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The Demonstration of the Superiority of the Dual Ni-Based Catalytic System for the Adjustment of the H₂/CO Ratio in Syngas for Green Fuel Technologies

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Abstract: A novel dual Ni-based catalytic process (DCP) to control the H₂/CO ratio of 2 in the syngas product within one step at temperature <700 °C was created and constructed. With the sequence of the catalysts located in the single reactor, the endothermic combined steam and CO₂ reforming of methane (CSCRM) reaction and the exothermic ultra-high-temperature water–gas shift (UHT-WGS) reaction work continuously. During the process, the H₂/CO ratio is raised suddenly at UHT-WGS after the syngas is produced from CSCRM, and CSCRM utilizes the heat released from UHT-WGS. Due to these features, DCP is more compact, enhances energy efficiency, and thus decreases the capital cost compared to reformers connecting with shift reactors. To prove this propose, the DCP tests were done in a fixed-bed reactor under various conditions (temperature = 500, 550, and 600 °C; the feed mixture (CH₄, CO₂, H₂O, and N₂) with H₂O/(CH₄ + CO₂) ratio = 0.33, 0.53, and 0.67). According to the highest CH₄ conversion (around 65%) with carbon tolerance, the recommended conditions for producing syngas with the H₂/CO ratio of 2 as a feedstock of Fischer–Tropsch synthesis include the temperature of 600 °C and the H₂O/(CH₄ + CO₂) ratio of 0.53.

Keywords: dual catalytic process; low temperature syngas production; methane reforming; Ni-based catalysts; ultra-high-temperature water–gas shift; Fischer–Tropsch synthesis

1. Introduction

The ongoing contamination of air by greenhouse gases has been a critical issue as it causes adverse environmental impacts around the world. GTL (gas-to-liquids) is a process that is considered as an alternative energy processing technology to convert natural gas into clean burning-liquid fuels such as gasoline, jet fuel, and diesel [1–3]. The one essential chemical reaction used in the commercial GTL process is the Fischer–Tropsch synthesis (FTs) which requires syngas (a mixture of H₂ and CO) with the H₂/CO ratio of about 2 [4,5]. Commercially, autothermal reforming and partial oxidation of natural gas, a major component of methane, are utilized to produce syngas with the H₂/CO ratio of 2 in the GTL process [6,7]. However, these reforming processes have some drawbacks, such as the requirement of an oxygen unit or oxygen-enriched facilities to adjust the H₂/CO ratio and the difficulty in process



control due to the presence of hot spots (a highly exothermic reaction), which brings about the potential explosion danger [6,8–11]. Consequently, the production of practical syngas is necessary to overcome the drawbacks of conventional reforming processes [12]. For this approach, the combined steam and CO_2 reforming of methane (CSCRM) has received considerable attention for syngas production in order to control the H₂/CO ratio of syngas by adjusting the feed composition of H₂O and CO₂ without the additional units of the oxygen supply [13,14].

Ni-based catalysts have been used for the CSCRM process because of their reasonable prices and acceptable activity compared to the expensive noble metal catalysts (Ru, Re, Rh, Pd, Pt, Ir) [1]. The barrier to this commercial process is the rapid deactivation of Ni catalysts due to carbon deposition and metal sintering during the reaction when the S/C ratio of the feed is lower than unity [15,16]. However, the CSCRM reaction is an intensive endothermic reaction that consumes a high amount of energy for the evaporation of a large amount of water and has a (high) operating temperature typically above 700 °C to produce the syngas with H₂/CO of around 2 [17–19]. For example, Jang et al. [20] investigated the CSCRM reaction (over Ni-MgO-Ce_{0.8}Zr_{0.2}O₂ catalyst) with the effects of the (CO₂ + H_2O)/CH₄ ratio (0.9–2.9), the CO₂:H₂O ratio (3:1–1:3), and the temperature range of 500 to 1000 $^{\circ}$ C. The authors concluded that with $(CO_2 + H_2O)/CH_4$ ratios above 1.2, the CO_2 : H_2O ratio of 1:2.1 and a temperature of at least 850 °C are preferable reaction conditions for the syngas production in the GTL process. Danilova et al. [21] studied the reaction of the CSCRM reaction under the atmospheric pressure at 750 °C over porous nickel-based catalysts. The results revealed that CH₄ conversion of 94%, the syngas yield of 90%, and the higher H₂/CO ratio (2.7–2.8) were achieved. Huang et al. [22] reported the effect of a steam in a feed composition on the activity of the 10wt%Ni/3wt%MgO/SBA-15 catalyst for the CSCRM reaction operated at 850 °C. The optimal CH₄:CO₂:H₂O molar ratio was 2:1:1.5 for CH₄ conversion of 98.7 %, the CO₂ conversion of 92%, and the H₂/CO ratio of approximately 1.79. Jabbour et al. [23] developed "one-pot" mesoporous nickel alumina-based catalysts using the EISA method for the CSCRM reaction operating at 800 °C. These high Ni dispersion catalysts enhanced activity and stability (CH₄ conversion of around 80%) with a sustainable H_2/CO molar ratio close to 2 in gas production. Bae et al. [24] studied the role of the CeO₂–ZrO₂ distribution on the Ni/MgAl₂O₄ catalyst in the CSCRM reaction at 850 °C. The homogeneous distribution of CeO₂–ZrO₂ on the Ni/MgAl₂O₄ catalyst demonstrated the highest CH_4 conversion of 86% and the highest CO_2 conversion of 58% with the H_2/CO ratio of 2.2.

