CO₂ methanation of biogas over 20 wt% Ni-Mg-Al catalyst: On the effect of N₂, CH₄, and O₂ on CO₂ conversion rate

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Abstract: Biogas contains more than 40% CO₂ that can be removed to produce high quality CH₄. Recently, CH₄ production from CO₂ methanation has been reported in several studies. In this study, CO₂ methanation of biogas was performed over a 20 wt% Ni-Mg-Al catalyst, and the effects of CO₂ conversion rate and CH₄ selectivity were investigated as a function of CH₄, O₂, H₂O, and N₂ compositions of the biogas. At a gas hourly space velocity (GHSV) of 30,000/h, the CO₂ conversion rate was ~79.3% with a CH₄ selectivity of 95%. In addition, the effects of the reaction temperature (200–450 °C), GHSV (21,000–50,000/h), and H₂/CO₂ molar ratio (3–5) on the CO₂ conversion rate and CH₄ selectivity over the 20 wt% Ni-Mg-Al catalyst were evaluated. The characteristics of the catalyst were analyzed using Brunauer-Emmett-Teller (BET) surface area analysis, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The catalyst was stable for approximately 200 h at a GHSV of 30,000/h and a reaction temperature of 350 °C. CO₂ conversion and CH₄ selectivity were maintained at 75% and 93%, respectively, and the catalyst was therefore concluded to exhibit stable activity.

Keywords: power to gas; CO₂ methanation; Ni catalyst, biogas utilization, CO₂ hydrogenation

1. Introduction

The recent years have witnessed a growing interest in the regulation of greenhouse gases and the quest for sustainable renewable energy to combat global warming. This has culminated in the demand for an efficient energy storage system (ESS) that can stabilize electric power systems with high output fluctuations. The lithium-ion battery is an ESS widely employed in various energy generation systems owing to its high energy density and efficiency; however, its short shelf life and low storage capacity limit long-term power storage [1]. The availability of organic waste, which is a sustainable energy source, can increase with economic and population growth. Consequently, much attention has been drawn to the utilization of biogas, as it can be easily obtained from livestock (organic) waste and urban solid waste. Biogas, which typically contains 40–65 vol% CH₄, 40–50 vol% CO₂, and minor quantities of (the subsequently removed) N₂, H₂S, O₂, and H₂O [2], is employed as a high-concentration CH₄ fuel after more than 40% of CO₂ is removed using absorbents or amines [3]. The power-to-gas technology generates H₂ from water by employing renewable energy and produces CH₄ via the methanation of H₂ and CO₂. Further, CO₂ methanation and reverse water gas shift (RWGS) are competing processes that occur during the production of CH₄ from CO₂, as described by Equations (1)–(3) [4]. This has become a topic of research considering the possibility of a ‘carbon-neutral fuel’ and the replacement of natural gas as well as ESSs [5].

\[
\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H_{298K} = -164 \text{kJ mol}^{-1}
\]
Biogas is initially subjected to purification to remove impurities such as H₂S, H₂O, and siloxanes. Subsequently, CO₂ and highly concentrated CH₄ are separated, so that CH₄ can be utilized as fuel [6]. In addition to being used as a fuel, biogas generated by catalytic reforming is also used to produce high-value-added chemicals (e.g., methanol, acetic acid, dimethyl ether, ammonia, and Fischer-Tropsch oil), which greatly contributes to the reduction of greenhouse gas emissions [7,8]. Moreover, biogas is an affordable and suitable raw material for syngas production, even though syngas is now largely produced through the CH₄ reforming of natural gas.

