Low-Rank Coal Supported Ni Catalysts for CO₂ Methanation

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Abstract: As renewable energy source integration increases, P2G technology that can store surplus renewable power as methane is expected to expand. The development of a CO₂ methanation catalyst, one of the core processes of the P2G concept, is being actively conducted. In this work, low-rank coal (LRC) was used as a catalyst support for CO₂ methanation, as it can potentially enhance the diffusion and adsorption behavior by easily controlling the pore structure and composition. It can also improve the process efficiency owing to its simplicity (no pre-reduction step) and high thermal conductivity, compared to conventional metal oxide-supported catalysts. A screening of single metals (Ni, Co, Ru, Rh, and Pd) on LRC was performed, which showed that Ni was the most active. When Ni on the LRC catalyst was doped with a promoter (Ce and Mg), the CO₂ conversion percentage increased by >10% compared to that of the single Ni catalyst. When the CO₂ methanation activity was compared at 250–500 °C, the Ce-doped Ni/Eco and Mg-doped Ni/Eco catalysts showed similar or better activity than the commercial metal oxide-supported catalyst. In addition, the catalytic performance remained stable even after the test for an extended time (~200 h). The results of XRD, TEM, and TPR showed that highly efficient LRC-based CO₂ methanation catalysts can be made when the metal dispersion and composition are modified.

Keywords: carbon support; CO₂ methanation; low-rank coal; nickel; ceria; magnesia

1. Introduction

Worldwide efforts are being made to develop sustainable energy systems that cope with the increase in energy consumption associated with anthropogenic CO₂ emissions. Renewable energy is of significant importance for achieving carbon neutrality, and power to gas (P2G) is attracting attention as a technology that complements the lack of grid stability caused by the use of renewables [1]. P2G can store surplus renewable energy in the form of methane and is expected to expand rapidly, as it can contribute to GHG reduction via the CO₂ utilization (CCU) through the combination of power and gas grids [2–5].

One of the core processes in P2G is CO₂ methanation (reaction of CO₂ and H₂), with large amounts of work conducted on this [6–12]. The development of catalysts that can promote high CO₂ conversion and high CH₄ selectivity has been actively attempted using Ni and Ru as active metals [13–20]. In exothermal CO₂ methanation, the stability of the catalysts is usually considered, and in order to ensure that, many studies have been conducted on catalyst supports with thermal stability and high surface area, such as Ni-MOF (metal-organic framework) on SiO₂ support, Ni/CoO₂ prepared by plasma decomposition, mesoporous ZrO₂-modified clays, MOF-derived Ru on nanosized ZrO₂, and modified mesoporous silica (MCM) supports [21–25]. However, the preparation of these samples requires a complex manufacturing process, which makes it difficult to scale-up. Instead, conventional metal oxide supports such as alumina and silica are usually used...
for commercialization. However, controlling their pore structure and surface composition is difficult, which limits the reaction enhancement in terms of diffusion and adsorption.

In contrast, the catalytic activity of carbon-based supports can be increased by relatively easy control of the pore structure and chemical composition. It can show high thermal efficiency in a scale-up reactor because of its high heat transfer rate. However, because it is oxidizable at elevated temperatures, its application is limited to reactions under reduced conditions, such as CO$_2$ methanation. Recently, several studies have been reported based on carbon-supported catalysts for CO$_2$ methanation, such as activated carbon (AC), biochar, and carbon nanotubes (CNTs) [26–29]. Ni on AC (Ni/AC) mixed with Rh/$\gamma$-Al$_2$O$_3$ and Ru (or Ni) on chemically modified activated biochar showed enhanced methane selectivity due to hydrogen adsorption by the support [26,28]. Alkali-metal-modified Fe on CNT supports showed high activity, comparable to the conventional oxide (Al$_2$O$_3$ and CeO$_2$) supports [30]. However, both AC and CNT lack heteroatoms that work as seeds for metal dispersion and provide a chemical variety, frequently inducing better activity [31]. In addition, the thermal stability of biochar is questionable when exposed to high temperatures for extended periods.

In this work, a CO$_2$ methanation catalyst was prepared using Indonesian low-rank coal (LRC), which contains many functional groups such as carboxyl, hydroxyl, ether, and amine. These functional groups enabled the nano-dispersion of active metals in the form of nanodots; therefore, deactivation due to sintering was expected to be minimal [32,33]. The BET surface area of LRC was increased by devolatilization upon heat treatment, and the generated pores can provide an improved diffusion pathway for reactants/products. In addition, LRC, which is composed of thousands of different polyaromatic hydrocarbons, exhibits heterogeneity by nature and, thus, structural discontinuity, resulting in many defect sites. These defects might lower the activation energy of hydrogen dissociation, which can minimize the delay in CO$_2$ hydrogenation [32].

In this study, the CO$_2$ methanation activity was evaluated after dispersing various metals on the LRC support, such as Ni, Ru, Co, Rd, and Pd, which have shown promising results [7,10,12,23]. Then, promoters were introduced into the system, and the catalyst behavior during the continuous run was tested. Furthermore, the physical and chemical properties of the catalyst were studied using BET analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM), and H$_2$ temperature-programmed reduction (TPR).

2. Experimental

2.1. Preparation of Catalysts

The catalyst support was prepared using Indonesia LRC (Eco), which was pulverized to 0.5–1.0 mm. Table 1 shows the proximate and ultimate analyses of Eco [34].

Table 1. Proximate and ultimate analysis of Low rank coal (LRC, Eco coal) (Data from reference [33]).

| Sample (wt.%) | Moisture | Volatile Matter * | Fixed Carbon * | Ash * | C ** | H ** | N ** | O ** | S ** |
|--------------|----------|------------------|---------------|-------|------|------|------|------|------|
| Eco          | 11.1     | 53.4             | 42.4          | 4.2   | 70.3 | 5.2  | 0.9  | 23.4 | 0.1  |

* dry basis, ** dry and ash-free basis.