The high operating temperature in the CSCRM reaction may result in the cost of the synthesis gas production being approximately 60% of the total capital cost [25]. Therefore, to reduce the operating cost in the syngas production and to lessen the concern about the catalyst deactivation under severe operating conditions, energy efficiency (low operating temperature) in the syngas production process should be developed [26–28]. An alternative solution would be combining the CSCRM operating at a relatively low S/C ratio with a mildly exothermic process (such as the UHT-WGS and/or partial oxidation of methane) without the supply of heat in an adiabatic reactor, and thus, making the process more energy efficient [29,30]. Nevertheless, the H₂/CO ratio is fixed at about 2 by adjusting the operating parameter to meet the requirements of the FTs. Furthermore, the catalyst deactivation could be suppressed by the milder operating conditions and adding an oxygen source in the feed.

In previous work [31], 5wt%Ni5wt%Co/MgO–Al₂O₃ (NiCo/Mg-Al) showed the higher metal dispersion, smaller metal particle size, and a high reducibility due to the effect of the metal–metal interaction. As a result, a valuable CRM catalytic activity in terms of CH₄ and CO₂ conversion was attained. The maintainability of the UHT-WGS catalytic performance at the temperature range of 500–600 °C over the catalyst with the composition of 10wt%Ni/5wt%CeO₂-Al₂O₃ (Ni/5Ce-Al) was also successful because of the high surface area, high metal dispersion, and practical Ni–Ce–Al interaction [32]. Using these developed Ni-based catalysts, the novel concept of the superior dual Ni-based catalytic process (DCP) that converts CH₄ and CO₂, the main greenhouse gases, into syngas with the H₂/CO ratio of about 2 at relatively low temperatures (<700 °C) was developed in this work. In DCP, the Ni/5Ce-Al catalyst is located next after the NiCo/Mg-Al catalyst. As a result, the CSCRM and the UHT-WGS are operated continuously in a single reactor. During the operation, the syngas

is produced on the catalyst for the CSCRM and then the H_2/CO ratio in the syngas is increased on the catalyst for the UHT-WGS. Moreover, the exothermic WGS can supply energy to the endothermic reactions above that take place on the CSCRM zone. Consequently, this original DCP is an alternative compact catalyst system that provides a very favorable H_2/CO ratio for the syngas product associated with energy efficiency. Based on the reactants in the feed (CH₄:CO₂:H₂O:N₂) and the thermodynamic favorability, the possible reactions are demonstrated in the Equations (1)–(4).

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO, \Delta H_{298 \text{ K}} = +261 \text{ kJ/mol}$$

$$\tag{1}$$

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO, \Delta H_{298 \text{ K}} = +206 \text{ kJ/mol}$$

$$\tag{2}$$

$$CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2, \Delta H_{298 K} = +165 \text{ kJ/mol}$$
(3)

$$CO + H_2O \leftrightarrow H_2 + CO_2, \Delta H_{298 \text{ K}} = -41 \text{ kJ/mol}$$
(4)

Regarding Equations (1)–(4), three representative reactions are endothermic except for Equation (4). The reaction temperature and the feed composition are significant to control the activity and the composition of the syngas product.

In this work, the DCP was constructed and demonstrated. All supported catalysts were prepared by the impregnation method. The physicochemical properties of prepared catalysts were characterized. The CRM and UHT-WGS catalytic performances were separately tested with temperature programmed from 500 to 600 °C. According to the well-known stoichiometry of the CSCRM equation ($3CH_4 + 2H_2O$ + $CO_2 \leftrightarrow 8H_2 + 4CO$) [6,14,19], the H₂/CO ratio of 2 can be achieved when managing the composition of the gas feed with S/C ratio close to 0.5 and performing under a severe temperature (\geq 700 °C). Then, the effects of the operating condition adjustments on the DCP catalytic performance and the H₂/CO ratio were examined for various temperatures (500, 550, and 600 °C) and the feed compositions (CH₄:CO₂:H₂O:N₂ molar ratio = 1:0.5:x:1; x = 0.5, 0.8, and 1 reflecting the S/C ratios of 0.33, 0.53, and 0.67, respectively).