In a recent study, Mohammad et al. [9] compared the activity of Al₂O₃-supported Ni, Co, Fe, and Mo catalysts during CO₂ methanation. Ni catalyst showed the highest CO₂ conversion and CH₄ selectivity, followed by Co, Fe, and Mo. The study by Aziz et al. [10] on the activity of mesostructured silica nanoparticle (MSN)-supported Ni, Fe, and Mo catalysts demonstrated that the Fe catalyst was active at high temperatures, whereas the Ni catalyst exhibited the highest catalytic activity at lower temperatures (<350 °C)[11]. Daroughegi et al. [12] conducted CO₂ methanation experiments on Al₂O₃-supported Ni catalysts with different metal loadings, and the results revealed that the specific surface area and CO₂ conversion increased with the increase in the Ni loading from 15, 20, and 25 wt%, whereas the specific surface area and CO₂ conversion decreased at 33 wt%. In the study on Ni/γ-Al₂O₃, Cho et al. [13] reported that the highest dispersion, CH₄ selectivity, and reaction rate were observed at 20 wt% Ni content when the Ni content was varied from 15 to 50 wt%.

Jaffar M.M et al. [9] compared the activities of the 10 wt% Ni catalysts supported on SiO₂, MCN, and Al₂O₃. Among the experiments performed at 360 °C, the Ni-Al₂O₃ catalyst showed the highest CO₂ conversion and CH₄ selectivities of 82.9 and 97.9%, respectively. Further, the SEM results confirmed that the Ni particles were more uniformly dispersed in the 10 wt% Ni-Al₂O₃ catalyst than those in the 10 wt% MCM and SiO₂ catalysts. It has also been reported that the catalytic activity of SiO₂-supported catalysts for methane production decreases in the presence of H₂O. On MCM, Aziz [14] reported that the CH₄ conversion and selectivity decrease because of the consumption of the carbonyl species by conversion to CO₂ in the presence of water vapor, via the water-gas shift reaction. Vetrivel et al. [15] and Wang et al.[16] reported that the fabrication of the catalysts by reduction on a CeO₂ support generated more surface oxygen vacancies, which resulted in high CO₂ conversion, CH₄ selectivity and enhanced catalyst stability.

Typically, promoters are used for improving the activity of supported catalysts. For example, the promoter MgO can increase carbon resistance [17], thermal stability [18], and the dispersion of Ni/Al₂O₃ catalysts [19,20], affording enhanced activity [21,22]. Thus, MgO, in combination with support materials such as Al₂O₃ or SiO₂ has been proposed as a support for methanation catalysts [23,24]. Bette et al. [25] demonstrated that the maximum CO₂ conversion of 74% was obtained with a 59 wt% Ni/(Mg,Al)O₂ catalyst, and the addition of MgO to Ni/SiO₂ resulted in a conversion of 66.5% [14]. In addition, MgO is a basic material that absorbs carbon dioxide and reduces catalyst deactivation via sintering and carbon deposition [26]. While catalysts become inactive because of the water produced during CO₂ methanation, MgO reacts with water to generate magnesium peroxide (Mg(OH)₂) and thereby mitigates catalyst deactivation [27,28].

The activation energy of Ni catalysts for methanation was 93.61 kJ/mol in Ni/ZrO₂ catalysts [29], 75 kJ/mol in Ni/Al₂O₃ catalysts [30], and 75 kJ/mol in Ni/Al hydrotalcite catalysts [31].

The present work studies the production of CH₄ by the reaction of biogas CO₂ with hydrogen over a 20 wt% Ni-Mg-Al catalyst and characterizes this catalyst by several instrumental analyses. The conditions for the reaction of biogas, including reaction temperature, space velocity, and H₂/CO₂ ratio, were varied to investigate their effects on CO₂ conversion, CH₄ yield, and selectivity. In addition, because biogas is a mixture of various gases and trace elements, the effect of the concentration of these components (N₂, O₂, CH₄, and CO₂) on CO₂ conversion, CH₄ yield, and selectivity were studied. Based on this, the optimal reaction conditions for producing CH₄ from
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biogas were determined, under which a stability test of the 20 wt% Ni-Mg-Al catalyst was performed for 200 h.

