



Article CO₂ Methanation of Biogas over Ni-Mg-Al: The Effects of Ni Content, Reduction Temperature, and Biogas Composition

Danbee Han¹, Wonjun Cho² and Youngsoon Baek^{1,*}

- ¹ Department of Environment-Energy Engineering, The University of Suwon, 17 Wauan-gil, Bongdam-eup, Hwaseong-si 18323, Korea
- ² Bio Friends Inc., Yuseong-gu, Daejeon 34028, Korea
- * Correspondence: ysbaek@suwon.ac.kr; Tel.: +82-31-220-2167

Abstract: Biogas is mainly composed of CH_4 and CO_2 , so it is used as an alternative energy to CH_4 with high energy density by separating and removing CO_2 from biogas. In addition, it can be utilized by producing synthesis gas (CO and H_2) through thermal decomposition of biogas or by synthesizing CH_4 by methanation of CO_2 . The technique of CO_2 methanation is a method that can improve the CH_4 concentration without CO_2 separation. This study aims to produce more efficient methane through CO_2 methanation of biogas over Ni-Mg-Al catalyst. So, the effect of Ni contents in catalyst, catalyst reduction temperature, CO_2 concentration in biogas, and the initial concentration of CH_4 on CO_2 conversion rate and CH_4 selectivity was investigated. In addition, the effect of increasing CO_2 concentration, H_2/CO_2 ratio, and GHSV (gas space velocity per hour) on H_2 conversion, CH_4 productivity, and product was investigated. In particular, the durability and stability of CO_2 methanation was tested over 60 wt% Ni-Mg-Al catalyst at 350 °C and 30,000/h for 130 h. From the long-term test results, the catalyst shows stability by maintaining a constant CO_2 conversion rate of 72% and a CH_4 selectivity of 95%.

Keywords: CO₂ methanation; CO₂ hydrogenation; Ni catalyst; biogas; carbon capture utilization storage; power to gas

1. Introduction

Because of the rapid development of the global economy, the severities of the energy crisis and environmental pollution are increasing. In 2020, fossil fuel consumption accounted for 10.3 Gt of CO_2 emissions. At the current rate, the Earth's temperature is predicted to rise by 6 °C before the end of 2050. To combat the threat of climate change, the Paris Climate agreement, in which countries around the world pledged carbon neutrality to limit the increase in the Earth's temperature to 1.5 °C by 2050, was adopted. Measures to minimize CO_2 in the atmosphere include the replacement of fossil fuels with alternative energy sources (e.g., hydrogen) and utilizing carbon capture, utilization, and storage (CCUS) technologies [1-3]. Among CCUS technologies, chemical conversion is the most convenient and effective [4] because the CO_2 generated from the fuel is converted to fuel through the aid of a catalyst and recycled, thereby ensuring carbon neutrality [5]. As CO₂ methanation, an important process that involves catalysis, has tremendous potential for commercial applications, it has received significant attention. The methanation reaction can reduce environmental pollution through the conversion of CO_2 to CH_4 , which is cleaner for the environment, and it can alleviate the energy shortage problem. Therefore, methanation is among the most effective processes for mitigating CO_2 emissions [6,7].

Catalytic processes involve a catalyst, a catalyst support, a catalytic promoter, and group VIII metals, such as Ru, Rh, Pd, Ni, Co, and Fe to provide active sites for the CO₂ methanation reaction. Among these metals, Pd, Rh, and Ru are precious metals that are characterized by low-temperature catalytic activity and high methane selectivity [8].



Citation: Han, D.; Cho, W.; Baek, Y. CO₂ Methanation of Biogas over Ni-Mg-Al: The Effects of Ni Content, Reduction Temperature, and Biogas Composition. *Catalysts* **2022**, *12*, 1054. https://doi.org/10.3390/ catal12091054

Academic Editor: Kuan Chang

Received: 22 July 2022 Accepted: 13 September 2022 Published: 16 September 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). However, because of their high cost and scarcity, these metals are unsuitable for largescale applications [9]. Conversely, Co-based catalysts exhibit low-temperature activity and stability but low methane selectivity [10,11]. Further, in the presence of Fe-based catalysts, carbon accumulates on the surface of the catalyst and liquid hydrocarbons are easily formed; however, these catalysts are unsuitable for low-temperature reactions [12]. Nibased catalysts have been extensively studied for application in CO2 methanation because of their excellent performance and low cost. Therefore, efforts have been devoted to identifying supports and promoters of Ni-based catalysts to address their low-temperature activity and sintering resistance limitations.

La³⁺, Pr³⁺, Sm³⁺ in to the crystal structure of cerium oxide created a higher population of oxygen vacant sites. Moreover, the co-presence of La³⁺, Mg²⁺ and La³⁺, Pr³⁺ into the CeO₂ increased the methos of moderate basic sites. These physicochemical properties increased the rate of CO₂ methanation reaction at a relatively low temperature. CO₂ conversion was observed at 350 °C, Ni/La-Pr-Ce (55%) > Ni/La-Sm-Ce (53%) > Ni/La-Mg-Ce (49%) > Ni Ce(39%) [13].

In a series of 5%X-12%Ni/ γ -Al2O3 (X = La, Ce, Pr, Eu & Gd) catalysts, 5%Pr-12%Ni/ γ -Al₂O₃ catalysts showed the highest CO₂ conversion of 98.2% with 100% CH₄ selectivity at 300 °C for investigated reaction conditions. Additionally, the catalyst was tested for 48h, which showed the stability of the catalyst for CO₂ conversion and CH₄ selectivity. CO₂ conversion was observed at 300 °C, 5%Pr-12%Ni/ γ -Al₂O₃ > 5% Ce-12% Ni/ γ -Al₂O₃ > Eu-12% Ni/ γ -Al₂O₃ > 5% La-12%Ni/ γ -Al₂O₃ 12% Ni/ γ -Al₂O₃ [14].

Types of bimetallic oxides act as catalysts and remarkably almost all of them present a catalytic activity superior to that of a commercial rhodium catalyst supported on alumina (5 wt% Rh/Al₂O₃) for the production of methane. CO₂ conversion increases until 350–400 °C and stabilizes or decreases over all the nickel-lanthanide bimetallic oxides at higher temperatures. At temperature above 350–400 °C there is an increase in the formation of CO by product, due to reversed WGS reaction [15].

Considering that structural properties, dispersion, and metal-support interactions are major factors affecting the low-temperature catalytic activity and sintering resistance of Nibased catalysts, designing and producing catalysts with adequate porosity, high potential for Ni dispersion, and elevated metal-support interaction is critical [1]. High Ni dispersion is generally achieved by using micro- or mesoporous supports characterized by excellent structural properties and the addition of promoters, such as Co, Zr, Sn, and Mg [16]. Supports can suppress or prevent sintering by enhancing the metal-support interaction and thus influence CO2 methanation by promoting the dissociation and adsorption of CO2 [17]. A catalytic support having a high specific surface area and an elevated pore volume can accommodate active Ni sites in a dispersed state [18]. Enhanced electron transfer between the support and the metal active sites increases the electron density of the metal and strengthens the Ni–C bond, which facilitates the dissociation of the C=O bond and the formation of CH_4 [19]. In addition, other physicochemical properties of the support as well as the particle size and surface characteristics of Ni affect the reducibility and properties of the catalyst. In general, substances such as Al₂O₃, TiO₂, SiO₂, and ZrO₂ are utilized as supports for Ni-based catalysts for CO₂ methanation [15].