2. Results and Discussion

2.1. Catalyst Characterization

2.1.1. Morphological Characterization

The diffraction patterns of the calcined NiCo/Mg-Al and Ni/5Ce-Al catalysts were investigated through the XRD as displayed in Figure 1. The NiCo/Mg-Al catalyst revealed characteristic diffraction peaks of MgAl₂O₄ spinel at 2θ angles of 36.8° 44.8°, and 65.3° (JCPDS 77-0435); these peaks could also be assigned to the spinel phases of NiAl₂O₄ (JCPDS 78-0552) and CoAl₂O₄ (JCPDS 82-2243) because Ni²⁺, Co²⁺, and Mg²⁺ can be incorporated into the identical lattice with Al₂O₃ [33]. However, these diffraction peaks were not easily to be identified because of either lower calcination temperatures or existing overlaps between the diffraction peaks of NiAl₂O₄ (or CoAl₂O₄) and the peaks of MgAl₂O₄ [34,35].

The Ni/5Ce-Al catalyst showed characteristic diffraction peaks of γ -Al₂O₃ at 2 θ angles of 37.5°, 45.6°, and 66.6° (JCPDS 50-0741). At the same time, the broad peaks at 2 θ angles of 28.5° and 47.5° (JCPDS 34-0394) are attributed to the cubic fluorite type structure of CeO₂. Diffraction peaks that correspond to the crystalline species of NiO (JCPDS 89-7131) and Co₃O₄ (JCPDS 76-1802) in cubic structures were not observed for all calcined catalysts. This occurrence indicates that the active metal species transformed into the spinel structure (especially the NiCo/Mg-Al catalyst) or the high dispersion of the active metal species on the surface of the support [36].



Figure 1. XRD patterns of calcined catalysts.

The N₂ adsorption–desorption isotherms of all catalysts are illustrated in Figure 2. According to the IUPAC classification, the NiCo/Mg-Al and Ni/5Ce-Al catalysts showed type IV isotherm curves with different hysteresis loops. The loop of NiCo/Mg-Al catalyst indicates a H3 hysteresis behavior associated with solids containing aggregates or agglomerations of particles, representing slit-like pores (plates or edged particles like cubes) with a non-uniform size and/or shape [2]. The H2 hysteresis behavior observed on Ni/5Ce-Al catalyst refers to pores with narrow mouths and an ink-bottle shape [37,38]. The pore size distributions of the NiCo/Mg-Al and the Ni/5Ce-Al catalysts comprise a mesoporous material with pore diameter ranges of 3–30 nm and 5–10 nm, respectively.



Figure 2. N₂ adsorption–desorption isotherms and BJH pore distributions of calcined. (**a**) NiCo/Mg-Al and (**b**) Ni/5Ce-Al catalysts.

The structural properties of calcined catalysts are summarized in Table 1. The NiCo/Mg-Al catalyst has a surface area of $130 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.4 \text{ cm}^3 \text{ g}^{-1}$, and an average pore size diameter of 11.2 nm, which is in agreement with other studies [2,39]. The Ni/5Ce-Al catalyst presented the surface area of $183 \text{ m}^2 \text{ g}^{-1}$ with a pore volume of $0.6 \text{ cm}^3 \text{ g}^{-1}$ and an average pore size diameter of 12.5 nm, which is located in the same range compared to other published research [36,40,41]. Moreover, these two catalysts disclosed the small metal particle size due to the high metal dispersion, as explained by the XRD results.

Catalysts	$\frac{S_{BET}}{(m^2 \ g^{-1})^{a}}$	$V_p (cm^3 g^{-1})^a$	Average Pore Size Diameter (nm) ^a	[%] D _m ^ь	<i>d</i> (nm) ^b	H ₂ -Uptakes (μ mol g ⁻¹)	
						Actual ^c	Theoretical ^d
NiCo/Mg-Al	130	0.4	11.2	32.2	2.0	1616	1700
Ni/5Ce-Al	183	0.6	12.5	23.8	2.7	1428	1704

 Table 1. Physicochemical properties of calcined catalysts.

^a Calculated by the BET Equation with about 5% systematic error; ^b calculated from H₂-TPD results with about 8% systematic error; H₂ consumption calculated experimentally (Actual ^c) from TPR profiles (with about 8% systematic error) after complete reduction at T = 900 °C and theoretical values (Theoretical ^d) determined based on metal loading.

