927. [CrossRef]
5. Zhao, B.; Chen, Z.; Chen, Y.; Ma, X. Syngas methanation over Ni/SiO_2 catalyst prepared by ammonia-assisted impregnation. Int. J. Hydrogen Energy 2017, 42, 27073–27083. [CrossRef]
6. Ishigaki, Y.; Uba, M.; Nishida, S.; Inui, T. Application of CoMnxOyRu catalyst to the process for producing high-calorie substitute natural gas from coke oven gas. Appl. Catal. 1989, 47, 197–208. [CrossRef]
7. Lee, Y.H.; Kim, H.; Choi, H.S.; Lee, D.-W.; Lee, K.-Y. Co-Mn-Ru/Al_2O_3 catalyst for the production of high-calorific synthetic natural gas. Korean J. Chem. Eng. 2015, 32, 2220–2226. [CrossRef]
8. Lee, Y.H.; Lee, D.-W.; Kim, H.; Choi, H.S.; Lee, K.-Y. Fe–Zn catalysts for the production of high-calorie synthetic natural gas. *Fuel* 2015, 159, 259–268. [CrossRef]

9. Lee, Y.H.; Lee, D.-W.; Lee, K.-Y. Production of high-calorie synthetic natural gas using copper-impregnated iron catalysts. *J. Mol. Catal. A Chem.* 2016, 425, 190–198. [CrossRef]

10. Lee, Y.H.; Lee, K.-Y. Effect of surface composition of Fe catalyst on the activity for the production of high-calorie synthetic natural gas (SNG). *Korean J. Chem. Eng.* 2017, 34, 320–327. [CrossRef]

11. Jo, S.B.; Chae, H.J.; Kim, T.Y.; Lee, C.H.; Oh, J.U.; Kang, S.-H.; Kim, J.W.; Jeong, M.; Lee, S.C.; Kim, J.C. Selective CO hydrogenation over bimetallic Co-Fe catalysts for the production of light paraffin hydrocarbons (C2–C4): Effect of H2/CO ratio and reaction temperature. *Catal. Commun.* 2018, 117, 74–78. [CrossRef]

12. Jo, S.B.; Kim, T.Y.; Lee, C.H.; Kang, S.-H.; Kim, J.W.; Jeong, M.; Lee, S.C.; Kim, J.C. Hybrid catalysts in a double-layered bed reactor for the production of C2–C3 paraffin hydrocarbons. *Catal. Commun.* 2019, 127, 29–33. [CrossRef]

13. Jo, S.B.; Kim, T.Y.; Lee, C.H.; Woo, J.H.; Chae, H.J.; Kang, S.-H.; Kim, J.W.; Lee, S.C.; Kim, J.C. Selective CO Hydrogenation Over Bimetallic Co-Fe Catalysts for the Production of Light Paraffin Hydrocarbons (C2–C4): Effect of Space Velocity, Reaction Pressure and Temperature. *Catalysts* 2019, 9, 779. [CrossRef]

14. Kim, T.Y.; Jo, S.B.; Lee, C.H.; Kang, S.-H.; Kim, J.W.; Lee, S.C.; Kim, J.C. Effect of reducibility on the performance of Co-based catalysts for the production of high-calorie synthetic natural gas. *Korean J. Chem. Eng.* 2020, 37, 1690–1698. [CrossRef]

15. Kim, T.Y.; Jo, S.B.; Woo, J.H.; Lee, J.H.; Dhanusuraman, R.; Lee, S.C.; Kim, J.C. Investigation of Co–Fe–Al Catalysts for High-Calorific Synthetic Natural Gas Production: Pilot-Scale Synthesis of Catalysts. *Catalysts* 2021, 11, 105. [CrossRef]