According to Romero-Sáez et al. [20], ZrO₂ is unable to activate and dissociate H₂, but it can activate CO₂ to produce CO. Therefore, H₂ molecules can be dissociated on the Ni surface, while CO₂ molecules are activated on the ZrO₂ surface [21]. Thus, interactions between hydrogen atoms and activated CO₂ molecules are facilitated, and this expands the Ni-ZrO₂ interface, thereby enhancing the CH₄ selectivity and reaction rate [22]. However, owing to its excellent stability, elevated CO₂ adsorption potential, and high oxygen storage capacity, CeO₂ likely has a superior low-temperature activity to supported Ni-based catalysts [23–26]. Al₂O₃ is a low-cost porous support with a high specific area that enables uniform dispersion of Ni on the catalyst surface [27,28]. In addition, Al₂O₃ and Ni can react to form NiAl₂O₄ because the strong Ni–O bond prevents the reduction of Ni²⁺. The fine size of the Ni particles on the catalyst surface hinders carbon deposition [29]. Moghaddam et al. [30] indicated that an additive (promoter), such as Fe, Co, Zr, La, or Cu, can improve the conversion of CO₂. Stangeland et al. [31] investigated CO₂ methanation under the reaction conditions of the catalyst. Conversely, Aziz et al. [32] highlighted the importance of the physicochemical properties, catalytic activity, and reaction mechanism of a catalyst, and discussed the developments in heterogeneous catalysts. Doping catalysts with Zr, Co, La, and Mg alters the CO₂ methanation reaction pathways by introducing alternative intermediates. Thus, CO formation can be prevented by effectively suppressing side reactions. MgO has been widely investigated as a basic modifier of Ni-based catalysts for CO₂ methanation [33]. In particular, the addition of a small amount of MgO to a catalyst promotes the chemisorption and dissociation of CO_2 [34]. MgO also improves the dispersion of Ni and modifies the oxidizing environment near its particles in the catalyst. Thus, severe aggregation at active Ni sites and carbon deposition on the catalyst surface can be prevented [35–37].

In this study, a Ni-Mg-Al catalyst with excellent redox properties was prepared. This Ni-based catalyst is inexpensive [38] and exhibits high activity, the Al support has high thermal stability and strong resistance to sintering and carbon deposition, and MgO enhances the adsorption behavior and dispersion of active Ni, thereby enhancing the catalytic activity [39]. In addition, MgO reduces catalyst deactivation, such as sintering and carbon formation, as well as negative effects on water on the catalyst. Since the reaction intermediate (CO) is converted to CH₄, using Ni-Mg-Al catalysts with sufficient Ni content of 20, 40, and 60 wt% to provide many reaction sites, high activity and selectivity of the catalyst for CO₂ methanation experiments improved [40]. In particular, the activation energy of the CO₂ methanation reaction for a Ni-Mg-Al catalyst containing 60 wt% Ni was investigated. Based on the experimental results, the influence of CO₂ concentration, GHSV (gas hourly space velocity) and H₂/CO₂ ratio for CH₄ productivity and product production was investigated. Durability and stability for 130 h was performed for CO₂ methanation over 60 wt% Ni-Mg-Al catalyst.

2. Results and Discussion

2.1. Effects of Temperature Reduction and Catalyst Loading on CO₂ Conversion

The effect of the Ni proportion in the Ni-Mg-Al catalyst at reduced temperatures of 450–700 °C on the CO₂ conversion is shown in Figure 1. Obviously, CO₂ conversion and CH₄ selectivity increased as the reduced temperature of the catalyst increased to 650–700 °C, indicating similarity in the behavior of the catalysts. However, 60 wt% Ni catalyst exhibited no significant change as the reduction temperature varied. This is consistent with the H₂-TPR analysis results (Figure 11), which revealed that the maximum reducibility of the catalysts occurred at 680–720 °C. Therefore, 700 °C was selected as the reduction temperature for the activity experiments under different conditions.



Figure 1. Effect of reduction temperature on CO₂ conversion and CH₄ selectivity at 350 °C (for 20 wt%, reference [41] was cited).

The 20, 40, and 60wt% Ni catalysts were reduced to 700 °C, and the results of the catalysts activity experiment with reaction temperature at a H₂/CO₂ ratio of 4 and GHSV of 30,000/h are shown in Table 1. The temperature at which CO₂ conversion reached 50% was 340, 298, and 291 °C, respectively, for the catalysts with 20, 40, and 60 wt% Ni, which indicates that the temperature decreases as the proportion of Ni increases. This behavior is attributed to the increase in active Ni sites as the proportion of Ni increases. This is in line with the XRD data and the TOF values, which showed an increase in active Ni sites, reflecting reactivity. In fact, a higher Ni loading promotes the production of CH₄. This behavior is likely associated with an increase in catalytic activity because a high Ni loading increases the number of active sites. According to Wierzbicki et al. [42], the metal loading determines the reduction properties of a catalyst. Zhang et al. [43] indicated that the RWGS side reaction competes with the CO₂ methanation reaction for active sites at a low Ni loading and thus a high Ni loading ($\geq 25\%$) promotes CO₂ methanation. Quindimil et al. [44] noted that an increase in the number of active sites (NiO) enhances CO₂ conversion, although increasing Ni loading beyond a certain limit can damage the structure of the catalyst through thermal agglomeration of active Ni sites.

Table 1. Reaction temperatures to reach 50% CO₂ conversion.

Ni Catalyst	20 wt% Ni-Mg-Al	40 wt% Ni-Mg-Al	60 wt% Ni-Mg-Al
Reaction temperature (°C)	340	298	291

2.2. Effect of Temperature Reaction on CO₂ Conversion

The reaction temperature is the dominant factor affecting the activity of Ni-based catalysts. Activation energy higher than the dissociation energy of CO_2 is required for CO_2 conversion at low temperatures. Therefore, increasing the reaction temperature enables the CO₂ molecules to attain the required activation energy and thus enhances the reactivity. The highest CO_2 conversion and CH_4 selectivity were achieved at temperatures ranging between 300 °C–400 °C. Beyond this temperature range, the CH₄ selectivity decreased. Mutz et al. [45] noted that, based on thermodynamics, the high-temperature and exothermic characteristics of the CO2 methanation process affect the equilibrium and deactivation of catalysts. High temperatures have been reported to promote the RWGS reaction and impede the CO₂ methanation reaction. In addition, as shown in the equilibrium curve in Figure 2, the limitation of the CO_2 conversion rate with temperature is also the cause of the lower CO_2 conversion rate. CO₂ conversion and CH₄ selectivity with reaction temperature at a GHSV of 30,000/h and an H_2/CO_2 ratio of 4 are shown in Figure 2. Evidently, CO_2 conversion increased as the temperature increased and peaked at 400 °C, while CH₄ selectivity and yield reached maximum values at 350 °C. This behavior is attributed to suppression of the methanation reaction and an increase in the RWGS reaction above 350 °C, which promotes the conversion of CO_2 to CO. In line herewith, Mohammad et al. [46] reported that the COconcentration increased and methane selectivity decreased at 400 °C because the RWGS reaction is enhanced at this temperature. In addition, Jia et al. [47,48] reported the highest CO2 conversion and CH4 yield at 350 °C, and CO2 conversion decreased beyond this temperature because of the thermodynamic equilibrium limitation. In the present study, the activation energy of 60 wt% Ni-Mg-Al catalyst was reduced and reacted at 200, 250, and 300 °C, and based on the data shown in Figure 3 the activation energy was reduced to approximately 59.7 kJ/mol. This demonstrates the excellent activity of our catalyst and this value is substantially lower than the 75 kJ/mol achieved with a Ni/Al_2O_3 catalyst as reported by Garbarino et al. [22].