2. Materials and Methods

2.1 Catalyst preparation

The catalyst used in this study is a 20 wt% Ni-Mg-Al catalyst (supported by Korea Institute of Energy Research). The catalyst was prepared on a Ni metal that exhibits high catalytic activity and CH₄ selectivity. The catalyst was prepared by mixing calculated ratios of Ni(NO₃)₂ · 6H₂O, Al(NO₃)₂ · 9H₂O, and Mg(NO₃)₂ · 6H₂O solutions at 60 °C until the Ni content was 20, 40 wt%, and a precipitate was obtained after adding a precipitant to the mixture and stirring for approximately 1 hour while maintaining a constant pH. The precipitated catalyst precursor was repeatedly washed with distilled water and filtered with a filter press until the pH reached approximately 7.0. The catalyst precursor was then dried in an oven at 150 °C for 12 h, and 20/40 wt% Ni-Mg-Al₂O₃ catalysts were prepared through a heat treatment process under an air atmosphere at 600 °C for 4 h. Prior to their use, all catalysts were heated to the reduction temperature under a gas flow of 100 ml/min (20% H₂, 80% N₂) for 2 h, and the catalysts were reduced while the temperature was maintained for 4 h.

Figure 1 illustrates the variations in catalytic activity of the 40 wt% Ni-Mg-Al₂O₃ catalysts at the reaction temperatures of 350 and 400 °C as a function of changes in the reduction temperatures to 450, 550, 700, and 800 °C. The CO₂ conversion initially showed a significant increase as the reduction temperature increased, while the CO₂ conversions at 700 and 800 °C were similar; therefore, 700 °C was used as the reduction temperature of the catalysts.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Effect of reduction temperature on CO₂ conversion and CH₄ selectivity over the 40 wt% Ni-Mg-Al catalyst.

2.2 CO₂ methanation apparatus and activity test

Isothermal CO₂ methanation experiments were conducted in a plug-flow system (Figure 2) at steady state with Ni catalysts loaded into the reactor. The catalytic reactor has an outer diameter of 12.7 mm (1/2”), a thickness of 1.257 mm, a length of 209 mm, and Inconel 800HT composed of 80% Ni, 14% Cr, and 6% Fe. During the experimentation, a mesh sieve was installed in the lower part of the reactor to support the catalyst layer, and 0.5 g of the catalyst was loaded. A back-pressure regulator (BPR) in the latter section of the reactor was used to control the reaction pressure from 1 to 9 atm. A water trap in the latter section of the BPR was used to remove the water generated from the reaction, and a high-pressure check valve was installed to prevent gas backflow. All tubes used were of SUS grade with an outer diameter of Φ3.2 mm and thickness of 0.8 t, and the products were
analyzed using gas chromatography (GC). To prevent the condensation of the products inside the tube during this process, a line heater was installed and maintained above 150 °C.

The reaction products were characterized using a GC (YL Instrument 6500), SS COL 10FT 1/8” PORAPACK N (Model: 13052-U) and Phase None Matrix 45/60 Molecular Sieve 13X were used for the GC columns, and argon was used as the carrier gas. Hydrogen, methane, and carbon monoxide were analyzed with a thermal conductivity detector (TCD), whereas carbon dioxide was analyzed using a flame ionization detector (FID). Characterization in the GC oven was conducted by maintaining the temperature initially at 35 °C for 0–6 min and raising it to approximately 170 °C at a ramp rate of 15 °C/min. FID characterization was performed at 250 °C by supplying 35 ml/min of hydrogen and 300 ml/min of oxygen, while TCD characterization was carried out at 150 °C under a gas flow rate of 35 ml/min of hydrogen and 20 ml/min of Ar. CO₂ conversion ($X_{\text{CO}_2}$), CH₄ selectivity ($S_{\text{CH}_4}$), and CH₄ yield ($Y_{\text{CH}_4}$) were calculated according to Equations (4)–(6)[32].

\[
X_{\text{CO}_2} (\%) = (1 - \frac{\text{CO}_2}{\text{CH}_4+\text{CO}+\text{CO}_2}) \times 100, \tag{4}
\]

\[
S_{\text{CH}_4} (\%) = \left(\frac{\text{CH}_4}{\text{CH}_4+\text{CO}}\right) \times 100, \tag{5}
\]

\[
Y_{\text{CH}_4} (\%) = \frac{\text{CO}_2 \times 5 \times \text{CH}_4}{100}, \tag{6}
\]

Using a reactant gas flow rate of 250 ml/min, reaction temperature of 350 °C, GHSV of 30,000/h, and H₂/CO₂ ratio of 4 as the basis, methanation reaction experiments were conducted by changing the experimental conditions, as listed in Table 1.