The dispersion was performed using the incipient wetness impregnation (IWI) method. The metal precursor was then dissolved in distilled water. Eco was placed on a Petri dish and mixed with the precursor solution. They were mixed well for ~30 min and dried in an oven (~100 °C) overnight, followed by heat treatment at 650 °C (ramp rate = 30 °C/min) for 30 min in an N$_2$ atmosphere.

For single-metal screening, a metal (Ni, Co, Ru, Rh, or Pd) was dispersed in Eco. The metal precursors were Ni(NO$_3$)$_2$·6H$_2$O (Samchun Chemical Co., Ltd., Pyeongtaek-si, Korea), Co(NO$_3$)$_2$·6H$_2$O (Samchun Chemical Co., Ltd., Pyeongtaek-si, Korea), RuCl$_3$ (Samchun Chemical Co., Ltd., Pyeongtaek-si, Korea), Rh(NO$_3$)$_3$ solution (SNS Co., Ltd., Seoul, Korea), and Pd(NO$_3$)$_2$·2H$_2$O (Samchun Chemical Co., Ltd., Pyeongtaek-si, Korea).
The target loading (before heat treatment and metal basis) was 10 wt.% for Ni and Co, and 3 wt.% for Ru, Rh, and Pd, respectively. During heat treatment at 650 °C, devolatilization occurred, resulting in the weight loss of the Eco support; therefore, the actual metal loading was 70–100% higher than the target loading described above.

In order to study the effect of promoters such as Mg, Ce, Zr, La, Ca, Fe, and Mo, either Ni or Ru was dispersed by the IWI method and the promoter precursor solution was then added. Drying and heat treatment were performed under the same conditions as stated above. Mg(NO₃)₂·6H₂O (Samchun Chemical Co., Ltd., Pyeongtaek-si, Korea), Ce(NO₃)₃·6H₂O (Samchun Chemical Co., Ltd., Pyeongtaek-si, Korea), ZrO(NO₃)₂·2H₂O (Samchun Chemical Co., Ltd., Pyeongtaek-si, Korea), La(NO₃)₃·6H₂O (Samchun Chemical Co., Ltd., Pyeongtaek-si, Korea), Ca(NO₃)₂·4H₂O (Samchun Chemical Co., Ltd., Pyeongtaek-si, Korea), Fe(NO₃)₃·9H₂O (Samchun Chemical Co., Ltd., Pyeongtaek-si, Korea), and MoO₃ (Samchun Chemical Co., Ltd., Pyeongtaek-si, Korea) were used as precursors. Ni (target loading = 15 wt.%) as an active metal was co-dispersed with a promoter (target loading = 3 wt.% for Mg, Ce, Zr, La, and Ca, 5 wt.% for Fe and Mo, and 1 wt.% for Ru). Various Mg loadings (1, 3, 5, and 10 wt.%) were tested to determine the optimal amount of the promoter together with 15 wt.% Ni. In addition, Ru (target loading = 3 wt.%) was mixed with a promoter (target loading = 3 wt.% for Mg, Ce, Zr, La, and Ca, and 1 wt.% for Ni, Fe, and Mo). The catalysts were named by combining the target loading (before heat treatment and metal basis) and the metal used, such that 15-Ni indicated 15 wt.% Ni on Eco. However, for simplicity, only the names of metals were given for the promoter-doped Ni/Eco catalysts, where the metal loading was as stated above. For example, Ni-Ce indicates a catalyst containing 15 wt.% Ni and 3 wt.% Ce on the Eco support.

2.2. Evaluation of CO₂ Methanation Activity

For the initial screening of active metals and their combination with promoters (Figures 1 and 2), CO₂ methanation was performed in a fixed-bed tubular quartz reactor (OD = 13 mm) [33]. The catalyst powder (0.2 g) was placed on a frit placed in the middle of the tube. Pre-reduction was performed at 550 °C for 1 h with 5% H₂ at a flow rate of 50 cc/min. The activity was measured at 400 °C and 16,000/h (GHSV) with 4% H₂ and 1% CO₂. The reactant and product gases (H₂, CH₄, CO₂, and CO) were quantitatively analyzed using GC 7890 B (Agilent Technologies, USA) with a TCD detector. Carbon conversion and CH₄ selectivity were calculated as follows:

\[
\text{Carbon conversion (\%)} = \frac{\text{CO}_2\text{ in} - \text{CO}_2\text{ out}}{\text{CO}_2\text{ in}} \times 100, \tag{1}
\]

\[
\text{CH}_4\text{ selectivity (\%)} = \frac{\text{CH}_4\text{ out}}{\text{CH}_4\text{ out} + \text{CO out}} \times 100. \tag{2}
\]

![Figure 1](image-url)  
**Figure 1.** CO₂ methanation activity of (a) single metals and (b) effect of Mg loading amount on 15-Ni/Eco (400 °C, GHSV = 16,000 /h, with 4% H₂ and 1% CO₂).
The temperature dependence of the catalysts was compared with that of a commercial methanation catalyst (METH 134, Clariant) at 200–500 °C using a high-throughput catalyst testing rig [20]. The rig consists of 48 parallel reactors running simultaneously and this configuration enabled a long-term continuous test to be conducted on Ni-Ce (15 wt.% Ni and 3 wt.% Ce on Eco) and Ni-Mg (15 wt.% Ni and 3 wt.% Mg on Eco) (Figures 3 and 4) [20]. The following conditions were used: flow rate per reactor = 3.6 cc/min, WHSV = 8700 mL/h/g, and reactant concentration = 73% H₂, 18% CO₂, and 9% Ar. The parallel reactors were loaded with approximately 25 mg of catalyst samples in duplicate, i.e., each sample was tested in two different reactors for validation purposes and average values were obtained for catalytic performance indicators. The test was performed at constant temperature steps, each step was maintained for a period of 24 h, and the output gas concentrations for each reactor were measured at 6 h intervals. Overall, experiments covering 200–500 °C took ~200 h, which provided information about the long-term stability of the sample.