16. Lögdberg, S.; Tristantini, D.; Borg, Ø.; Iver, L.; Gevert, B.; Järäs, S.; Blekkan, E.A.; Holmen, A. Hydrocarbon production via Fischer–Tropsch synthesis from H2-poor syngas over different Fe-Co/γ-Al2O3 bimetallic catalysts. *Appl. Catal. B Environ.* 2009, 89, 167–182. [CrossRef]

17. Griboval-Constant, A.; Butel, A.; Ordomsky, V.V.; Chernavskii, P.A.; Khodakov, A. Cobalt and iron species in alumina supported bimetallic catalysts for Fischer–Tropsch reaction. *Appl. Catal. A Gen.* 2014, 481, 116–126. [CrossRef]

18. Kustov, A.; Frey, A.M.; Larsen, K.E.; Johannessen, T.; Nørskov, J.K.; Christensen, C.H. CO methanation over supported bimetallic Ni–Fe catalysts: From computational studies towards catalyst optimization. *Appl. Catal. A Gen.* 2007, 320, 98–104. [CrossRef]

19. Feyzi, M.; Mirzaei, A.A.; Bozorgzadeh, H.R. Effects of preparation and operation conditions on precipitated iron nickel catalysts for Fischer–Tropsch synthesis. *J. Nat. Gas Chem.* 2010, 19, 341–353. [CrossRef]

20. Wang, L.; Li, D.; Koike, M.; Kosu, S.; Nakagawa, Y.; Xu, Y.; Tomishige, K. Catalytic performance and characterization of Ni-Fe catalysts for the steam reforming of tar from biomass pyrolysis to synthesis gas. *Appl. Catal. A Gen.* 2011, 392, 248–255. [CrossRef]

21. Li, T.; Wang, H.; Yang, Y.; Xiang, H.; Li, Y. Study on an iron–nickel bimetallic Fischer–Tropsch synthesis catalyst. *Fuel Process. Technol.* 2014, 118, 117–124. [CrossRef]

22. Cheng, C.; Shen, D.; Xiao, R.; Wu, C. Methanation of syngas (H2/CO) over the different Ni-based catalysts. *Fuel* 2017, 189, 419–427. [CrossRef]

23. Li, Z.; Zhao, T.; Zhang, L. Promotion effect of additive Fe on Al2O3 supported Ni catalyst for CO2 methanation. *Appl. Organomet. Chem.* 2018, 32, e4328. [CrossRef]

24. Liu, Q.; Wang, J.; An, K.; Zhang, S.; Liu, G.; Liu, Y. Highly Dispersed Ni–Fe Alloy Catalysts on MgAl2O4 Derived from Hydroaluminate for Direct Ethanol Synthesis from Syngas. *Energy Technol.* 2020, 8, 2000205. [CrossRef]

25. Liang, B.; Suzuki, T.; Hamamoto, K.; Yamaguchi, T.; Fujiyoshi, Y.; Awano, M.; Ingram, B.J.; Cater, J.D. Effect of the adding ferrum in nickel/GDC anode-supported solid-oxide fuel cell in the intermediate temperature. *Int. J. Hydrogen Energy* 2011, 36, 10975–10980. [CrossRef]

26. Nematomlali, B.; Rezaei, M.; Lay, E.N. Selective methanation of carbon monoxide in hydrogen rich stream over Ni/CeO2 nanocatalysts. *J. Rare Earth* 2015, 33, 619–628. [CrossRef]

27. Meng, F.; Li, X.; Li, M.; Cui, X.; Li, Z. Catalytic performance of CO methanation over La-promoted Ni/Al2O3 catalyst in a slurry-bed reactor. *Chem. Eng. J.* 2017, 313, 1548–1555. [CrossRef]

28. Al-Fatesh, A.; Fakeeha, A.; Khan, W.; Ibrahim, A.; He, S.; Seshan, K. Production of hydrogen by catalytic methane decomposition over alumina supported mono-, bi- and tri-metallic catalysts. *Int. J. Hydrogen Energy* 2016, 41, 22932–22940. [CrossRef]