### Table 1. Experimental condition for CO₂ methanation reaction.

<table>
<thead>
<tr>
<th>Items</th>
<th>Condition</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction Temperature (°C)</td>
<td>200–450</td>
<td></td>
</tr>
<tr>
<td>CH₄ and CO₂ composition ratio (%)</td>
<td>65:35, 50:50, 40:60</td>
<td></td>
</tr>
<tr>
<td>Variable</td>
<td>GHSV (/h)</td>
<td>21,000–50,000</td>
</tr>
<tr>
<td>H₂/CO₂ mole ratio</td>
<td>3.5, 4, 4.5, 5</td>
<td></td>
</tr>
<tr>
<td>O₂ (cc/min)</td>
<td>10.5 (4%)</td>
<td></td>
</tr>
</tbody>
</table>

### 2.3. Catalyst characterization

#### 2.3.1 Brunauer-Emmett-Teller (BET) measurement

The BET specific surface area, which is one of the key catalyst properties, was measured using ASAP 2020 Plus Physisorption (Center for advanced materials analysis, Suwon University).
known amount of catalyst sample was added to the BET measurement tube, and the moisture in the catalyst was removed through a pretreatment process under a vacuum of 10 µm Hg by heating to 250 °C at a ramp rate of 10 °C/min for 12 h, after which the weight of the catalyst sample was measured.

Measurements of the specific surface area, pore-volume, and pore size of the fresh (20 and 40 wt% Ni-Mg-Al) and spent (20 wt% Ni-Mg-Al catalyst after 200 h of use) catalysts are summarized in Table 2. The BET surface area of the spent catalyst decreased in comparison with that of the fresh catalyst. In addition, an increase in the Ni content led to a decrease in the specific surface area, which is attributed to the blocking of catalyst pores with increasing Ni content, similar to the results reported by Daroughegi et al. [12] with catalysts containing greater than 20 wt% of Ni. In addition, these observations were similar to the results obtained by A. Zhao et al. [33]—the Ni metal crystal size increased in the catalysts comprising Ni loadings greater than 20 wt%. For this reason, the 20 wt% catalyst showed a higher CO2 conversion than the 40 wt% catalyst (Table 3).

Table 2. Brunauer-Emmett-Teller (BET) surface area, pore volume, and pore size of 20 wt% Ni-Mg-Al catalyst (fresh and spent).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET(m2/g)</th>
<th>Total pore volume (m3/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt% Ni-Mg-Al</td>
<td>Fresh 180.33</td>
<td>0.36</td>
<td>81.530</td>
</tr>
<tr>
<td></td>
<td>spent 148.9</td>
<td>0.3</td>
<td>81.15</td>
</tr>
<tr>
<td>40 wt% Ni-Mg-Al</td>
<td>Fresh 152.61</td>
<td>0.31</td>
<td>82.13</td>
</tr>
</tbody>
</table>

Table 3. CO2 conversion & selectivity of CH4 with different Ni loadings.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction temperature (°C)</th>
<th>CO2 conversion (XCO2)</th>
<th>CH4 selectivity (SCH4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt% Ni-Mg-Al</td>
<td>350</td>
<td>75.0</td>
<td>94.2</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>75.6</td>
<td>93.0</td>
</tr>
<tr>
<td>40 wt% Ni-Mg-Al</td>
<td>350</td>
<td>61.2</td>
<td>96.4</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>72.2</td>
<td>95.3</td>
</tr>
</tbody>
</table>