Figure 2. CO₂ methanation activity of (a) promoter-doped Ni/Eco and (b) promoter-doped Ru/Eco (400 °C, GHSV = 16,000 /h, 4% H₂ and 1% CO₂).

Figure 3. Temperature dependence of promoter-doped Ni/Eco catalysts for CO₂ methanation. (a) CO₂ conversion and (b) CH₄ selectivity (Flow rate 3.6 cc/min, WHSV = 8700 mL/h/g, 73% H₂, 18% CO₂, and 9% Ar).
Figure 4. Long-term stability of (a) Ni-Mg/Eco and (b) Ni-Ce/Eco. ((Flow rate 3.6 cc/min, WHSV = 8700 mL/h/g, 73% H\textsubscript{2}, 18% CO\textsubscript{2}, and 9% Ar).

2.3. Instrumental Analysis

The BET surface area was analyzed using ASAP 2420 V2.09 (Micromeritics, USA) and Autosorb IQ (Quantachrome, Boynton Beach, FL, USA). The chemical composition was characterized using D-Max 2500-PC XRD, Cu K\textsubscript{α1} wavelength (Rigaku, Tokyo, Japan). TEM images were obtained using a Tecnai G2-20 S-twin TEM (FEI Company, Hillsboro, OR, USA). H\textsubscript{2} temperature-programmed reduction (H\textsubscript{2} TPR) was performed using Belcat-Basic (BEL Inc., Osaka, Japan). The samples were pretreated with Ar (30 cc/min) at 150 °C for 30 min prior to the analysis, and then reduced using 10% H\textsubscript{2} in Ar (30 cc/min) as the temperature increased from 50 to 900 °C (10 °C/min ramp rate).

3. Results and Discussion

3.1. Metal Screening for CO\textsubscript{2} Methanation

Representative active metals for CO\textsubscript{2} methanation, such as Ni, Co, Ru, Rh, and Pd, were dispersed in Eco [35]. Among the metals, Ni showed the highest activity (~61% CO\textsubscript{2} conversion) at 400 °C, and the conversion decreased in the order of Co > Rh > Ru > Pd (Figure 1a).

Ni is most often used for CO\textsubscript{2} methanation owing to its high activity and low price [35]. Ru showed unexpectedly low conversion (<30%) when dispersed in carbonaceous LRC [13]. This was also the case for Rh and Pd, showing ~35% and ~10% conversion, respectively [36,37]. In this experiment, the metals were impregnated by the IWI method using an aqueous precursor solution. The penetration of the aqueous solution into the interior pores of the LRC support may be limited by the hydrophobic repulsion of the LRC. A large portion of metals would remain on the external surface of the LRC, degrading the activity [38]. The effect of solvent polarity on the metal dispersion seemed to matter, and one might expect better metal dispersion with less polar solvents.

Thermal degradation of Ni may occur because of hot spots generated by exothermic CO\textsubscript{2} methanation. Many efforts have been made to develop a support with a high surface area and thermal stability that can maintain high activity for a long time [39–45]. Conventional carbon materials such as activated carbon and carbon black are thermally stable with regard to their chemical composition and structure [46]. However, LRC support that is composed of a lot of volatile matter containing heteroatomic (O, H, and N) molecules might lose relatively small molecules, accompanying the change in the carbon structure [40]. Therefore, the LRC-supported catalysts were calcined at a relatively high temperature (~650 °C) to minimize the effect of devolatilization in this work.

To evaluate the influence of promoter loading on the Ni/Eco catalyst, the activity was evaluated by varying the amount of Mg dopant. As shown in Figure 1b, Ni/Eco showed the highest activity when 3 wt.% Mg was added. A solid solution of NiO-MgO is
known to occur when Mg loading is high, and the availability of active metallic Ni may decrease [47]. Accordingly, the screening of the promoter for Ni/Eco was studied mostly with the addition of 3 wt.% dopants.

The CO\textsubscript{2} conversion percentage of Ni/Eco was evaluated after 3–5 wt.% impregnation of Mg, Ce, Zr, La, Ca, Ru, Fe, and Mo (Figure 2a).

Relatively high activity (~70% conversion) was observed with Mg and Ce doping, followed by Zr and La (~65%). However, the conversion was less than 60% when doped with Ca, Fe, and Mo. When Ru was mixed with Ni, the activity decreased significantly, giving only ~38% conversion. It is known that CO\textsubscript{2} methanation usually proceeds through either CO formation or formate formation pathways, depending on the intrinsic properties of the catalyst [48,49]. Regardless of the reaction route, an active site for the adsorption and dissociation of H\textsubscript{2} and CO\textsubscript{2} is required. In general, Ni provides an active site for H\textsubscript{2} dissociation, and oxides of Ce, Mg, and Zr provide an active site (oxygen vacancy) for CO\textsubscript{2} dissociation [50]. LRC tends to be oxidized by taking oxygen from the surrounding metal oxides. Therefore, it might increase the number of oxygen vacancies in the promoter and, thus, CO\textsubscript{2} dissociation [48]. Moreover, it is known that CeO\textsubscript{2} and ZrO\textsubscript{2} can induce better Ni dispersion, and La\textsubscript{2}O\textsubscript{3} can increase the reducibility of Ni [51]. The interaction of inert carbon supports with metals is generally weak, and thus, uninterrupted interaction between the active metal (Ni) and the promoter is expected, which is probably different from that of a general metal oxide-supported system [52]. Further experiments were conducted using Ni-based catalysts, as they are advantageous in terms of activity and cost.