2.1.2. Physical Characterization

Figure 3 presents the H₂-TPR profiles of NiCo/Mg-Al and Ni/5Ce-Al catalysts. The TPR profile of NiCo/Mg-Al catalyst displayed shoulder peaks at lower temperatures (a range of 150 to 450 °C), which correlate to the reduction of Co_3O_4 to CoO and CoO to metallic Co^0 . The broad peak centered at 520 °C relates to the reduction of Ni²⁺ to Ni⁰ [3]. The peak at a high temperature of around 840 °C indicates the reduction of Ni or Co species with strong interactions due to the metal alloy effect and/or SMSI effect regarding the NiCo-based catalyst [33]. A similar trend of H₂-TPR behavior was also reported in Li et al. [42], indicating high reduction temperature (825 °C) with a NiCo catalyst has been assigned as the reduction of small active metal particles and possibly the reduction of nickel and cobalt aluminate-like compounds (NiAl₂O₄ and CoAl₂O₄ spinel structures) [43].



Figure 3. H₂-TPR profiles of calcined catalysts.

For the TPR profile of the Ni/5Ce-Al catalyst, small broad peaks from 200 °C to 400 °C were observed. The peak at around 270 °C can be ascribed to the reduction of the CeO₂ and the NiO interacting with the partial bulk CeO₂, while the peak at around 370 °C correlates to the reduction of free NiO on the catalyst support [41]. In accordance with the XRD analyses from Figure 1, the high intensity peak at 700 °C illustrates the reduction of Ni²⁺ ions in the amorphous spinel phases with non-stoichiometry of nickel aluminate (NiAl_xO_y) and stoichiometry of nickel aluminate (NiAl₂O₄) [44]. Actual H₂-uptakes calculated from H₂-TPR profiles for the prepared catalysts were close to the theoretical H₂-uptake, are listed in Table 1. The result implies that the Ni²⁺ species were fully reduced. Although the TPR profiles suggest a reduction temperature of over 650 °C, the temperature for the reduction of all catalysts was limited at 650 °C to avoid the agglomeration of active metal according to the calcination temperature of the NiCo/Mg-Al catalyst [45].

2.2. Catalytic Performance

2.2.1. Catalytic Performance for CRM and UHT-WGS Reactions

The CRM and the UHT-WGS reactions were performed separately over NiCo/Mg-Al and Ni/5Ce-Al catalysts, respectively, for 8 h at each operating temperature (500, 550, and 600 °C). The CH₄ conversion obtained from the NiCo/Mg-Al catalyst with different temperatures is provided in Figure 4a. As seen in Figure 4a, the CH₄ conversion increased from ~29% at 500 °C to ~52% at 600 °C because of a highly endothermic process by nature. Furthermore, the sustainable CH₄ conversion as functions of time-on-stream for each studied temperature was observed and also close to the thermodynamic equilibrium conversions (23% at 500 °C, 39% at 550 °C, and 59% at 600 °C) calculated using the reactivity test conditions. These results are in good agreement with the published literature when considering the same studied temperature range [41,46,47].



Figure 4. (a) CH₄ conversion over the NiCo/Mg-Al catalyst in the CRM and (b) CO conversion over the Ni/5Ce-Al catalyst in the UHT-WGS with a continue reaction temperature programmed. (500 °C to 600 °C).

The catalytic activity of the Ni/5Ce-Al catalyst in the UHT-WGS reaction is presented in Figure 4b. It was found that the CO conversion performance decreased from ~65% at 500 °C to ~55% at 600 °C due to an exothermic reaction. Although the CO conversions obtained from UHT-WGS tests are different from the thermodynamic equilibrium conversions (92% at 500 °C, 89% at 550 °C, and 86% at 600 °C), a similar tendency was observed in the case of increasing operating temperature. Nonetheless, this catalytic behavior demonstrated the appropriate range of CO conversion and an expected trend of CO conversion compared to other studies [48–50]. The maintainability of CO conversion in each studied temperature was also attained. To further study the combination of the CSCRM and the UHT-WGS reactions as a dual catalytic process, the operating temperature should be limited at 600 °C to maintain the activity of the UHT-WGS due to its nature of exothermic reaction catalyst, while the CH₄ conversion from the methane reforming reaction (this case refers to CRM result) is acceptable [34].

2.2.2. Catalytic Performance for DCP

Figure 5a,b exhibits the CH₄ and CO₂ conversions against time-on-stream with different operating temperatures (500, 550, and 600 °C) at a fixed S/C ratio of 0.67. As seen in Figure 5a, the CH₄ conversion increases when the operating temperature increases because the CSCRM is the endothermic process and high temperature encourages the reactions [12]. This trend was also found for CO₂ conversion (Figure 5b); the extent of the CO₂ conversion rose from ~15% at 500 °C to ~35% at 600 °C. It should be noted that the appearance of the low CO₂ conversion at 500 °C could involve the

fact that CO_2 is a product of the WGS reaction. Nevertheless, these CH_4 and CO_2 conversions were reliable compared to the results at a similar operating temperature range demonstrated by previously published works [2,12,51]. The obtained H₂/CO ratios for different operating temperatures, displayed in Figure 5c, were close to 2 for all operating temperatures according to these conditions.