Figure 2. Effect of reaction temperature on CO₂ conversion and CH₄ selectivity.



Figure 3. Arrhenius plot for CO₂ methanation over 60 wt% Ni-Mg-Al catalyst.

2.3. Effects of CO₂ and H₂ Concentrations on CO₂ Conversion

Figure 4 shows the effects of the CO₂ concentration (6, 10, 16, and 20 vol%) on CO₂ conversion and CH₄ selectivity for 60 wt% Ni catalyst with an H₂/CO₂ ratio of 4 and a GHSV of 30,000/h. CH₄ selectivity essentially remained constant at approximately 98% as the CO₂ concentration increased, while CO₂ conversion increased because of the increase in reactants and the decrease in N₂, which enhance the likelihood of reactions. At a CO₂ concentration of approximately 15 vol%, the H₂/CO₂ ratio varied between 3.5 and 5 in increments of 0.5 under the same GHSV. The effects of the H₂ concentration increased, CH₄ selectivity are shown in Figure 5. As the H₂ concentration increased at a level comparable to that observed for the effect of the CO₂ concentration. Therefore, to enhance CH₄ production, high CO₂ and H₂ concentrations are required.



Figure 4. Effect of CO₂ concentration on CO₂ conversion and CH₄ selectivity.



Figure 5. Effect of H₂/CO₂ ratio on CO₂ conversion and CH₄ selectivity.

2.4. Effect of CH₄ Concentration on CO₂ Conversion

The effect of the initial CH₄ concentration on the production of CH₄ from CO₂ in biogas is shown in Figure 6. As the CH₄ concentration increased from 0% to 16.8%, CO₂ conversion and CH₄ production decreased. According to Le Chatelier's principle, if CH₄ is present among the reactants, CO₂ conversion to CH₄ is hindered after equilibrium is attained, and thus an increase in the initial concentration of CH₄ decreases CH₄ production. Therefore, CH₄ production decreases at a higher rate than the increase in the overall flow as the concentration of CH₄ increases. Based on a simulation study, Jürgensen [49] found that CO₂ conversion decreases as the initial CH₄ concentration increases. H₂ conversion showed minimal changes, indicating that it is essentially unaffected by the initial CH₄ concentration.



Figure 6. Effect of initial CH₄ concentration on CO₂ and H₂ conversion and CH₄ selectivity.

2.5. Effect of CO₂ Concentration, H₂/CO₂ Ratio and GHSV on CH₄ Productivity and Product

Effect of CO₂ concentration, H_2/CO_2 ratio, and GHSV on CH₄ productivity and product at 350 °C are shown in Figures 7–9, respectively. As mentioned before, the increase in the CO₂ reactant not only increases the CO₂ conversion rate but also increases the productivity and product due to the increase in reaction opportunity with a decrease in inert nitrogen. As shown in Figure 7, as the H_2/CO_2 ratio increased, H_2 conversion decreased, while the CH₄ product and productivity remained almost unchanged. It is important and necessary to find the optimization of the reaction from the above results. Figure 9 shows the effect of increasing GHSV on CH₄ productivity and product. As shown in Figure 9, as GHSV increased, H_2 conversion and CH₄ productivity slightly decreased, but CH₄ product increased. The CH₄ productivity and product were different, depending on the presence or absence of a reaction in the balance of N₂. In the reaction without N₂, CH₄ productivity and product decreased by 1.1% and increased by 0.37 mol.



Figure 7. Effect of CO₂ concentrations on the H₂ conversion and CH₄ production.(GHSV = 30,000/h, H₂/CO₂ = 4).



Figure 8. Effect of H_2/CO_2 ratio on the H_2 conversion and CH_4 production.(GHSV = 30,000/h).



Figure 9. Effect of GHSV on the CH_4 productivity and CH_4 products ($H_2/CO_2 = 4$).

2.6. Catalytic Activity and Stability Tests

The activity and stability of the catalyst were evaluated for approximately 130 h under a GHSV of 30,000/h, a temperature of 350 °C, and a CO₂ concentration of 16 vol% at H₂/CO₂ ratios of 3.3, 3.6, and 4.0 (Figure 10). The maximum CO₂ conversion and CH₄ selectivity were 72% and 95%, respectively, during the 130 h. During the test period of 130 hours for CO₂ methanation, almost no carbon was produced. These results confirm that the Ni-Mg-Al catalyst provides adequate activity and stability for CO₂ methanation.



Figure 10. The durability and activity test of the catalyst for 130 h.

3. Characterization of the Catalysts

3.1. Surface Area Analysis

The surface area, which is a critical catalyst property, was measured by the Brunauer– Emmett–Teller (BET) method using an ASAP 2020 Plus Physisorption instrument (Micromeritics Instrument Corporation, Norcross, GA, USA). The surface area, pore volume, and pore size of fresh (20 and 40 wt% Ni-Mg-Al) and spent (20 wt% Ni-Mg-Al, 200 h of use) catalysts are presented in Table 2. Evidently, the BET surface area decreased as the Ni content increased, and the surface area, pore volume, and pore size of the spent catalysts were lower than those of the fresh catalysts. It is thought to be due to catalyst agglomeration and pore breakage through reduction and reaction.

Ni Ca	italyst	BET (m ² /g)	Total Pore Volume (m ³ /g)	Pore Size (Å)
* 20	fresh	180.3	0.36	81.5
(wt%)	spent	148.9	0.30	81.1
40	fresh	155.8	0.31	77.4
(wt%)	spent	107.8	0.32	82.4
60	fresh	140.9	0.32	91.5
(wt%)	spent	110.8	0.23	85.9

Table 2. BET specific surface area, pore volume, and pore size of Ni-Mg-Al catalysts containing different proportions of Ni before (fresh) and after (spent) experiments.

* 20 wt%, 40 wt% data was cited reference [41].

3.2. H_2 -Temperature Programmed Reduction (TPR) and H_2 -Chemisorption Analyses

The results of H₂-TPR analysis before and after reduction of the 20, 40, and 60 wt% Ni-Mg-Al catalysts at 600 °C using an Auto Chem II 2920 chemisorption analyzer are shown in Figures 11a and 11b, respectively. Two peaks are observed in the low-temperature (<200 °C) and near-high-temperature (700 °C) regions, with the latter being substantially larger. The larger peak is attributed to a higher H₂ concentration because of the higher Ni proportion, and it shifted toward lower temperatures. Conversely, in Figure 11b, only one peak is visible between 150–180 °C, demonstrating the complete reduction of the catalysts in the reactor. The peak observed for the spent catalyst is smaller than that for the same catalyst before the reduction. The temperature associated with peaks decreases as the proportion of Ni increases, which indicates improved reducibility. The low-temperature behavior observed during the reduction of the catalysts suggests the presence of some amorphous substances or decreased interaction because of the strongly reducing MgO. These observations were consistent with those obtained by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) (see below).



Figure 11. H₂-TPR profiles of (**a**) fresh and (**b**) spent catalysts (* reference [41] was cited).