Ru supported on LRC (Ru/Eco) showed very different behavior from the doped Ni/Eco (Figure 2b). A significant increase in activity was observed for most of the doped samples. Conversion of 50–55% was obtained by the addition of Zr, La, and Ca and ~40% conversion by Mg and Ce. Ni, Fe, and Mo also showed relatively high conversion (38–45%) compared to Ru only (<30%).

3.2. Temperature Dependence of Promoter-Doped Ni/Eco

The catalytic performances of Ni/Eco, Ni-Mg/Eco, Ni-Ce/Eco, Ni-Zr/Eco, Ni-Fe/Eco, and Eco support only (support) were compared with that of commercial methanation catalyst (commercial, METH 134, Clariant, Muttenz, Switzerland) at 250–500 °C (Figure 3).

The commercial catalyst showed relatively high activity at 300 °C and below (~59% at 250 °C and ~94% at 300 °C) but relatively low activity at 400 °C and above (~87% at 400 °C and ~78% at 500 °C), compared to some of the Ni/Eco series. Among the LRC-supported samples, Ni-Ce/Eco exhibited the best performance. It showed a slightly lower activity (~86% at 300 °C) than commercial catalysts but showed higher activity in the high-temperature region (~95% at 350 °C, 92% at 400 °C, and 83% at 500 °C). Ni-Mg/Eco showed similar activity to Ni-Ce/Eco at >350 °C, but was relatively low at <300 °C. Ni-Zr/Eco showed higher activity than other LRC-supported systems at 250 °C, but showed 5–30% lower conversion than Ni-Ce/Eco at 300 °C or higher. The conversion of Ni-Fe/Eco was as low as 42–75%, even at 350–500 °C. Ni/Eco also showed a relatively low conversion at <350 °C (~33%). As expected, the Eco support showed a low conversion (~20%).

The commercial catalyst showed 100% CH\textsubscript{4} selectivity at all temperatures (250–500 °C). Ni-Ce/Eco and Ni-Mg/Eco showed 95–100% CH\textsubscript{4} selectivity at >300 °C and 75–90% at 250 °C. Other Eco-supported catalysts also showed relatively low selectivity at low temperatures.

The results of the continuous 200 h test of Ni-Ce/Eco and Ni-Mg/Eco are shown in Figure 4. The catalytic performance was monitored at 200–500 °C, where the samples were maintained for 24 h at each temperature. The overall duration in the reactor was ~200 h. At <300 °C, data fluctuations were observed, probably due to slow kinetics. However, at >350 °C, the difference between the measurement points became small (within 3%). Previous work also reported that the activity of the LRC-supported Ni catalyst was stable upon exposure at 400 °C for 1000 h, which confirmed the thermal stability of Ni/Eco-based
catalysts [32]. An extended long-term test should be, however, conducted to ensure the stability of the LRC-supported catalyst during CO₂ methanation.

3.3. Characterization of Catalysts

The N₂ adsorption isotherms of Ni/Eco, Ni-Ce/Eco, and Ni-Mg/Eco are shown in Figure 5a.

![N₂ adsorption isotherm](image1.png)

![BJH pore size distribution](image2.png)

**Figure 5.** Pore structure analysis of Ni/Eco, Ni-Ce/Eco, and Ni-Mg/Eco catalyst. (a) N₂ adsorption isotherm and (b) BJH pore size distribution.

The general shapes of the plots were similar to each other, as they were made using the same support. This indicated the presence of mixed pores on the micro- and mesoscale. The steep increase at p/p₀ < 0.1, and a plateau at 0.1 < p/p₀ < 0.9, occurred by micropore filling and a sharp increase at p/p₀ > 0.9 by mesopores [53,54]. BET surface area (S_BET), pore volume (V_p), micropore volume (V_micro), and pore size were calculated, based on the BET equation and t-plot analysis, and are given in Table 2. The characteristic values of the pore structures were somewhat different from each other. BET surface area (S_BET) was in the range of 290–370 m²/g, V_p was 1.6–1.9 cm³/g, and V_micro was 0.09–0.12 cm³/g. Most notably, the V_micro ratio of Ni-Ce and Ni-Mg was 15–20% lower than that of Ni only. A previous study reported that the S_BET of Ni-Ce/Al₂O₃ decreased with an increase in ceria [55].

| Catalyst  | S_BET (m²/g) | V_p (cm³/g) | V_micro (cm³/g) | V_micro Ratio (%) | Pore Size (nm) |
|-----------|--------------|-------------|-----------------|-------------------|----------------|
| Ni only   | 308          | 0.163       | 0.120           | 73.6              | 2.1            |
| Ni-Ce     | 286          | 0.163       | 0.090           | 55.2              | 2.6            |
| Ni-Mg     | 373          | 0.187       | 0.110           | 58.8              | 3.5            |

This was probably due to partial blocking of micropores by the addition of the promoter [56]. A decrease in the V_micro ratio was also observed when Zr and Fe were doped on Ni/Eco (data not shown). An average pore size of Ni-Ce/Eco, and Ni-Mg/Eco (2.4 nm and 3.5 nm, respectively) was higher than that of Ni/Eco (2.1 nm). The adsorbates move through the mesopores and macropores to the micropores, where adsorption and subsequent reactions mostly occur [40]. However, the correlation between the activity and pore structure was unclear in this study. The adsorption behavior is typically influenced by the surface composition. LRC contains a large amount of oxygen, which can be controlled to some extent quantitatively by changing the heat treatment conditions [34]. This control of the LRC composition can be a tool to secure custom-made support according to the
hydrophobicity of the reactants. In addition, the results of the BJH pore size distribution showed that the pore diameters of all three catalysts were mainly ~4 nm (Figure 5b).