2.3.2 X-ray diffraction (XRD) characterization

The elemental composition of the catalysts was characterized using an XRD diffractometer (ThermoFisher Scientific, ARL Equinox 3000). The catalyst powder samples were pretreated at 250 °C for 5 h to remove moisture, and the crystals of the catalysts were analyzed. Cu-Kα radiation was used to fix the axis of the sample, and measurements were performed at 30 mA and 40 kV over a 20 range 10°–80° using a scanning speed of 80/min. The XRD analysis results of the catalytic supports and Ni catalysts before and after the reaction are shown in Figure 3. Diffraction peaks that appear at 20 values of 37.3°, 43.3°, 62.9°, and 75.4° are associated with the NiO phase, whereas those at 44.5°, 51.8°, and 76.3° are associated with Ni metal. The 20 values of 45.86 and 66.91 correspond to MgO, whereas the diffraction peaks at 20 values of 37.4°, 46.07°, and 66.9° are associated with the alumina phase. Figure 3 shows the XRD characterization of the catalysts before and after reduction at 700 °C and on the spent catalyst 200 h after the reaction. As shown in the figure, peaks corresponding to Ni metal were not observed in the fresh catalyst prior to the reaction, whereas NiO peaks were observed[34]. In contrast, the reduction catalyst and spent catalyst exhibited prominent Ni metal peaks at 20 values of 51.85° and 76.3°, respectively [30].
2.3.3 H$_2$-TPR analysis

The interaction and reduction between the catalyst metal and support were characterized by H$_2$-temperature-programmed reduction (H$_2$-TPR). As shown in Figure 4, the H$_2$ consumption of the catalysts appeared between 300, 400, and 450–1,000 °C. The two peaks correspond to the reduction of the NiO particles. The first peak refers to the reduction of NiO particles that exhibit a weak interaction due to MgO, and the second peak that appears at high temperatures corresponds to the reduction of NiO. Al$_2$O$_3$ particles with spinel structures that exhibit a strong interaction between the NiO particles and the Al$_2$O$_3$ support. An improved H$_2$ consumption was observed as the Ni content of the catalysts increased.

2.3.4 XPS characterization

To investigate the oxidation state of the catalysts, X-ray photoelectron spectroscopy (XPS, K-Alpha plus, Thermo Scientific, Center for advanced materials analysis, Suwon University) was used to measure the binding energy. XPS characterization was performed under vacuum using Al-Ka radiation on a fresh catalyst and on the spent catalyst after 200 h of reaction, without any separate sample pretreatment process (Figure 5). The oxidation state of Ni can be determined from
The binding energy (BE) of the XPS Ni2p3/2 spectrum. The Ni2p3/2 BE of NiO is 855–856 eV, and that of the Ni metal is 852.3–852.6 eV[35]. As shown in the figure, the XPS spectrum for the BE of the fresh catalyst displayed peaks 854.9 and 855.7 eV that are associated with NiO (peaks at 853.4 and 855.3 eV), and a small amount of Ni(OH): (peaks at 861.5 eV). The XPS pattern of the spent catalyst revealed the presence of Ni metal near 851.8 eV in addition to NiO and Ni(OH)2.

![XPS spectrum](image)

Figure 5. X-ray photoelectron spectra of (a) fresh and (b) spent 20 wt% Ni-Mg-Al catalysts.

2.3.5 Scanning electron microscopy (SEM)–energy-dispersive X-ray spectroscopy (EDX) characterization

SEM-EDX was used to investigate the surface morphology of the catalysts and the dispersion of Ni. FEI APREO SEM(Center for advanced materials analysis, Suwon University) was used to obtain images at 20,000 × magnification of the catalyst samples prepared by removing powders and dust, drying at 120 °C for 1 h, and coating with metal (Au). SEM images of the fresh catalyst and the spent catalyst after 420 h of reaction are presented in Figure 6. As shown in the SEM images, nanoscale particles were uniformly dispersed throughout the surface. Owing to the decomposition of Mg(NO3)2·6H2O to MgO at temperatures above 600 °C, it was confirmed that spherical [36] particles were uniformly dispersed.

![SEM images](image)
Figure 6. Scanning electron microscopy images of (a) fresh and (b) spent 20 wt% Ni-Mg-Al catalysts.

The results of the elemental composition analysis of the catalyst using EDX and of the surface morphology characterization from the SEM image are shown in Figure 7. The contents of Ni, Mg, and Al metals from the cross-section of the catalysts are summarized in Table 4.