The Ni dispersion, particle size, and turnover frequency (TOF) of the 20, 40, and 60 wt% Ni-Mg-Al catalysts at 250 °C measured through H₂-chemisorption analysis are presented in Table 3. As the Ni content increases, the Ni dispersion increased slightly and then decreased slightly. According to many researchers [50], increasing the catalyst content tends to significantly decrease the dispersion of Ni, but in this paper the dispersion of the catalyst is maintained uniformly. The strong interaction between MgO and Ni-species appears to maintain the formation of well-dispersed small Ni particles [51–54]. In addition, the increase in TOF value is consistent with the activity test results. The particle size remained quite stable (28.3–29.6 nm). The increases were the most pronounced at the highest proportion of Ni (60 wt%) because of the higher reactivity of the catalyst.

Ni Catalyst	Ni Dispersion (%)	Ni Particle Size (nm)	TOF (s $^{-1}$)
20 wt% *	3.57	28.3	0.01093
40 wt% *	3.68	27.5	0.02366
60 wt%	3.42	29.6	0.02593

Table 3. Ni dispersion, particle size, and TOF for the 20, 40, and 60 wt% Ni-Mg-Al catalysts.

* Reference [41] was cited.

3.3. XRD Analysis

The elemental composition of the catalysts was determined with an X-ray diffractometer. The catalyst powder samples were heated at 250 °C for 5 h to remove moisture, and the catalyst crystals were analyzed. Cu-K α radiation was used to fix the axis of the sample, and measurements were performed at 30 mA and 40 kV over a 2 θ range of 10–80°. The XRD analysis results of the catalytic supports and Ni catalysts before and after the reaction are shown in Figure 12. The fresh catalysts (Figure 12a–c) produced no Ni peaks but rather were characterized by NiO peaks, whereas Ni peaks were evident in the patterns of the spent catalysts (Figure 12d–f). The Ni peaks (37.4°, 44.7°, 51.7°, and 76.3°), gamma Al₂O₃ diffraction peaks (39.5°, 46.1°, and 66.9°), and MgO were observed at 37.2°, 43.2°, and 62.4° (JCPDS No.04-0850). As the Ni loading was increased, the intensity of metallic Ni peaks increased (51.7° and 76.3°) [55]. The XRD MgO peak overlapped with the NiO and Al₂O₃ peaks, making it difficult to distinguish them, and no difference was found except for the intensity of the MgO peak before and after the reaction.





Figure 12. XRD patterns of fresh Ni-Mg-Al catalysts (a) 20 wt% Ni (b) 40 wt% Ni, or (c) 60 wt% Ni and spent catalysts (d) 20 wt% Ni (e) 40 wt% Ni, or (f) 60 wt% Ni ((A) fresh, (B) spent)(* reference [41] was cited).

3.4. XPS Analysis

An X-ray photoelectron spectrometer (Thermo Scientific, Waltham, MA, USA, K-Alpha plus model) was used to determine binding energy (BE) values, which were used to evaluate the oxidation states of the catalysts. BE values for fresh and spent catalysts without pre-treatment measured under vacuum using Al-K α (50 mV) radiation are shown in Figure 13. The oxidation states of Ni can be determined from the BE of the XPS Ni2p3/2, which varies 855 to 856 eV for NiO, 852.3 to 852.6 eV for metallic Ni and 861.5 to 865.6 for Ni(OH)₂. All of the catalyst were calcined in the presence of atmospheric air, and humidity could be formed Ni(OH)₂. As shown in Figure 13, the BE values in the fresh catalysts appeared mainly NiO and Ni(OH)₂. In the spent catalysts, in addition to NiO and Ni(OH)₂, metallic Ni emerged at 852.3 eV [56,57]. Metallic Ni was formed during reduction; however, this Ni species is stable and it can be easily oxidized when it is exposed to air, generating NiO and Ni(OH)₂.



Figure 13. Cont.



Figure 13. XPS patterns of fresh Ni-Mg-Al catalysts (**a**) 20 wt% Ni, (**b**) 40 wt% Ni, (**c**) 60 wt% Ni, (**d**) 60wt% Mg and spent catalysts (**e**) 20 wt% Ni, (**f**) 40 wt% Ni, and (**g**) 60 wt% Ni, (**h**) 60wt% Mg (* for 20 wt%, Reference [41] was cited.).

3.5. Transmission Electron Microscopy (TEM) Characterization

The metallic Ni particle size of the fresh and spent catalyst with 20, 40, and 60 wt% Ni were analyzed using a TEM. As shown in Figure 14a–f, the metallic Ni particles were suitably dispersed over the supports. The size of the Ni particle were approximately 27~32 nm, Which matched with the metallic Ni particle size obtained using the H₂ chemisorption. It can be confirmed that there is no change and no carbon deposition, when compared with the fresh catalyst.



(a)

Figure 14. Cont.



Figure 14. Cont.



0

10

15

20

Nanoparticle size, nm

30

Figure 14. TEM images of reduced Ni-Mg-Al catalysts (**a**) 20 wt%, (**b**) 40 wt%, (**c**) 60 wt% Ni and spent Ni-Mg-Al catalyst (**d**) 20 wt%, (**e**) 40 wt%, (**f**) 60 wt%.

SEM-energy-dispersive X-ray spectroscopy (EDX) was used to investigate the surface morphology of the catalysts and the dispersion of Ni. An APREO SEM system (FEI, Hillsboro, OR, USA) was used to acquire images of the catalyst samples prepared by removing powders and dust, drying at 120 °C for 1 h and coating with metal (Au) at a magnification of $20,000 \times$. Because of the decomposition of Mg(NO₃)₂·6H₂O to MgO at temperatures above 600 °C, spherical particles were uniformly dispersed, as has been previously reported [40].

The results of the elemental composition analysis of the catalysts using EDX are shown in Table 4. The contents of Ni, Mg, and Al metals in cross-sections of the catalysts are summarized. The EDX analysis data indicated that the actual Ni contents of the catalysts used in the experiment were close to the theoretical values of 20, 40, and 60 wt%.

Items	Ni (wt%)	Mg (wt%)	Al ₂ O ₃ (wt%)
20 wt%	15.9 (20)	3.2 (5)	79.8 (75)
40 wt%	36.8 (40)	2.0 (5)	61.2 (55)
60 wt%	41.5 (60)	1.0 (5)	57.5 (35)
(): theoretical amount			

Table 4. SEM-EDX analysis results for fresh Ni-Mg-Al catalysts.

(): theoretical amount

(f)

4. Experimental Methods

4.1. Methanation Reaction

 CO_2 methanation, which was proposed by Sabatier in 1902, is a high-pressure, lowtemperature process for efficiently converting CO_2 to CH_4 . In this process, hydrogen produced using a renewable energy source (e.g., solar) and CO_2 produced from biomass are reacted to produce CH_4 [38,39]. Because of the significant heat released (-165 kJ/mol) during the methanation process, CO_2 conversion and CH_4 selectivity decrease at temperatures above 627 °C. This is because, under such conditions, the change in Gibbs free energy is > 0, and thus CO_2 is produced through the reaction of CH_4 and H_2O [40]. In theory, to ensure high CO_2 conversion and CH_4 selectivity, the process requires a low temperature [58,59]. In addition, a catalyst with a high efficiency at a low temperature is required to ensure optimal catalytic activity.