The XRD spectra of Ni/Eco, Ni-Ce/Eco, and Ni-Mg/Eco are shown in Figure 6a.

Figure 6. X-ray diffraction (XRD) patterns of (a) Ni/Eco, Ni-Ce/Eco, and Ni-Mg/Eco and (b) 15-Ni, x-Mg series (Ni metal: PDF# 00-004-0850, NiO: PDF# 00-004-0835, and MgO: PDF# 01-071-6452).

The general profiles of Ni/Eco and Ni-Ce/Eco were similar, showing metallic Ni peaks at 2θ = 44.5° and 51.9°. The peak at 26.2° was identified as graphite. As reported previously, nickel particles dispersed on LRC were mostly reduced by LRC, which was readily oxidized by taking oxygen from neighboring molecules [32]. Auer et al. (1998) pointed out that a small amount of oxidized metal remained on the carbonaceous support [48]. The metal particles dispersed on the metal oxide support should be reduced to an active metallic form before the reaction, typically through an H₂ pre-reduction step [57]. This step could be skipped for LRC-supported catalysts, giving improved process efficiency. On the other hand, Ni-Mg/Eco showed relatively intense NiO peaks at 2θ = 37.3°, 43.3°, and 62.3°.

Bacariza et al. (2017) showed that the addition of a small amount of Mg (<2.5%) reduced Ni, pointing out that a small amount of oxidized metal remained on the carbonaceous support. Auer et al. (1998) noted that a small amount of oxidized metal remained on the carbonaceous support. In this work, the target loading of Mg was 3 wt.% (based on before heat treatment), resulting in >5 wt.% Mg after heat treatment at 650 °C as a result of the loss of volatile matter. A part of Ni in Ni-Mg/Eco was probably oxidized by the relatively high Mg concentration. It is expected that improved activity can be obtained when the loading of Mg and Ni, as well as the synthesis conditions, are optimized. The particle size of metallic Ni was calculated using the Scherrer equation: 7.8 nm for Ni/Eco, 23.1 nm Ni-Ce/Eco, and 15.7 nm for Ni-Mg/Eco.

Figure 6b shows the XRD spectra of Ni/Eco doped with 1–10 wt.% Mg. When 1 wt.% Mg was added, metallic Ni peaks at 2θ = 44.5° and 51.9° were dominant with minor NiO peaks. As the loading of Mg increased from 3 wt.% to 10 wt.%, the intensity of the metallic Ni peak decreased, while that of the NiO peak increased. The MgO peaks (2θ = 42.5° and 61.8°) overlapped with the NiO peaks. Nevertheless, it seemed that the formation of NiO increased with Mg loading. The LRC-supported Ni catalysts prepared by incipient wetness impregnation (IWI) in the present work showed much stronger NiO peaks than those prepared by conventional wet impregnation (Imp) [32,33]. This was likely due to the presence of segregated surface NiO as a result of insufficient diffusion of the precursor solutions when the IWI method was used.

Figure 7 shows the TEM images and single metal mapping results of the Ni/Eco, Ni-Ce/Eco, and Ni-Mg/Eco catalysts.
Ni/Eco prepared by the IWI method in this work resulted in 2–3 nm larger particle size than Ni/Eco by the Imp method (Figure 7a) [34]. In addition, more aggregated particles (>10 nm in size) by IWI were found than by Imp. As mentioned above, IWI usually leads to relatively poor dispersion quality, compared to Imp, owing to relatively low-quality diffusion, resulting in non-uniformity. However, a large portion of particles existed in the <5 nm dot form, similar to the samples dispersed by Imp. The average Ni particle size of the promoter-doped Ni/Eco was 2–3 times larger than that of undoped Ni/Eco (according to the Scherrer equation from the XRD data).

According to the results of single metal mapping (Figure 7d,e,g,h), the aggregated particles were mainly Ni. In contrast, the particle sizes of Ce and Mg were relatively small and evenly dispersed. It is believed that the quality of Ni dispersion can be improved further by adjusting the synthesis conditions, such as the impregnation method and the polarity of the precursor solution [40].

H\textsubscript{2} temperature-programmed reduction (H\textsubscript{2}-TPR) of Ni/Eco, Ni-Ce/Eco, and Ni-Mg/Eco was performed, as shown in Figure 8.
The TPR results distinguished the effect of metal-promoter interactions on the reducibility of Ni. The profiles of all three samples were generally similar, showing unsymmetrical major peaks at 450–700 °C and relatively weak overlapped peaks at 150–400 °C. The low temperature (<400 °C) peaks correspond to the free or weakly bound NiO present on the surface without significant interaction with the promoter or support [58]. These were not influential on Ni reduction at higher temperatures [59]. The intense peaks at 450–700 °C were most likely due to NiO bound to the LRC support, and the peak maximum was shifted to a higher temperature (10–50 °C) via the interaction between Ni and Ce (or Mg) [60]. The unknown amount of H2 was probably generated as a pyrolysis product of LRC in the high-temperature region and seemingly contributed to the peak intensity [34]. The relative intensity of the peaks at the high temperature (HT, 450–700 °C), compared to those at the low temperature (LT, 150–400 °C), decreased when the promoter (Ce or Mg) was introduced. In particular, Ni-Mg/Eco consumed 37% H2 for LT peaks and 63% for HT peaks, whereas Ni/Eco consumed 19% H2 for LT peaks and 81% for HT peaks. This was probably due to the increased concentration of surface NiO by Mg addition and in agreement with the XRD results, indicating that the relatively strong NiO peak observed in Figure 6 arose from the surface NiO. Meanwhile, MgO was not reduced up to 1000 °C [61]. In addition, the reduction of surface CeO2 occurred at ~520 °C [62]. However, the general profile of Ni-Ce/Eco showed no significant contribution from the Ce reduction.