Table 4. Elemental composition of 20 wt% Ni-Mg-Al catalyst determined by scanning electron microscopy–energy-dispersive X-ray spectroscopy.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Ni</th>
<th>Mg</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (%)</td>
<td>4.82</td>
<td>36.99</td>
<td>16.80</td>
<td>2.59</td>
<td>38.80</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1 Effect of reaction temperature on CO$_2$ conversion

The dependence of CO$_2$ conversion and CH$_4$ selectivity on reaction temperature at a GHSV of 30,000/h and H$_2$/CO$_2$ ratio of 4 is displayed in Figure 8. As shown in the figure, CO$_2$ conversion increased as the temperature increased and reached a maximum at 400 °C, whereas CH$_4$ selectivity and yield showed the highest values at 350 °C. This trend is probably the result of CO$_2$ methanation suppression above 350 °C, whereas the RWGS reaction is enhanced, which resulted in the conversion of CO$_2$ to CO. This result was confirmed in a study by Mohammad et al. [9], in which the CO concentration increased as the RWGS reaction increased at 400 °C, whereas the methane selectivity decreased. A study by Jia et al. [29] also reported that the highest CO$_2$ conversion and CH$_4$ yield were observed at 350 °C as the temperature increased, and a further increase in temperature decreased the CO$_2$ conversion because of the thermodynamic equilibrium limit [37].

In addition, the activation energy obtained from the 20 wt% Ni-Mg-Al catalyst was
approximately 74.2 kJ/mol, which was similar to the 75 kJ/mol obtained as the value with the use of Ni/Al₂O₃ in the study by Carbarino [30].

3.2 Effect of H₂/CO₂ ratio on CO₂ conversion

Figure 9 shows the effects of the H₂/CO₂ ratio at a reaction temperature of 350 °C and a GHSV of 30,000/h on CO₂ conversion and CH₄ selectivity/yield. Figure 9(a) shows the results obtained for different H₂/CO₂ ratios by increasing the amount of H₂ at a given amount of CO₂ and by increasing the amount of CO₂ at a given amount of H₂. Figure 9(b) shows the effects of increasing the reactant amounts at a given H₂/CO₂ ratio. As shown in Figure 9(a), the CO₂ conversion and CH₄ yield increased by approximately 15% when the ratio of H₂ increased from 3.5 to 5, whereas the CH₄ selectivity remained almost constant. As shown in Figure 9(b), the same H₂/CO₂ ratio led to similar CO₂ conversion and CH₄ selectivity and yield, regardless of the amount of reactants. These results were similar to those from a study by Rahmani [38] in which a 15% increase was observed when the H₂/CO₂ ratio was increased from 3 to 4, and the study by Aziz et al. [39] also reported that the concentration of hydrogen affects the catalytic activity because of hydrogen adsorption onto the surface of the catalyst and the conversion to methane via hydrogenation.

Figure 9. Effect of H₂/CO₂ mole ratio along with (a) CO₂ or H₂ variation; (b) reactant amount variation.

3.3 Effect of GHSV on CO₂ conversion

The effects of increasing GHSV on CO₂ conversion and CH₄ selectivity and yield at a reaction temperature of 350 °C and H₂/CO₂ ratio of 4 are shown in Figure 10(a) and (b). The effect of increasing the reactant flow rate to change the GHSV to 21,000–50,000/h is shown in Figure 10(a), and the effect of increasing the amount of nitrogen at a given reactant flow rate to change the GHSV to 9,000–38,000/h is shown in Figure 10(b). As shown in the figure, CO₂ conversion and CH₄ yield/selectivity showed a general decreasing trend as the GHSV increased, and the effect for (b) was larger than that for (a). This is because an increase in GHSV shortens the time during which the reactants CO₂ and H₂ are in contact with the catalyst, thus reducing the amount of reactants adsorbed onto the surface of the catalyst. These results were consistent with the experimental results reported by Abate et al. [40].
Figure 10. Effect of increased gas hourly space velocity & $N_2$ concentration at $H_2/CO_2$ ratio of 4 and reaction temperature of 350 °C (a) total reactant flow rate (b) $N_2$ flow rate ($N_2$ concentration).