The CO_2 methanation process can be divided into two steps. The first step involves the formation of carbonaceous intermediates through the reaction of CO_2 with the catalyst. In the second step, CH_4 is formed through the reaction of the carbonaceous intermediates on the catalyst surface with hydrogen species. Various reaction intermediates produced during

 CO_2 methanation have been reported [60]. CO, which is produced through the adsorption of CO_2 on the catalyst surface and subsequent decomposition, is reportedly the most likely intermediate during the methanation process [61]. The CO is then dissociated into C and O species, and the former is hydrogenated to produce CH_4 [62,63]. The CO_2 methanation process can be summarized as equations (1)–(3), with the reverse water gas shift (RWGS) reaction producing CO, which is then converted to CH_4 via CO methanation [64].

$$CO_2 + 4 H_2 \rightarrow CH_4 + H_2O$$
 $\Delta H = -165 \text{ kJ/mol}$ (1)

$$CO_2 + H_2 \rightarrow CO + H_2O$$
 $\Delta H = 42.1 \text{ kJ/mol}$ (2)

$$CO + 3 H_2 \rightarrow CH_4 + H_2O$$
 $\Delta H = -206 \text{ kJ/mol}$ (3)

In the CO₂ methanation process, the H_2/CO_2 ratio required for CH₄ production is 4, and the reaction occurs at temperatures above 250 °C. Although the RWGS reaction is endothermic, it occurs more readily than the methanation reaction at temperatures above 350 °C because of its low enthalpy. However, because the CO methanation reaction is exothermic and its enthalpy is very high, the overall CO₂ methanation process is exothermic, which is disadvantageous for reaction at high temperatures. Therefore, a high-activity catalyst suitable for low-temperature reactions is desirable for CO₂ methanation.

4.2. Catalyst Synthesis and Experimentation

In the present study, Ni-Mg-Al catalysts characterized by a high activity and CH₄ affinity were utilized. The synthesis process is illustrated in Figure 15. The catalysts were synthesized by mixing Ni(NO₃)₂·6H₂O, Al(NO₃)₂·9H₂O and Mg(NO₃)₂·6H₂O, followed by stirring at 60 °C to produce catalysts with 20, 40, and 60 wt% Ni loadings. A precipitant was added to the mixture while maintaining a constant pH, and the solution was stirred for 1 h to induce precipitation. The precipitated catalyst precursor was repeatedly washed with distilled water and filtered using a press until the pH was approximately 7.0. The catalyst precursor was dried in an oven at 150 °C for 12 h and then heated at 600 °C for 4 h to obtain the 20, 40, and 60 wt% Ni-Mg-Al catalysts. The prepared catalyst is used as a reaction catalyst after raising the reduction temperature within 2 h, while flowing a mixed gas of 20% H₂ and 80% N₂ at 100 mL/min and maintaining it for 4 h. The CO₂ conversion significantly increased as the reduction temperature of the Ni-Mg-Al catalysts increased in the 450–700 °C range, while changes in the 600–700 °C range were minor [41]. Therefore, 700 °C was selected as the reduction temperature in the present study.



Figure 15. Block diagram of the process for synthesizing the Ni-catalyst used for CO₂ methanation.

The plug-flow system utilized as a reactor for experiments in the present study is shown in Figure 16. A temperature sensor was installed in the reactor, and an isothermal experiment was performed, while maintaining the reaction temperature with an error of \pm 1.0 °C by the PID controller under atmospheric conditions (1 bar). The catalyst (0.5 g) was layered on the bottom of the reactor and a mesh was installed to support this layer. A water trap at the outlet of the reactor served for the removal of water generated as a byproduct, and a check valve was installed to prevent the backflow of gas. The products from the reactor were characterized using a gas chromatography (GC) system (YL Instrument 6500, Youngin chromass, Anyang, Korea), which was equipped with an SS COL 10 ft 1/8" Matrix Porapak N (model: 13052-U) column with a 13X 45/60 mesh. The H₂, CH₄, and CO concentrations were measured using a thermal conductivity detector, while the CO_2 concentration was analyzed using a flame ionization detector with a CO_2 methanizer. For analyses, the GC oven was maintained at 35 °C for 6 min and then the temperature was raised to 170 °C at a ramp rate of 15 °C /min. Approximately 35 mL/min of H_2 and 300 mL/min of O_2 were injected into the flame ionization detector for analysis at 250 °C, while 35 and 20 mL/min of H_2 and Ar, respectively, were analyzed using the thermal conductivity detector at 150 °C.



① MFC ② Water pump ③ Line heater ④ Mixing chamber ⑤ Reactor ⑥ Catalyst bed ⑦ BPR ⑧ Water trap ⑨ Check Valve ⑩ G.C ⑪ Temperature sensor ⑫ Control panel

Figure 16. Schematic representation of the plug-flow system used for CO₂ methanation.

Experiments were conducted with a reactant gas flow rate of 250 mL/min, a reaction temperature of 350 °C, a GHSV of 30,000/h, and an H_2/CO_2 ratio of 4. Other parameters were varied as indicated in Table 5. The reaction temperature was varied between 200 °C and 450 °C and the GHSV between 10,000 and 50,000/h at different H_2/CO_2 ratios to evaluate their effects on CO_2 and H_2 conversion. The H_2/CO_2 ratio was adjusted with the balance gas N_2 . The effect of the initial CH_4 concentration (0%~16.8%) of biogas was investigated by CO_2 and H_2 conversion and CH_4 production.

 CO_2 conversion (X_{CO2}, %) [21], H₂ conversion (X_{H2}, %), CH₄ selectivity (S_{CH4}, %), CH₄ productivity (P_{CH4}, %), and product (mole) were calculated using Equations (4)–(8).

$$X_{CO2}(\%) = 1 - \frac{CO_{2,O}}{CH_{4,o} + CO_O + CO_{2,O}} \times 100$$
(4)

$$X_{CO2}(\%) = 1 - \frac{CO_{2,O}}{CH_{4,o} + CO_O + CO_{2,O}} \times 100$$
(5)

$$S_{CH4}(\%) = \frac{CH_4}{CH_4 + CO} \times 100$$
 (6)

$$P_{CH4}(\%) = \frac{CH_{4, product}}{CO_2 + H_2 + N_2 + (CH_4 \text{ or } CO)} \times 100$$
(7)

$$Product(mole) = CO_2(mole) \times X_{CO2} \times S_{CH4}$$
(8)

Table 5. Experimental conditions used for the methanation reaction.

Parameter	Conditions
Temperature (°C)	200~450
Pressure(bar)	1
GHSV (/h)	10,000~50,000
N2 (vol%)	Balance gas
CO ₂ (vol%)	6, 10, 16, 20
H _{2/} CO ₂	3.5, 4, 4.5, 5
CH4 (vol%)	0, 6.3, 10.8, 16.8

5. Conclusions

In the present study, CO_2 methanation experiments were conducted over a Ni-Mg-Al catalyst to produce CH_4 from biogas. The following results were obtained through experiments on the effect of catalyst reduction temperature, catalyst content, initial CH_4 concentration in biogas, CO_2 concentration, GHSV, and H_2/CO_2 ratio on CH_4 production.