4. Conclusions

Low Rank Coal (LRC) can provide improved process efficiency in many different ways because of its unique characteristics, including its high thermal conductivity and reducing ability, controllable pore structure and composition, and heterogeneous surface providing numerous defects. In our current work, LRC-supported Ni catalysts demonstrated similar or better conversion compared to a commercial metal oxide-supported catalyst, such that Ni (with Ce or Mg promoter) dispersed on LRC achieved the conversion of >95% and the selectivity of >98% at 350–400 °C. In addition, stable performance was observed during ~200 h continuous run at 200–500 °C. With further optimization of the synthesis method and metal composition, the catalytic behavior is expected to be improved significantly.

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**References**

1. Zhou, S.; Sun, K.; Wu, Z.; Gu, W.; Wu, G.; Li, Z.; Li, J. Optimized operation method of small and medium-sized integrated energy system for P2G equipment under strong uncertainty. Energy 2020, 199, 117269. [CrossRef]

2. Götz, M.; Lefebvre, J.; Mörs, F.; Koch, A.M.; Graf, F.; Bajohr, S.; Reimert, R.; Kolb, T. Renewable Power-to-Gas: A technological and economic review. Renew. Energy 2016, 85, 1371–1390. [CrossRef]

3. Guandalini, G.; Campanari, S.; Romano, M.C. Power-to-gas plants and gas turbines for improved wind energy dispatchability: Energy and economic assessment. Appl. Energy 2015, 147, 117–130. [CrossRef]

4. Baysal, Z.; Kureti, S. CO2 methanation on Mg-promoted Fe catalysts. Appl. Catal. B Environ. 2020, 262, 118300. [CrossRef]

5. Beuls, A.; Swaluys, C.; Jacquemin, M.; Heyen, G.; Karelovic, A.; Ruiz, P. Methanation of CO2: Further insight into the mechanism over Rh/γ-Al2O3 catalyst. Appl. Catal. B Environ. 2012, 113, 2–10. [CrossRef]

6. Bassano, C.; Deiana, P.; Lietti, L.; Visconti, C.G. P2G movable modular plant operation on synthetic methane production from CO2 and hydrogen from renewables sources. Fuel 2019, 253, 1071–1079. [CrossRef]

7. Mebrahtu, C.; Krebs, F.; Abate, S.; Perathoner, S.; Cendi, G.; Palkovits, R. CO2 Methanation: Principles and Challenges. Rapid Aging Antidepressants 2019, 178, 85–103. [CrossRef]

8. 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]

9. Schlereth, D.; Hinrichsen, O. A fixed-bed reactor modeling study on the methanation of CO2. Chem. Eng. Res. Des. 2014, 92, 702–712. [CrossRef]

10. Ocampo, F.; Louis, B.; Kiwi-Minsker, L.; Roger, A.-C. Effect of Ce/Zr composition and noble metal promotion on nickel based CeZr1–xOx catalysts for carbon dioxide methanation. Appl. Catal. A Gen. 2011, 392, 36–44. [CrossRef]

11. Hidalgo, D.; Martín-Marroquin, J. Power-to-methane, coupling CO2 capture with fuel production: An overview. Renew. Sustain. Energy Rev. 2020, 132, 110057. [CrossRef]

12. Esa, Y.A.M.; Sapawe, N. A short review on carbon dioxide (CO2) methanation process. Mater. Today Proc. 2020, 31, 394–397. [CrossRef]

13. Renda, S.; Ricca, A.; Palma, V. Precursor salts influence in Ruthenium catalysts for CO2 hydrogenation to methane. Appl. Energy 2020, 279, 115767. [CrossRef]

14. Nam, H.; Kim, J.H.; Kim, H.; Kim, M.J.; Jeon, S.-G.; Jin, G.-T.; Won, Y.; Hwang, B.W.; Lee, S.-Y.; Baek, J.-I.; et al. CO2 methanation in a bench-scale bubbling fluidized bed reactor using Ni-based catalyst and its exothermic heat transfer analysis. Energy 2021, 214, 118895. [CrossRef]

15. Song, H.; Yang, J.; Zhao, J.; Chou, L. Methanation of Carbon Dioxide over a Highly Dispersed Ni/La2O3 Catalyst. Chin. J. Catal. 2010, 31, 21–23. [CrossRef]

16. 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, 116059–116068. [CrossRef]

17. Liu, Q.; Tian, Y. One-pot synthesis of NiO/SBA-15 monolith catalyst with a three-dimensional framework for CO2 methanation. Int. J. Hydrogen Energy 2017, 42, 12295–12300. [CrossRef]

18. Aziz, M.; Jalil, A.; Triwahyono, S.; Mukti, R.; Taufiq-Yap, Y.; Sazegar, M. Highly active Ni-promoted mesostructured silica nanoparticles for CO2 methanation. Appl. Catal. B Environ. 2014, 147, 359–368. [CrossRef]

19. Yin, S.; Zhu, L.; Liu, Y.; Wang, X.; Liu, Y.; Wang, S. Effect of Ni Precipitation Method on CO Methanation over Ni/TiO2 Catalysts. Chem. Res. Chin. Univ. 2018, 34, 296–301. [CrossRef]

20. Lippi, R.; Howard, S.C.; Barron, H.; Easton, C.D.; Madsen, I.C.; Waddington, L.J.; Vogt, C.; Hill, M.R.; Sumby, C.J.; Doonan, C.J.; et al. Highly active catalyst for CO2 methanation derived from a metal organic framework template. J. Mater. Chem. A 2017, 5, 12990–12997. [CrossRef]

21. Ye, R.-P.; Liao, L.; Reina, T.R.; Liu, J.; Chevella, D.; Jin, Y.; Fan, M.; Liu, J. Engineering Ni/SiO2 catalysts for enhanced CO2 methanation. Fuel 2021, 282, 119151. [CrossRef]