Figure 5. (a) CH₄ conversion, (b) CO₂ conversion, and (c) H_2/CO ratio with the effect of operating temperature for the DCP with a fixed S/C ratio of 0.67.

The influence of the feed composition (S/C ratio = 0.33, 0.53, and 0.67) for the DCP was investigated. Reactant conversions and the H₂/CO ratio at a fixed operating temperature of 600 °C (Figure 6) illustrate that an increased S/C ratio from 0.33 to 0.53 resulted in an increase in the CH₄ conversion from ~55 %to ~65 % (Figure 6a). This result implies the raising of reforming rates by the addition of the oxidizing agents [34]. Alternatively, the increased S/C ratio from 0.53 to 0.67 decreased the CH₄ conversion from \sim 65 % to \sim 50 %, suggesting an excess adsorbed steam on the catalyst surface. This behavior could be explained by the work of Gensterblum et al. [52], who reported that gas sorption (CH_4 or CO_2) capacity decreases with increasing H_2O content on coal surfaces, and the interaction of H_2O with natural coal is more complex than the interactions of non-polar gases (CH_4 , CO_2 , and N_2). It is speculated that the duration of the H₂O dissociative adsorption is longer than said duration for other gases, which agrees with the results of Tan et al. [53]. They revealed that the adsorption energies of the H₂O molecules $(61-80 \text{ kJ mol}^{-1})$ on metal-MOF-74 (metal = Ni, Co, and Mg) are higher than that of the adsorption energies of CH₄ (19-20 kJ mol⁻¹) and CO₂ (37-48 kJ mol⁻¹) molecules. Zhou et al. [54] also pointed out that the adsorption capacity of H_2O molecules (7.552 mmol g^{-1}) is higher than that of the adsorption capacities of CH₄ (0.001 mmol g^{-1}) and CO₂ (0.241 mmol g^{-1}) molecules, resulting in a significant decrease of the adsorption sites for the CH₄ and CO₂ molecules at a higher H₂O content. Nevertheless, the experimental CH₄ conversions for all feed compositions were slightly higher than those of the



thermodynamic equilibrium (45% for S/C ratio of 0.33, 51% for S/C ratio of 0.53, and 55% for S/C ratio of 0.67).

Figure 6. The effect of the feed composition (S/C ratio = 0.33, 0.53, and 0.67) in the DCP at a fixed temperature of 600 °C; (a) CH₄ conversion, (b) CO₂ conversion, and (c) H₂/CO ratio.

Figure 6b represents the CO₂ conversion as a function of time-on-stream. The CO₂ conversion decreased from approximately 52% to 35% with an increasing S/C ratio from 0.33 to 0.67. The increase in S/C ratio caused a considerable decrease of CO₂ conversion. This circumstance can be attributed to CH₄ reacting with H₂O instead of the CO₂ at high H₂O content in the feed composition (S/C ratio), since both CO₂ and H₂O act as co-oxidants in the DCP, but CO₂ is more stable (its thermodynamic effect) with an increasing amount of H₂O in the feed gas [22]. Meanwhile, the CO₂ conversion in the thermodynamic equilibrium (35% for S/C ratio of 0.33, 17% for S/C ratio of 0.53, and 6% for S/C ratio of 0.67) decreased with the increase of the S/C ratio and lower than experimental CO₂ conversions for all S/C ratios. The difference between the experimental and the thermodynamic equilibrium results could be caused by the side reactions (RWGS reaction) considering the similar reaction temperature [55]. The maintainable CO₂ conversions after 160 min of time-on-stream were observed for all feed compositions. However, the obtained CH₄ and CO₂ conversions in this work were higher than those of the CH₄ and CO₂ conversions reported in the literature, because of relatively low feed composition and the Ni-based catalyst. For instance, Álvarez M et al. [56] examined the combined dry-steam reforming of

methane with the feed composition S/C ratio of 0.4 over the Ni/MgO–Al₂O₃ catalyst. The received CH₄ and CO₂ conversions during about 20 h testing time were approximately 35% and 25%, respectively.

The effect of the feed composition towards the syngas production is displayed in Figure 6c; it was observed that the greater S/C ratio in the feed provided the higher H₂/CO ratio in the syngas product. The H₂/CO ratio of the syngas reached 2 for the S/C ratios of 0.53 and 0.67. The increase of H₂ content in the syngas product represented more effect of steam reforming in CSCRM. For all S/C ratios, the H₂/CO ratios gained from the tests were slightly lower than the thermodynamic equilibrium values (1.9 for S/C ratio of 0.33, 2.4 for S/C ratio of 0.53, and 2.8 for S/C ratio of 0.67) due to the side reactions such as the RWGS and coke forming reactions [23]. Notwithstanding, these experimental H₂/CO ratios refer to a practical feedstock for FTs, as reported in Lillebø et al. [57], who studied the FTs with different H₂/CO ratios (between 1.04 and 2.56) on the 20wt%Co-0.5wt%Re/Al₂O₃ catalyst at 210 °C. The results demonstrated that the hydrocarbon C₅₊ selectivity of at least 85% can be accomplished for the syngas reactant with the H₂/CO ratios above 2.1 without a significant short-term deactivation or a loss of selectivity. Therefore, the feed composition with the S/C ratio of 0.53 accompanied with the operating temperature of 600 °C is a preferable condition for the DCP (consideration of the CH₄ conversion and practical consumption) to produce the syngas for FTs in the GTL technology.