(1) As the reaction temperature increased, the CO₂ conversion rate increased and then decreased after 400 °C. The highest CH₄ selectivity and yield were obtained at approximately 350 °C. CO₂ conversion decreased at temperatures above 400 °C because of the thermodynamic equilibrium limitation, while CH₄ selectivity decreased at temperatures above 350 °C because of the RWGS reaction. These processes suppressed the methanation reaction and thus increased the amount of CO generated. The activation energy obtained for the methanation process in the present study was 59.7 kJ/mol;

(2) As the Ni content increased, the CO₂ conversion rate, H₂ conversion rate, and CH₄ product increased. A CO₂ conversion of 72% and H₂ conversion of 45% were obtained using the catalyst containing 60 wt% Ni. This is because the Ni active sites increased as the Ni content increased and the Ni dispersion was well maintained uniformly; this was consistent with the increase in active Ni sites revealed by XRD analysis and the increase in TOF values, which reflect the reactivity;

(3) An increase in the initial CH_4 concentration in the biogas from 0 to 16.8 vol% decreased CO_2 conversion by 20%. This behavior is explained by Le Chatelier's principle, where the conversion to CH_4 is suppressed because of the initial CH_4 among the reactants;

(4) As CO₂ concentration in the reaction gas increased, H₂ conversion, CH₄ productivity and product increased. As the H₂/CO₂ ratio increased, H₂ conversion decreased, while CH₄ productivity and product increased slightly. As GHSV increased, H₂ and CH₄ productivity decreased slightly, while CH₄ product increased with or without N₂;

(5) A stability test of CO_2 methanation over the Ni-Mg-Al catalyst containing 60 wt% Ni conducted at 350 °C for 130 h revealed a constant CO_2 conversion and CH_4 selectivity of 71% and 95%, respectively. These results demonstrated that the catalyst has good stability during CO_2 methanation.

Author Contributions: Data curation: D.H.; investigation and writing—original draft: D.H.; writing—review and editing: Y.B. and D.H.; funding acquisition: W.C., validation: W.C. and Y.B.; supervision: Y.B. All authors have read and agreed to the published version of the manuscript.

Funding: This study was conducted with the support of the Korea Institute of Planning and Evaluation for Technology in Food, Agriculture, and Forest (IPET) and the Korean government (Ministry of Agriculture, Feed and Rural Affairs, 2021, grant No. 421038-03, Development of energy high-efficiency circulation and CO_2 from fuel cell and carbon capture utilization for smart farm research

project). Further, this study received support from the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Korean government (Ministry of Trade, Industry and Energy, 2021, grant No. 20213030040270, Development and demonstration of hydrogen production process based on waste plastic non-oxidative pyrolysis).

Data Availability Statement: Not applicable.

Acknowledgments: We are grateful to Eun-Duk Park, a professor of chemical engineering at Ajou University, for help with the catalyst analysis and to Myeong-won Seo of the Korea Institute of Energy Research (KIER) for providing the catalyst.

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

References

- 1. Gac, W.; Zawadzki, W.; Słowik, G.; Sienkiewicz, A.; Kierys, A. Nickel catalysts supported on silica microspheres for CO₂ methanation. *Microporous Mesoporous Mater.* **2018**, 272, 79–91. [CrossRef]
- Zhang, G.; Liu, J.; Xu, Y.; Sun, Y. A review of CH₄CO₂ reforming to synthesis gas over Ni-based catalysts in recent years (2010–2017). *Int. J. Hydrogen Energy* 2018, 43, 15030–15054. [CrossRef]
- Li, W.; Liu, Y.; Mu, M.; Ding, F.; Liu, Z.; Guo, X.; Song, C. Organic acid-assisted preparation of highly dispersed Co/ZrO₂ catalysts with superior activity for CO₂ methanation. *Appl. Catal. B Environ.* 2019, 254, 531–540. [CrossRef]
- Bian, Z.; Chan, Y.M.; Yu, Y.; Kawi, S. Morphology dependence of catalytic properties of Ni/CeO₂ for CO₂ methanation: A kinetic and mechanism study. *Catal. Today* 2020, 347, 31–38. [CrossRef]
- Benson, E.E.; Kubiak, C.P.; Sathrum, A.J.; Smieja, J.M. Electrocatalytic and homogeneous approaches to conversion of CO₂ to liquid fuels. *Chem. Soc. Rev.* 2009, *38*, 89–99. [CrossRef]
- Solis-Garcia, A.; Louvier-Hernandez, J.F.; Almendarez-Camarillo, A.; Fierro-Gonzalez, J. Participation of surface bicarbonate, formate and methoxy species in the carbon dioxide methanation catalyzed by ZrO₂-supported Ni. *Appl. Catal. B Environ.* 2017, 218, 611–620. [CrossRef]
- Gnanakumar, E.S.; Chandran, N.; Kozhevnikov, I.V.; Grau-Atienza, A.; Fernández, E.V.R.; Sepulveda-Escribano, A.; Shiju, N.R. Highly efficient nickel-niobia composite catalysts for hydrogenation of CO₂ to methane. *Chem. Eng. Sci.* 2019, 194, 2–9. [CrossRef]
- 8. Panagiotopoulou, P. Hydrogenation of CO₂ over supported noble metal catalysts. Appl. Catal. A Gen. 2017, 542, 63–70. [CrossRef]
- Chai, S.; Men, Y.; Wang, J.; Liu, S.; Song, Q.; An, W.; Kolb, G. Boosting CO₂ methanation activity on Ru/TiO₂ catalysts by exposing (001) facets of anatase TiO₂. J. CO₂ Util. 2019, 33, 242–252. [CrossRef]
- 10. Li, W.; Nie, X.; Jiang, X.; Zhang, A.; Ding, F.; Liu, M.; Liu, Z.; Guo, X.; Song, C. ZrO₂ support imparts superior activity and stability of Co catalysts for CO₂ methanation. *Appl. Catal. B Environ.* **2018**, *220*, 397–408. [CrossRef]
- Liu, H.; Xu, S.; Zhou, G.; Xiong, K.; Jiao, Z.; Wang, S. CO₂ hydrogenation to methane over Co/KIT-6 catalysts: Effect of Co content. *Fuel* 2018, 217, 570–576. [CrossRef]
- 12. Veselovskaya, J.V.; Parunin, P.D.; Netskina, O.V.; Kibis, L.S.; Lysikov, A.I.; Okunev, A.G. Catalytic methanation of carbon dioxide captured from ambient air. *Energy* **2018**, *159*, 766–773. [CrossRef]
- Siakavelas, G.I.; Charisiou, N.D.; AlKhoori, A.; AlKhoori, S.; Sebastian, V.; Hinder, S.J.; Baker, M.A.; Yentekakis, I.V.; Polychronopoulou, K.; Goula, M.A. Highly selective and stable Ni/La-M (M=Sm, Pr, and Mg)-CeO₂ catalysts for CO₂ methanation. *J.* CO₂ Util. 2021, 51, 101618. [CrossRef]
- 14. Ahmad, W.; Younis, M.N.; Shawabkeh, R.; Ahmed, S. Synthesis of lanthanide series (La, Ce, Pr, Eu & Gd) promoted Ni/γ-Al₂O₃ catalysts for methanation of CO₂ at low temperature under atmospheric pressure. *Catal. Commun.* **2017**, *100*, 121–126.
- 15. Ferreira, A.C.; Branco, J.B. Methanation of CO₂ over nanostructured nickel-4f block element bimetallic oxides. *Int. J. Hydrogen Energy* **2019**, *44*, 6505–6513. [CrossRef]
- Li, S.; Liu, G.; Zhang, S.; An, K.; Ma, Z.; Wang, L.; Liu, Y. Cerium-modified Ni-La₂O₃/ZrO₂ for CO₂ methanation. *J. Energy Chem.* 2020, 43, 155–164. [CrossRef]
- Ye, R.-P.; Gong, W.; Sun, Z.; Sheng, Q.; Shi, X.; Wang, T.; Yao, Y.; Razink, J.J.; Lin, L.; Zhou, Z.; et al. Enhanced stability of Ni/SiO₂ catalyst for CO₂ methanation: Derived from nickel phyllosilicate with strong metal-support interactions. *Energy* 2019, 188, 116059. [CrossRef]
- 18. Bacariza, M.C.; Graça, I.; Bebiano, S.S.; Lopes, J.M.; Henriques, C. Micro- and mesoporous supports for CO₂ methanation catalysts: A comparison between SBA-15, MCM-41 and USY zeolite. *Chem. Eng. Sci.* **2018**, 175, 72–83. [CrossRef]
- 19. Liu, W.; Li, L.; Zhang, X.; Wang, Z.; Wang, X.; Peng, H. Design of Ni-ZrO₂@SiO₂ catalyst with ultra-high sintering and coking resistance for dry reforming of methane to prepare syngas. *J. CO*₂ *Util.* **2018**, *27*, 297–307. [CrossRef]
- Romero-Sáez, M.; Dongil, A.; Benito, N.; Espinoza-González, R.; Escalona, N.; Gracia, F. CO₂ methanation over nickel-ZrO₂ catalyst supported on carbon nanotubes: A comparison between two impregnation strategies. *Appl. Catal. B Environ.* 2018, 237, 817–825. [CrossRef]
- 21. Ocampo, F.; Louis, B.; Kiwi-Minsker, L.; Roger, A.-C. Effect of Ce/Zr composition and noble metal promotion on nickel based CexZr₁-xO₂ catalysts for carbon dioxide methanation. *Appl. Catal. A Gen.* **2011**, *392*, 36–44. [CrossRef]