22. Rui, N.; Zhang, X.; Zhang, F.; Liu, Z.; Cao, X.; Xie, Z.; Zou, R.; Senanayake, S.D.; Yang, Y.; Rodriguez, J.A.; et al. Highly active Ni/Co2O3 catalysts for CO2 methanation: Preparation and characterization. Appl. Catal. B Environ. 2021, 282, 119581. [CrossRef]

23. Lu, H.; Yang, X.; Gao, G.; Wang, J.; Han, C.; Liang, X.; Li, C.; Li, Y.; Zhang, W.; Chen, X. Metal (Fe, Co, Ce or La) doped nickel catalyst supported on ZrO2 modified mesoporous clays for CO and CO2 methanation. Fuel 2016, 183, 335–344. [CrossRef]

24. Taherian, Z.; Khataee, A.; Orooji, Y. Promoted nickel-based catalysts on modified mesoporous silica support: The role of yttria and magnesia on CO2 methanation. Microporous Mesoporous Mater. 2020, 306, 110455. [CrossRef]
25. Lippi, R.; D’Angelo, A.M.; Li, C.; Howard, S.C.; Madsen, I.C.; Wilson, K.; Lee, A.F.; Sumbay, C.J.; Doonan, C.J.; Patel, J.; et al. Unveiling the structural transitions during activation of a CO₂ methanation catalyst Ru/ZrO₂ synthesised from a MOF precursor. Catal. Today 2020. [CrossRef]

26. Swalus, C.; Jacquemin, M.; Poleunis, C.; Bertrand, P.; Ruiz, P. CO₂ methanation on Rh/γ-Al₂O₃ catalyst at low temperature: “In situ” supply of hydrogen by Ni/activated carbon catalyst. Appl. Catal. B Environ. 2012, 125, 41–50. [CrossRef]

27. Wang, X.; Liu, Y.; Zhu, L.; Li, Y.; Wang, K.; Qiu, K.; Tippayawong, N.; Aggarangsi, P.; Reubroycharoen, P.; Wang, S. Biomass derived N-doped biochar as efficient catalyst supports for CO₂ methanation. J. CO₂ Util. 2019, 34, 733–741. [CrossRef]

28. Wang, X.; Yang, M.; Zhu, X.; Zhu, L.; Wang, S. Experimental study and life cycle assessment of CO₂ methanation over biochar supported catalysts. Appl. Energy 2020, 280, 115919. [CrossRef]

29. 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]

30. Wang, J.; You, Z.; Zhang, Q.; Deng, W.; Wang, Y. Synthesis of lower olefins by hydrogenation of carbon dioxide over supported iron catalysts. Catal. Today 2013, 215, 186–193. [CrossRef]

31. Kwak, J.H.; Kovarik, L.; Szanyi, J. Heterogeneous Catalysis on Atomically Dispersed Supported Metals: CO₂ Reduction on Multifunctional Pd Catalysts. ACS Catal. 2013, 3, 2094–2100. [CrossRef]

32. Kim, S.; Prajitto, H.; Yoo, J.; Kim, S.; Chun, D.; Lim, J.; Choi, H.; Lee, S.; Im, H. Dispersion behavior of various single metals on carbonaceous co supports and their reactivity in methanol steam reforming. J. Ind. Eng. Chem. 2021, 94, 317–325. [CrossRef]

33. Kim, S.; Chun, D.; Lim, Y.; Kim, S.; Choi, H.; Lee, S.; Yoo, J. Catalytic reforming of toluene using a nickel ion-exchanged catalyst. Int. J. Hydrogen Energy 2015, 40, 11855–11862. [CrossRef]

34. Ruhsuwurmova, N.; Kim, S.; Yoo, J.; Chun, D.; Rhim, Y.; Lim, J.; Kim, S.; Choi, H.; Lee, S. Nickel supported on low-rank coal for steam reforming of ethyl acetate. Int. J. Hydrogen Energy 2018, 43, 15880–15890. [CrossRef]

35. Frontera, P.; Macario, A.; Ferraro, M.; Antonucci, P. Supported Catalysts for CO₂ Methanation: A Review. Catalysts 2017, 7, 59. [CrossRef]

36. Karelovic, A.; Ruiz, P. CO₂ hydrogenation at low temperature over Rh/γ-Al₂O₃ catalysts: Effect of the metal particle size on catalytic performances and reaction mechanism. Appl. Catal. B Environ. 2012, 113, 237–249. [CrossRef]

37. Veith, G.M.; Lupini, A.R.; Rashkeev, S.; Pennycook, S.J.; Mullins, D.R.; Schwartz, V.; Bridges, C.A.; Dudney, N.J. Thermal stability and catalytic activity of gold nanoparticles supported on silica. J. Catal. 2009, 262, 92–101. [CrossRef]

38. Rodriguez-Reinoso, F. The role of metal materials in heterogeneous catalysis. Carbon 1998, 36, 159–175. [CrossRef]

39. Takano, H.; Shinomiya, H.; Izumiya, K.; Kumagai, N.; Habazaki, H.; Hashimoto, K. CO₂ methanation of Ni catalysts supported on tetragonal ZrO₂ doped with Ca²⁺ and Ni²⁺ ions. Int. J. Hydrogen Energy 2015, 40, 8347–8355. [CrossRef]

40. Tada, S.; Shimizu, T.; Kameyama, H.; Haneda, T.; Kikuchi, R. Ni/CO₂ catalysts with high CO₂ methanation activity and high CH₄ selectivity at low temperatures. Int. J. Hydrogen Energy 2012, 37, 5527–5531. [CrossRef]