2.2.3. TGA/DTG Analysis of Spent Catalysts

The quantity and types of deposited carbon with the effect of the feed composition over the spent NiCo/Mg-Al and the spent Ni/5Ce-Al catalysts in DCP were characterized using the TGA/DTG technique, flowing air, and temperature programmed from 100 to 800 °C. The TGA/DTG profiles are presented in Figure 7a,b for spent NiCo/Mg-Al and Ni/5Ce-Al catalysts, respectively. As depicted in Figure 7a,b, three types of the carbon species were detected. The peaks at the temperature range of 300 to 420 °C are attributed to the oxidation of the weakly stable amorphous carbon (sp² C-atoms or graphene-like species). The coexistence in two types of carbon species at a high temperature corresponds to the oxidation of carbon nanotubes (450 to 550 °C) and the oxidation of graphitic carbon (sp³ C-atoms, >550 °C) [23]. As seen in Figure 7a, the weight loss of the spent NiCo/Mg-Al catalyst decreased from 65% to 27% with an increasing S/C ratio from 0.33 to 0.53 and then increased from 27% to 33% with an increasing S/C ratio from 0.53 to 0.67. These combined results indicate that the S/C ratio of 0.53 has a tendency to remove a deposited carbon in the case of a low S/C ratio, which can reduce the graphitic carbon. The formation of graphitic carbon existed when adjusting the S/C ratio to equal 0.67. This evidence reflected the longer time of deposited carbon grown on the surface of the NiCo/Mg-Al catalyst for the S/C ratio of 0.67 compared to the S/C ratio of 0.53. It means that the dissociative adsorption of H₂O on the NiCo/Mg-Al catalyst requires time before the gasification step to contribute oxygen species in order to remove carbon on the surface. Therefore, fewer active sites for the oxidizing agents were available for the S/C ratio of 0.67 than for the S/C ratio of 0.53, resulting into less oxygen species on the surface, allowing more deposited carbon to polymerization on the surface of Ni.

At the same time, the Ni/5Ce-Al catalyst (Figure 7b) displays the main peak range of 450 to 650 °C, which refers to carbon nanotubes and graphitic carbon. A decrease in weight loss is evident from 25% to 12% with an increasing S/C ratio noted from 0.33 to 0.67. The weight loss for the S/C ratio of above 0.53 is acceptable. From these results, it was found that the content of H₂O in the feed composition plays a major role in the removal of carbon species on the surface of the WGS catalyst. By comparison, the UHT-WGS catalyst shows a lower amount of carbon deposition than that of the CSCRM catalyst since the carbon deposition on the Ni-based catalysts is not critical in the WGS reaction [58].



Figure 7. TGA/DTG profiles of spent (**a**) NiCo/Mg-Al and (**b**) Ni/5Ce-Al catalysts for the effect of feed composition at 600 °C.

3. Material and Methods

3.1. Catalyst Preparation

3.1.1. CRM Catalyst Preparation

The MgO–Al₂O₃ support was synthesized by the sol–gel method. Magnesium ethoxide (Mg(OC₂H₅)₂, Sigma Aldrich, St. Louis, MO, USA), was dissolved in distilled water (denoted as solution A) at ambient temperature (25 ° to 30 °C) and stirred for 20 h. At the same time, aluminum isopropoxide (Al[OCH(CH₃)₂]₃, Sigma Aldrich) was dissolved in distilled water (denoted as solution B) and continually stirred at 80 °C for 1 h. Subsequently, concentrated nitric acid was added by drops into the solution B and vigorously stirred for 20 h. Next, solution A was added to solution B and stirred for 2 h to form a homogeneous solution. The obtained mixed solution was dried at 50 °C overnight and calcined at 650 °C for 5 h under an air atmosphere with a ramp rate of 3 °C min⁻¹ to decompose contaminants. The 5wt %Ni5wt %Co/MgO–Al₂O₃ (NiCo/Mg-Al) catalyst was prepared by co-impregnation using nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Sigma Aldrich) and cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, Sigma Aldrich) as precursors for the nickel solution and cobalt solution, respectively. These aqueous solutions were mixed and added by drops onto the support. The obtained solid cake was then dried at 50 °C for 2 h and calcined at 650 °C for 5 h using the ramping rate of 3 °C min⁻¹.