3.4 Effect of initial concentration of biogas components on CO$_2$ conversion

3.4.1 Effect of initial CH$_4$ concentration on CO$_2$ conversion

The effect of changing the initial CH$_4$ concentration to 0, 50, and 65 vol% for CO$_2$ conversion at a reaction temperature of 400 °C, GHSV of 30,000/h, and $H_2/CO_2$ ratio of 4 is shown in Figure 11. As shown in the figure, increasing the content of CH$_4$ in the reactant gas to 40, 50, and 65 vol% led to low CO$_2$ conversions of approximately 67, 64, and 54%, respectively, resulting in up to a 20% decrease in the CO$_2$ conversion compared to that in the absence of CH$_4$. This phenomenon is attributed to the Le Chatelier principle, in which the initial CH$_4$ present in the reactant gas inhibits the conversion to CH$_4$. These results were also reported in a simulation study by Jurgensen [41], wherein CO$_2$ conversion decreased as the initial methane concentration increased.

Figure 11. Effect of biogas composition (CH$_4$:CO$_2$ = 65:35, 50:50).

3.4.2 Effect of initial CO$_2$ concentration on CO$_2$ conversion

The effect of increasing the initial CO$_2$ concentration on CO$_2$ conversion and CH$_4$ selectivity at a reaction temperature of 350 °C, GHSV of 30,000/h, and $H_2/CO_2$ ratio of 4 are presented in Figure 12. As shown in the figure, an increase of CO$_2$ in biogas from 10 to 14 vol% at a GHSV of 30,000/h resulted in a 2% increase in CO$_2$ conversion and a 3% increase at a GHSV of 50,000/h. This is
probably due to the increase in reaction temperature from the exothermic reaction of CO\textsubscript{2} methanation with increasing amounts of the reactants, such that the increase in CO\textsubscript{2} conversion is greater at a GHSV of 50,000/h than at 30,000/h, because more reactants are present in the former case than in the latter.

**Figure 12.** Effect of reactant concentration [= CO\textsubscript{2}/(H\textsubscript{2}+CO\textsubscript{2}+N\textsubscript{2})] at a reaction temperature of 350 °C.

3.4.3 Effect of initial N\textsubscript{2} concentration on CO\textsubscript{2} conversion

Approximately 15% of N\textsubscript{2} exists in landfill gas—a type of biogas—and is used as an inactive gas to prevent the deactivation of catalysts caused by the spot exothermic reaction of CO\textsubscript{2} methanation. The effect of the presence of 0, 10, and 30% N\textsubscript{2} in the reactant gas on CO\textsubscript{2} conversion at a GHSV of 15,000/h and H\textsubscript{2}/CO\textsubscript{2} ratio of 4 is shown in Figure 13. When nitrogen concentrations were 10 and 30% in the reactant, the respective CO\textsubscript{2} conversions were approximately 3 and 5% lower than that in the absence of N\textsubscript{2}. This is believed to be due to the decrease in reactant concentration as the N\textsubscript{2} concentration increases, resulting in less heat generation, which, in turn, lowers the reaction temperature.

**Figure 13.** Effect of N\textsubscript{2} in biogas at reaction temperature of 350 °C.

3.4.4 Effect of initial oxygen concentration on CO\textsubscript{2} conversion
The effects of the presence of oxygen in the reactant gas on CO\textsubscript{2} conversion at a GHSV of 30,000/h, an H\textsubscript{2}/CO\textsubscript{2} ratio of 4, and reaction temperatures of 300 and 400 °C are shown in Figure 14. When 4% oxygen was present in the reactant gas, CO\textsubscript{2} conversion and selectivity decreased by approximately 5 and 3%, respectively. This is thought to be a protected re-oxidation reaction due to the presence of oxygen in the reactant gas, which prevents the forward reaction in CH\textsubscript{4} synthesis paths (1) and (2). According to the mechanism proposed by Lin et al. [21], CO\textsubscript{2} is separated from the oxygen vacancies on the Ni metal and support material, which are produced during the reduction of catalysts, and it is reported that a decrease in the oxygen vacancies on the catalyst and support reduces the catalytic activity. Therefore, it is considered that the CO\textsubscript{2} conversion and selectivity decrease in the presence of oxygen because of the decrease in the amount of oxygen vacancies on the Ni catalyst and support, which prevents CO\textsubscript{2} from being converted to CO or carbon species, or because of the re-oxidation of CO.