41. Wang, X.; Zhen, T.; Yu, C. Application of Ni-Al/hydrotalcite-derived catalyst modified with Fe or Mg in CO₂ methanation. Appl. Petrochem. Res. 2016, 6, 217–223. [CrossRef]

42. Pan, Z.; Dong, M.; Meng, X.; Zhang, X.; Mu, X.; Zong, B. Integration of magnetically stabilized bed and amorphous nickel alloy catalyst for CO methanation. Chem. Eng. Sci. 2007, 62, 2712–2717. [CrossRef]

43. Ashok, J.; Ang, M.; Kawi, S. Enhanced activity of CO₂ methanation over Ni/CO₂-ZrO₂ catalysts: Influence of preparation methods. Catal. Today 2017, 281, 304–311. [CrossRef]

44. Westermann, A.; Azamble, B.; Bacariza, M.; Graça, I.; Ribeiro, M.; Lopes, J.; Henriques, C. Insight into CO₂ methanation mechanism over NiUSY zeolites: An operando IR study. Appl. Catal. B Environ. 2015, 174–175, 120–125. [CrossRef]

45. Rahmani, S.; Rezaei, M.; Meshkani, F. Preparation of promoted nickel catalysts supported on mesoporous nanocrystalline gamma alumina for carbon dioxide methanation reaction. J. Ind. Eng. Chem. 2014, 20, 4176–4182. [CrossRef]

46. Auer, E.; Freund, A.; Pietsch, J.; Tacke, T. Carbons as supports for industrial precious metal catalysts. Appl. Catal. A Gen. 1998, 173, 259–271. [CrossRef]

47. Bacariza, M.C.; Graça, I.; Bebiano, S.S.; Lopes, J.M.; Henriques, C. Magnesium as Promoter of CO₂ Methanation on Ni-Based USY Zeolites. Energy Fuels 2017, 31, 9776–9789. [CrossRef]

48. Karelovic, A.; Ruiz, P. Mechanistic study of low temperature CO₂ methanation over Rh/TiO₂ catalysts. J. Catal. 2013, 301, 141–153. [CrossRef]

49. Marwood, M.; Doepfer, R.; Renken, A. In-situ surface and gas phase analysis for kinetic studies under transient conditions the catalytic hydrogenation of CO₂. Appl. Catal. A Gen. 1997, 151, 223–246. [CrossRef]

50. Cárdenas-Arenas, A.; Cortés, H.S.; Bailón-García, E.; Davó-Quinonero, A.; Lozano-Castelló, D.; Bueno-López, A. Active, selective and stable NiO-CoO nanoparticles for CO₂ methanation. Fuel Process. Technol. 2021, 212, 106637. [CrossRef]

51. Cai, M.; Wen, J.; Chu, W.; Cheng, X.; Li, Z. Methanation of carbon dioxide on Ni/ZrO₂-Al₂O₃ catalysts: Effects of ZrO₂ promoter and preparation method of novel ZrO₂-Al₂O₃ carrier. J. Nat. Gas Chem. 2011, 20, 318–324. [CrossRef]

52. Fu, T.; Li, Z. Review of recent development in Co-based catalysts supported on carbon materials for Fischer–Tropsch synthesis. Chem. Eng. Sci. 2015, 135, 3–20. [CrossRef]

53. Stereck, S.; Breitinger, H.; Maier, W.F. Characterization of micro- and mesoporous solids by physisorption methods and pore-size analysis. Appl. Catal. A Gen. 1998, 174, 137–146. [CrossRef]
54. Sotomayor, F.; Cychosz, K.A.; Thommes, M. Characterization of Micro/Mesoporous Materials by physisorption: Concepts and Case Studies. *Acc. Mater. Surf. Res.* 2018, 3, 24–50.

55. Wang, S.; Lu, G.M. Role of CeO$_2$ in Ni/CeO$_2$–Al$_2$O$_3$ catalysts for carbon dioxide reforming of methane. *Appl. Catal. B Environ.* 1998, 19, 267–277. [CrossRef]

56. Wang, C.-Y.; Li, S.-Y.; Yang, X.-R.; Ren, J.; Chen, Y.-G. CH4 CO$_2$ reforming anti-carbon deposition catalyst. *Energy Convers. Manag.* 1996, 37, 1357–1361. [CrossRef]

57. Zangouei, M.; Moghaddam, A.Z.; Arasteh, M. The influence of nickel loading on reducibility of NiO/Al$_2$O$_3$ catalysts synthesized by sol-gel method. *Chem. Eng. Res. Bull.* 2010, 14, 97–102. [CrossRef]

58. Clause, O. Effect of the preparation method on the thermal stability of silica-supported nickel oxide as studied by EXAFS and TPR techniques. *J. Catal.* 1992, 138, 195–205. [CrossRef]

59. Marconi, E.; Tuti, S.; Luisetto, I. Structure-Sensitivity of CO$_2$ Methanation over Nanostructured Ni Supported on CeO$_2$ Nanorods. *Catalyst* 2019, 9, 375. [CrossRef]

60. Diskin, A.M.; Cunningham, R.H.; Ormerod, R. The oxidative chemistry of methane over supported nickel catalysts. *Catal. Today* 1998, 46, 147–154. [CrossRef]

61. Kumar, M.; Aberuagba, F.; Gupta, J.; Rawat, K.; Sharma, L.; Dhar, G.M. Temperature-programmed reduction and acidic properties of molybdenum supported on MgO–Al$_2$O$_3$ and their correlation with catalytic activity. *J. Mol. Catal. A Chem.* 2004, 213, 217–223. [CrossRef]

62. Laguna, O.; Centeno, M.A.; Sarria, F.R.; Odriozola, J.A. Oxidation of CO over gold supported on Zn-modified ceria catalysts. *Catal. Today* 2011, 172, 118–123. [CrossRef]