3.1.2. UHT-WGS Catalyst Preparation

The 5wt % CeO₂-Al₂O₃ (Ce-Al) support was first synthesized by the sol–gel method using cerium (III) acetylacetonate hydrate (Ce(C₅H₇O₂)₃·*x*H₂O, Sigma Aldrich) and aluminum isopropoxide precursors. The desired quantities of the precursors were dissolved in a mixture of distilled water and isopropanol according to a molar ratio of 1:1. The saddle brown solution was refluxed at 70 °C for 2 h to form the gel product. The product was dried at 50 °C overnight and calcined at 600 °C for 6 h with a ramp of 3 °C min⁻¹. Secondly, an amount of nickel (II) nitrate hexahydrate corresponding to 10 wt % of Ni was impregnated onto the calcined support followed by drying at 50 °C for 2 h and calcination at 600 °C for 6 h using the heating rate of 3 °C min⁻¹. For this purpose, the synthesized UHT-WGS catalyst was labeled as Ni/5Ce-Al.

3.2. Catalyst Characterization

3.2.1. Morphological Characterization

The crystalline phases of the catalyst samples were examined by XRD analysis using an X-ray diffractometer (PANalytical X'Pert-Pro, Almelo, The Netherlands) with nickel-filtered Cu K α (λ = 1.54178 Å, 2 θ range from 10° to 80°), a monochromatized radiation source, operated at 40 kV and 30 mA, having the scanning rate of 0.02° with 0.5 s per step.

The specific surface area (S_{BET} , $m^2 g^{-1}$), pore volume (Vp, $cm^3 g^{-1}$), and average pore size diameter (nm) were characterized by N₂ adsorption/desorption isotherms, which were measured at –196 °C using BELSORP-mini II instrument (Osaka, Japan). The pore size distribution curve was calculated from the analysis of the desorption branch of the isotherm by the BJH method.

3.2.2. Physical Characterization

According to the stoichiometry of 1:1 for the chemisorbed hydrogen atom on the Ni surface, the metal dispersion (D_m , %) and the metal particle size (d, nm) were calculated from Equations (5) and (6), respectively, using the H₂-TPD results [59,60]. In these equations, V_{chem} is an amount of hydrogen desorption (cm³); SF is a stoichiometry factor; MW is an atomic weight of metal (g mol⁻¹); m is a sample weight (g); w is a wt % of supported metal content; σ_m is a cross-sectional area of one metal atom (nm²); and ρ is a density of metal (g cm⁻³).

$$\%D_{\rm m} = \frac{\left(\frac{V_{\rm chem}}{22414}\right) \times SF \times MW}{\left(\frac{m \times w}{100}\right)} \times 100 \tag{5}$$

$$d = \frac{6000}{\left(\frac{V_{chem}}{22414}\right) \times SF \times 6.02 \times 10^{23} \times \rho \times \sigma_{m} \times 10^{-18}}{\left(\frac{m \times w}{100}\right)}}$$
(6)

Before analysis, 50 mg of the calcined catalyst was reduced in situ at 600 °C in a H₂ flow of 50 mL min⁻¹ for 2 h, followed by cooling to 100 °C in Ar flow of 50 mL min⁻¹. Consequently, H₂ was isothermally chemisorbed on the surface of the sample at 100 °C for 0.5 h and the sample was cooled to ambient temperatures in Ar flow of 50 mL min⁻¹. The desorbed H₂ was measured by a TCD during the temperature programmed from 40 °C to 900 °C under Ar flow of 50 mL min⁻¹.

The reducibility of the calcined catalyst was evaluated via the H₂-TPR technique performed in the BELCAT-basic system (Osaka, Japan). In this analysis, 50 mg of the calcined catalyst was degassed at 220 °C for 1 h in Ar flow of 30 mL min⁻¹, followed by cooling to 40 °C. After, the sample was reduced in the temperature programmed from 40 °C to 900 °C under 5%H₂/Ar flow of 50 mL min⁻¹. The H₂ consumption was detected by the TCD.

The quantity and nature of the deposited carbon over the spent catalyst were measured by TGA and DTG using a METTLER TOLEDO thermogravimetric analyzer (Columbus, Ohio, United States). The catalyst sample weight loss and the derivative thermogravimetric curve of the weight loss versus temperature were collected continuously under flowing air up to 800 °C with a heating rate of 10 °C min⁻¹.