- 22. Garbarino, G.; Wang, C.; Cavattoni, T.; Finocchio, E.; Riani, P.; Flytzani-Stephanopoulos, M.; Busca, G. A study of Ni/La-Al₂O₃ catalysts: A competitive system for CO₂ methanation. *Appl. Catal. B Environ.* **2019**, 248, 286–297. [CrossRef]
- Tada, S.; Shimizu, T.; Kameyama, H.; Haneda, T.; Kikuchi, R. Ni/CeO₂ catalysts with high CO₂ methanation activity and high CH₄ selectivity at low temperatures. *Int. J. Hydrogen Energy* 2012, *37*, 5527–5531. [CrossRef]
- Löfberg, A.; Guerrero-Caballero, J.; Kane, T.; Rubbens, A.; Jalowiecki-Duhamel, L. Ni/CeO₂ based catalysts as oxygen vectors for the chemical looping dry reforming of methane for syngas production. *Appl. Catal. B Environ.* 2017, 212, 159–174. [CrossRef]
- 25. Ratchahat, S.; Sudoh, M.; Suzuki, Y.; Kawasaki, W.; Watanabe, R.; Fukuhara, C. Development of a powerful CO₂ methanation process using a structured Ni/CeO₂ catalyst. *J. CO₂ Util.* **2018**, *24*, 210–219. [CrossRef]
- Yan, X.; Hu, T.; Liu, P.; Li, S.; Zhao, B.; Zhang, Q.; Jiao, W.; Chen, S.; Wang, P.; Lu, J.; et al. Highly efficient and stable Ni/CeO₂-SiO₂ catalyst for dry reforming of methane: Effect of interfacial structure of Ni/CeO₂ on SiO₂. *Appl. Catal. B Environ.* 2019, 246, 221–231. [CrossRef]
- 27. Akbari, E.; Alavi, S.M.; Rezaei, M. CeO₂ Promoted Ni-MgO-Al₂O₃ nanocatalysts for carbon dioxide reforming of methane. *J. CO₂ Util.* **2018**, *24*, 128–138. [CrossRef]
- 28. Ray, K.; Bhardwaj, R.; Singh, B.; Deo, G. Developing descriptors for CO₂ methanation and CO₂ reforming of CH₄ over Al₂O₃ supported Ni and low-cost Ni based alloy catalysts. *Phys. Chem. Chem. Phys.* **2018**, 20, 15939–15950. [CrossRef]
- Ahn, J.Y.; Chang, S.W.; Lee, S.M.; Kim, S.S.; Chung, W.J.; Lee, J.C.; Cho, Y.J.; Shin, K.S.; Moon, D.H.; Nguyen, D.D. Developing Ni-based honeycomb-type catalysts using different binary oxide-supported species for synergistically enhanced CO₂ methanation activity. *Fuel* 2019, 250, 277–284. [CrossRef]
- Moghaddam, S.V.; Rezaei, M.; Meshkani, F.; Daroughegi, R. Carbon dioxide methanation over Ni-M/Al₂O₃ (M: Fe, CO, Zr, La and Cu) catalysts synthesized using the one-pot sol-gel synthesis method. *Int. J. Hydrogen Energy* 2018, 43, 16522–16533. [CrossRef]
- Stangeland, K.; Kalai, D.; Li, H.; Yu, Z. CO₂ Methanation: The Effect of Catalysts and Reaction Conditions. *Energy Procedia* 2017, 105, 2022–2027. [CrossRef]
- 32. Aziz, M.A.A.; Jalil, A.A.; Triwahyono, S.; Ahmad, A. CO₂ methanation over heterogeneous catalysts: Recent progress and future prospects. *Green Chem.* **2015**, *17*, 2647–2663. [CrossRef]
- 33. Guo, M.; Lu, G. The effect of impregnation strategy on structural characters and CO₂ methanation properties over MgO modified Ni/SiO₂ catalysts. *Catal. Commun.* **2014**, *54*, 55–60. [CrossRef]
- Tan, J.; Wang, J.; Zhang, Z.; Ma, Z.; Wang, L.; Liu, Y. Highly dispersed and stable Ni nanoparticles confined by MgO on ZrO₂ for CO₂ methanation. *Appl. Surf. Sci.* 2019, 481, 1538–1548. [CrossRef]
- Al-Fatesh, A.S.; Abu-Dahrieh, J.K.; Atia, H.; Armbruster, U.; Ibrahim, A.A.; Khan, W.U.; Abasaeed, A.E.; Fakeeha, A.H. Effect of pre-treatment and calcination temperature on Al₂O₃-ZrO₂ supported Ni-Co catalysts for dry reforming of methane. *Int. J. Hydrogen Energy* 2019, 44, 21546–21558. [CrossRef]
- 36. Feng, X.; Feng, J.; Li, W. Insight into MgO promoter with low concentration for the carbon-deposition resistance of Ni-based catalysts in the CO₂ reforming of CH₄. *Chin. J. Catal.* **2018**, *39*, 88–98. [CrossRef]
- Vázquez, F.V.; Kihlman, J.; Mylvaganam, A.; Simell, P.; Koskinen-Soivi, M.-L.; Alopaeus, V. Modeling of nickel-based hydrotalcite catalyst coated on heat exchanger reactors for CO₂ methanation. *Chem. Eng. J.* 2018, 349, 694–707. [CrossRef]
- Su, X.; Xu, J.; Liang, B.; Duan, H.; Hou, B.; Huang, Y. Catalytic carbon dioxide hydrogenation to methane: A review of recent studies. J. Energy Chem. 2016, 25, 553–565. [CrossRef]
- Champon, I.; Bengaouer, A.; Chaise, A.; Thomas, S.; Roger, A.-C. Carbon dioxide methanation kinetic model on a commercial Ni/Al₂O₃ catalyst. J. CO₂ Util. 2019, 34, 256–265. [CrossRef]
- 40. Hu, F.; Tong, S.; Lu, K.; Chen, C.-M.; Su, F.-Y.; Zhou, J.; Lu, Z.-H.; Wang, X.; Feng, G.; Zhang, R. Reduced graphene oxide supported Ni-Ce catalysts for CO₂ methanation: The support and ceria promotion effects. *J.* CO₂ *Util.* **2019**, *34*, 676–687. [CrossRef]
- Han, D.; Kim, Y.; Byun, H.; Cho, W.; Baek, Y. CO₂ Methanation of Biogas over 20 wt% Ni-Mg-Al Catalyst: On the Effect of N₂, CH₄, and O₂ on CO₂ Conversion Rate. *Catalysts* 2020, *10*, 1201. [CrossRef]
- Wierzbicki, D.; Baran, R.; Debek, R.; Motak, M.; Grzybek, T.; Gálvez, M.E.; Da Costa, P. The influence of nickel content on the performance of hydrotalcite-derived catalysts in CO₂ methanation reaction. *Int. J. Hydrogen Energy* 2017, 42, 23548–23555. [CrossRef]
- Zhang, Z.; Tian, Y.; Zhang, L.; Hu, S.; Xiang, J.; Wang, Y.; Xu, L.; Liu, Q.; Zhang, S.; Hu, X. Impacts of nickel loading on properties, catalytic behaviors of Ni/γ–Al₂O₃ catalysts and the reaction intermediates formed in methanation of CO₂. *Int. J. Hydrogen Energy* 2019, 44, 9291–9306. [CrossRef]
- Quindimil, A.; De-La-Torre, U.; Pereda-Ayo, B.; Davó-Quiñonero, A.; Bailón-García, E.; Lozano-Castelló, D.; González-Marcos, J.A.; Bueno-López, A.; González-Velasco, J.R. Effect of metal loading on the CO₂ methanation: A comparison between alumina supported Ni and Ru catalysts. *Catal. Today* 2019, 356, 419–432. [CrossRef]
- 45. Mutz, B.; Carvalho, H.W.; Mangold, S.; Kleist, W.; Grunwaldt, J.-D. Methanation of CO₂: Structural response of a Ni-based catalyst under fluctuating reaction conditions unraveled by operando spectroscopy. *J. Catal.* **2015**, 327, 48–53. [CrossRef]
- 46. Peymani, M.; Alavi, S.M.; Rezaei, M. Synthesis Gas Production by Catalytic Partial Oxidation of Propane on Mesoporous Nanocrystalline Ni/Al₂O₃Catalysts. *Appl. Catal. A Gen.* **2017**, *529*, 1–9. [CrossRef]
- 47. Jia, X.; Zhang, X.; Rui, N.; Hu, X.; Liu, C. Structural effect of Ni/ZrO₂ catalyst on CO₂ methanation with enhanced activity. *Appl. Catal. B Environ.* **2019**, 244, 159–169. [CrossRef]