![Figure 14. Effect of O\textsubscript{2} in reaction gas.](image)

3.5 Stability and activity of catalyst test

To evaluate the activity and stability of the catalysts, CO\textsubscript{2} methanation was conducted at a GHSV of 30,000/h, reaction temperature of 350 °C, and H\textsubscript{2}/CO\textsubscript{2} ratio of 4 for 200 h. As shown in Figure 15, the CO\textsubscript{2} conversion was constant at 75%, and CH\textsubscript{4} selectivity was 93% for 200 h. These results confirmed the activity and stability of the 20 wt% Ni-Mg-Al catalyst for the CO\textsubscript{2} methanation reaction.

![Figure 15. Stability test over 20 wt% Ni-Mg-Al catalysts at reaction temperature of 350 °C, a gas hourly space velocity of 30,000/h, and a H\textsubscript{2}/CO\textsubscript{2} ratio of 4.](image)
4. Conclusion

In this study, the reaction between H₂ and the CO₂ present in biogas was explored, and the experiments on CO₂ methanation for producing CH₄ were conducted over a 20 wt% Ni-Mg-Al catalyst. The optimal conditions for CO₂ methanation over the 20 wt% Ni-Mg-Al catalyst were determined based on the effects of the reaction temperature, GHSV, and H₂/CO₂ ratio on CO₂ conversion. Furthermore, experiments investigating the effects of CO₂, CH₄, N₂, and O₂ concentrations (i.e., biogas composition) on CO₂ conversion led to the following conclusions.

1) CO₂ conversion increased as the reaction temperature increased, but decreased beyond 400 °C, and the highest values of CH₄ selectivity and yield were obtained near 350 °C. This is due to the thermodynamic equilibrium limit that reduces the CO₂ conversion at temperatures above 400 °C [29] and inhibits the methanation reaction above 350 °C via the RWGS reaction, which increases the production of CO and decreases the CH₄ selectivity. The activation energy at this point was 72.4 kJ/mol.

2) CO₂ conversion and CH₄ selectivity increased as the H₂/CO₂ ratio increased from 3.5 to 5.0, whereas the CO₂ conversion resulted in similar values as long as the H₂/CO₂ ratio remained the same regardless of the H₂ and CO₂ concentrations when the H₂/CO₂ ratio was varied. Increasing the GHSV of the reactant gas and its N₂ concentration shortened the contact time between the reactant and catalyst and reduced the CO₂ conversion.

3) A higher initial concentration of CO₂ in the biogas led to a slightly higher CO₂ conversion, but increasing the initial CH₄ concentration to 40, 50, and 65 vol% decreases the CO₂ conversion by up to 20% compared to that in the absence of CH₄. This trend is believed to be the result of Le Chatelier's principle, in which the conversion of CH₄ was suppressed by the initial concentration of CH₄ in the reactant gas. The selectivity was shown to be independent of CH₄ concentration and remained constant.

4) Investigation of the effect of the concentrations of N₂ and O₂ components of biogas revealed that CO₂ conversion decreased by approximately 5% in the presence of 10 vol% N₂. In the presence of O₂, the CO₂ conversion decreased as a result of the decrease in the number of active sites of the Ni catalyst due to oxygen, which also reduced the CH₄ selectivity because of the re-oxidation reaction.

5) The stability of the 20 wt% Ni-Mg-Al catalyst for CO₂ methanation was evaluated from experiments at 350 °C for 200 h. The catalyst is expected to exhibit stable activity, because the CO₂ conversion and CH₄ selectivity were maintained at constant values of 75 and 93%, respectively.

In future, we plan to (i) apply the developed strategy to power plants (which generate much CO₂) and food waste treatment plants (which generate much anaerobic digestion gas) to produce methane gas and (ii) carry out demonstration tests for use in natural gas grids and natural gas-powered vehicles.

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