3.3. Catalytic Activity Test

Catalytic tests were carried out in a stainless steel tubular fixed-bed reactor at atmospheric pressure. Before the DCP reaction, the catalytic performances of CRM and UHT-WGS catalysts were demonstrated separately with a continued reaction temperature programmed (500, 550, and 600 °C); each temperature was held for 8 h. Prior to the CRM test with the composition of CH₄:CO₂:N₂ = 1:1.7:1.3 molar ratio with GHSV of 1.8×10^4 mL g_{cat}⁻¹ h⁻¹, the 200 mg of CRM catalyst diluted with 1000 mg of fused silica was packed (diluted catalyst height of 1.4 cm) and the in situ reduced

was at 650 °C for 6 h under a H₂ flow of 30 mL min⁻¹; the temperature was then decreased to the reaction temperature in N₂ at a flow rate of 30 mL min⁻¹. For the UHT-WGS tests using the GHSV of 2.0×10^5 mL g_{cat}⁻¹ h⁻¹ with H₂O/CO ratio of three, the 30 mg of UHT-WGS catalyst diluted with 1000 mg of fused silica (diluted catalyst height of 1.2 cm) was preactivated and cooled using a similar reduction condition to the CRM catalyst.

For the DCP reaction, the diluted UHT-WGS catalyst as previously mentioned was charged first and the quartz wool was then placed on the top of the UHT-WGS catalyst. Subsequently, the diluted CRM catalyst as mentioned was loaded second. When the effect of the operating temperature was evaluated, the different reaction temperatures (500, 550, and 600 °C) were used under the feed composition with the S/C ratio of 0.67. The effect of H₂O content in the feed composition was investigated using the feed composition of CH₄:CO₂:H₂O:N₂ molar ratio = 1:0.5:x:1; *x* = 0.5, 0.8, and 1 (corresponding to the S/C ratio of 0.33, 0.53, and 0.67, respectively) with the fixed reaction temperature of 600 °C employing the GHSV rang of 1.6×10^4 – 1.8×10^4 mL g_{cat}⁻¹ h⁻¹. The conversions of CH₄ and CO₂ and the H₂/CO ratio were calculated using the following Equations (Equations (7)–(9)). The scheme of the experimental setup is presented in Figure 8.

$$X_{CH_4} = \frac{n_{CH_4,in} - n_{CH_4,out}}{\dot{n}_{CH_4,in}} \times 100$$
(7)

$$X_{\rm CO_2} = \frac{\dot{n}_{\rm CO_2,in} - \dot{n}_{\rm CO_2,out}}{\dot{n}_{\rm CO_2,in}} \times 100$$
(8)

$$\frac{H_2}{CO} ratio = \frac{mole of H_2 produced}{mole of CO produced}$$
(9)



Figure 8. Schematic diagram of the experimental setup.

4. Conclusions

The Ni/5Ce-Al catalyst was developed for UHT-WGS and allowed a DCP, including a CSCRM reaction followed by the UHT-WGS reaction over Ni-based catalysts in a single reactor to be created and investigated. For the individual catalyst, the catalytic performances of the CRM and the UHT-WGS

catalysts with temperatures programmed from 500 to 600 °C were separately tested. The results revealed that the CH₄ conversion in the CRM reaction increased with increasing reaction temperature from 500 to 600 °C because the CRM reaction is an endothermic process that is favored at a high temperature. By contrast, a decrease in the CO conversion in the UHT-WGS reaction with an increasing process temperature from 500 to 600 °C was found due to the exothermic reaction by nature. The convergences of the conversions in the CRM and the UHT-WGS reactions were accomplished at 600 °C. The DCP with the influences of operating temperature (500, 550, and 600 °C) and the feed composition (S/C ratio = 0.33, 0.53, and 0.67) was examined. It was discovered that the operating temperature and the feed composition have significant impacts on conversions, the H₂/CO ratio, and the carbon formation in the DCP. The achievement of the optimum DCP condition was a S/C ratio of 0.53 at 600 °C with not only the appropriate H₂/CO ratio of about 2 but also the prevention of carbon formation. Therefore, it can be concluded that, at the relative low operating temperature, the DCP on the NiCo/Mg-Al and the Ni/5Ce-Al catalyst could be developed for the commercial production of syngas to be fed to FTs.

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Nomenclature

List of acrony	/ms
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
CRM	CO ₂ reforming of methane
CSCRM	combined steam and CO ₂ reforming of methane
DCP	dual Ni-based catalytic process
DTG	derivative thermogravimetric analysis
EISA	evaporation-induced self-assembly
FTs	Fischer–Tropsch synthesis
GHSV	gas hourly space velocity
GTL	gas-to-liquids
H ₂ -TPD	hydrogen temperature programmed desorption
H ₂ -TPR	hydrogen temperature programmed reduction
RWGS	reverse water gas shift
S/C ratio	steam-to-carbon ($H_2O/(CH_4 + CO_2)$ ratio
SMSI	strong metal support interaction
TCD	thermal conductivity detector
TGA	thermogravimetric analysis
UHT-WGS	ultra-high-temperature water–gas shift
XRD	X-ray diffraction

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