- Dannesboe, C.; Hansen, J.B.; Johannsen, I. Catalytic methanation of CO₂ in biogas: Experimental results from a reactor at full scale. *React. Chem. Eng.* 2020, *5*, 183–189. [CrossRef]
- Jürgensen, L.; Ehimen, E.A.; Born, J.; BoHolm-Nielsena, J. Dynamic biogas upgrading based on the Sabatier process: Thermodynamic and dynamic process simulation. *Bioresour. Technol.* 2015, 178, 323–329. [CrossRef]
- Jaffar, M.M.; Nahil, M.A.; Williams, P.T. Parametric study of CO₂ methanation for synthetic natural gas production. *Energy Technol.* 2019, 7, 1900795. [CrossRef]
- Erdöhelyi, A.; Pásztor, M.; Solymosi, F. Catalytic hydrogenation of CO₂ over supported palladium. J. Catal. 1986, 98, 166–177. [CrossRef]
- 52. Agnelli, M.; Kolb, M.; Mirodatos, C. Co Hydrogenation on a Nickel Catalyst: 1. Kinetics and Modeling of a Low-Temperature Sintering Process. J. Catal. 1994, 148, 9–21. [CrossRef]
- Tan, M.; Wang, X.; Wang, X.; Zou, X.; Ding, W.; Lu, X. Influence of calcination temperature on textural and structural properties, reducibility, and catalytic behavior of mesoporous γ-alumina-supported Ni–Mg oxides by one-pot template-free route. *J. Catal.* 2015, 329, 151–166. [CrossRef]
- 54. Nakayama, T.; Ichikuni, N.; Sato, S.; Nozaki, F. Ni/Mgo catalyst prepared using citric acid for hydrogenation of carbon dioxide. *Appl. Catal. A Gen.* **1997**, *158*, 185–199. [CrossRef]
- Carbarino, G.; Riani, P.; Magistri, L.; Busca, G. A study of the methanation of carbon dioxide on Ni/Al₂O₃ catalysts at atmospheric pressure. *Int. J. Hydrogen Energy* 2014, 39, 11557–11565. [CrossRef]
- Song, F.; Zhong, Q.; Yu, Y.; Shi, M.; Wu, Y.; Hu, J.; Song, Y. Obtaining well-dispersed Ni/Al₂O₃ catalyst for CO₂ methanation with a microwave-assisted method. *Int. J. Hydrogen Energy* 2017, *42*, 4174–4183. [CrossRef]
- 57. Biesinger, M.C.; Payne, B.P.; Lau, L.W.M.; Gerson, A.; Smart, R.S.C. X-ray photoelectron spectroscopic chemical state quantification of mixed nickel metal, oxide and hydroxide systems. *Surf. Interface Anal.* **2009**, *41*, 324–332. [CrossRef]
- Jiang, H.; Gao, Q.; Wang, S.; Chen, Y.; Zhang, M. The synergistic effect of Pd NPs and UiO-66 for enhanced activity of carbon dioxide methanation. J. CO₂ Util. 2019, 31, 167–172. [CrossRef]
- Ou, Z.; Qin, C.; Niu, J.; Zhang, L.; Ran, J. A comprehensive DFT study of CO₂ catalytic conversion by H₂ over Pt-doped Ni catalysts. *Int. J. Hydrogen Energy* 2018, 44, 819–834. [CrossRef]
- Lim, J.Y.; McGregor, J.; Sederman, A.; Dennis, J. Kinetic studies of CO₂ methanation over a Ni/γ-Al₂O₃ catalyst using a batch reactor. *Chem. Eng. Sci.* 2016, 141, 28–45. [CrossRef]
- 61. Westermann, A.; Azambre, B.; Bacariza, M.C.; Graça, I.; Ribeiro, M.F.; Lopes, J.M.; Henriques, C. Insight into CO₂ methanation mechanism over NiUSY zeolites: An operando IR study. *Appl. Catal. B Environ.* **2015**, *174–175*, 120–125. [CrossRef]
- Miguel, C.; Mendes, A.; Madeira, L. Intrinsic kinetics of CO₂ methanation over an industrial nickel-based catalyst. *J. CO₂ Util.* 2018, 25, 128–136. [CrossRef]
- 63. Li, Y.; Zhang, H.; Zhang, L.; Zhang, H. Bimetallic Ni–Pd/SBA-15 alloy as an effective catalyst for selective hydrogenation of CO₂ to methane. *Int. J. Hydrogen Energy* **2019**, *44*, 13354–13363. [CrossRef]
- Li, W.; Wang, H.; Jiang, X.; Zhu, J.; Liu, Z.; Guo, X.; Song, C. A short review of recent advances in CO₂ hydrogenation to hydrocarbons over heterogeneous catalysts. *RSC Adv.* 2018, *8*, 7651–7669. [CrossRef]