High-Pressure Hydrogenation: A Path to Efficient Methane Production from CO₂

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Abstract: Methane has a rather relevant role in the “Power-to-Gas” concept, which is central in the current paradigm of climate change and renewable energies. Methane, the main component of natural gas, can be produced by catalytic hydrogenation reactions, particularly of CO₂. A very effective catalyst in this reaction, hydrotalcite-derived nickel nanoparticles supported on alumina, Ni/Al₂O₃-HTC, can be employed in a high-pressure flow reactor to convert CO₂ and H₂ into CH₄ at 100% selectivity and 84% conversion, whereas at atmospheric pressure, methane can be obtained with up to 90% selectivity. The high-pressure aspect also allows fast-paced production—over 5 m³ h⁻¹ kg⁻¹ of CH₄ can be generated.

Keywords: methanation; Power-to-Gas; catalysis; CO₂ conversion; hydrotalcite

1. Introduction

The recent shifts in geopolitics have had a profound impact on energy transition policies. Natural gas has, for many, been seen as a gradual path toward decarbonization. However, recent developments, especially in Europe, have led to an increase in natural gas prices and the exploration of alternative energy sources to meet current demands [1]. In this context, hydrogen has emerged as an attractive option to fuel the European economy, with numerous projects for its production underway across Europe [2]. However, hydrogen faces challenges such as low power density and storage difficulties, which hinder its widespread adoption. Nonetheless, hydrogen can be readily converted into other products that can seamlessly integrate into existing energy pipelines. The production of synthetic methane is one of the valuable outcomes achievable through the hydrogenation of CO₂ [3]. This process not only facilitates the global utilization of hydrogen but also plays a crucial role in decarbonization efforts. This is because the CO₂ used in the production of synthetic methane can originate from specific industrial processes, thereby becoming part of a sustainable cycle that ultimately reduces carbon emissions [4].

Therefore, CO₂ methanation is relevant in the context of carbon utilization and sustainable energy and it fits into the “Power-to-Gas” concept as a way to store energy produced by intermittent renewable sources such as solar or wind [5]. The hydrogenation of CO₂ to CH₄ over nickel-based catalysts is particularly effective and is currently employed at industrial scale, since it has a good combination of the low cost of non-noble metals and high catalytic activity [6–9]. Particularly, catalysts of the composition Ni/Al₂O₃ are often studied for this reaction [10,11]. The catalytic activity of Ni/Al₂O₃ is rather sensitive to the synthesis methodology [12]. Ni/Al₂O₃ synthesized from hydrotalcite (HTC) has been demonstrated to be a distinctly active catalyst for the CO₂ methanation reaction. Ni/Al₂O₃-HTC has been
shown to contain more basic active sites, which leads to a higher CO$_2$ conversion when compared with Ni/Al$_2$O$_3$ synthesized by the wet impregnation method [13]. Additionally, the strong metal-support interaction present in hydrotalcite-derived catalysts leads to an intrinsically high dispersion of the metal on the support, even at high loadings, which helps prevent sintering and catalyst deactivation [14].

The CO$_2$ methanation reaction has a complex relationship with temperature. On the one hand, the thermodynamic equilibrium of this reaction indicates that low temperatures favor higher CO$_2$ conversion and selectivity to CH$_4$, but the kinetic barriers demand higher temperatures to be overcome [15]. High pressure could be a powerful tool to increase the methane yield and avoid carbon deposition. In a thermodynamic equilibrium analysis of the CO$_2$ methanation, Jürgensen et al. found that at increased pressures, carbon deposition can be inhibited, which could delay catalyst deactivation [16]. Mutz et al. also verified experimentally that increasing pressure from 1 to 10 bar improved CO$_2$ conversion and methane selectivity [17]. Here, an efficient process for the hydrogenation of CO$_2$ to CH$_4$ over hydrotalcite-derived Ni/Al$_2$O$_3$ is evaluated over a broad range of temperatures (200–800 °C) and pressures (1–80 bar). The demonstration of the positive effect of high pressure on the conversion and selectivity of the CO$_2$ methanation process is a highlighted topic in this work. Likewise, the stability and reusability of the catalyst is evaluated through the characterization of spent samples with the objective of establishing a consistent understanding of the design of heterogeneous catalysts for the competitive production of synthetic methane from CO$_2$ emissions.

2. Results

The hydrotalcite-derived Ni/Al$_2$O$_3$-HTC catalyst contained 15 wt% Al and 43 wt% Ni, as revealed by ICP-OES elemental analysis, which is in agreement with the theoretical molar ratio. The BET surface area of the as-prepared catalyst was found to be 175 m$^2$·g$^{-1}$, with a pore volume of 0.50 cm$^3$·g$^{-1}$ and pore radius of 2 nm. After thermal treatment under H$_2$ at 500 °C for 1 h, the BET surface area increased to 247 m$^2$·g$^{-1}$, the pore volume increased to 0.57 cm$^3$·g$^{-1}$ and the pore radius increased to 2.7 nm. The pore size distributions were measured with the BJH method over the adsorption isotherm. The N$_2$ adsorption-desorption isotherms can be found in the Supplementary Materials, along with the graphs of BJH pore-size distributions (Figures S1–S4). This difference in surface area may be related to changes in the proportion of amorphous NiAl$_2$O$_4$ or Al$_2$O$_3$ and metallic Ni, which is caused by the reduction process and leads to different morphologies [18].

The temperature-programmed reduction of the hydrotalcite-derived Ni/Al$_2$O$_3$-HTC catalyst can be found in Figure 1a. A small and broad peak of hydrogen consumption is present around 250 °C, which can be attributed to the reduction of NiO species with low interaction with the Al$_2$O$_3$ support, and a sharp increase in H$_2$ consumption starts around 500 °C and with a maximum at 558 °C, which may be due to the reduction of a different species of Ni of stronger interaction with the Al$_2$O$_3$ support. Similar TPR results have been reported for another Ni/Al$_2$O$_3$ catalyst by Xu et al. [19]. Since H$_2$ consumption starts to increase at 500 °C, this was the temperature chosen for the pre-reduction step performed prior to reaction.

The XRD of the as-prepared and reduced catalysts (Figure 1b) showed no sign of Al$_2$O$_3$, which indicates that the alumina support is amorphous. The catalyst as prepared contained peaks matched to NiO (ICSD 76959) at 37.6°, 43.7°, 63.6°, 76.3°, and 80.4°. The average crystallite size of NiO phases on the catalyst as prepared was 3.9 nm. When the catalyst was reduced at 500 °C under H$_2$, the XRD peaks matched metallic Ni (ICSD 52265) at 44.5°, 51.9°, and 76.5°, with an average crystallite size of metallic Ni of 7.6 nm, although some broadened and low intensity peaks related to NiO were still visible, which suggests nickel was not fully reduced. These crystallite sizes are smaller than reported for Ni/Al$_2$O$_3$ catalysts of similar Ni weight content but synthesized from γ-Al$_2$O$_3$—i.e., Hu et al. found a 14.1 nm crystallite size for a Ni/γ-Al$_2$O$_3$ catalyst of 40 wt% Ni [11], which emphasizes the effect of the hydrotalcite precursor [11]. The average crystallite size of the Ni particles...
was estimated through Rietveld refinement of the XRD analyses for the reduced and spent catalysts, performed with Profex software version 5 [20]. The parameters obtained for the Rietveld refinement can be found in Table 1. Transmission electronic microscopy (TEM) images of the reduced catalyst were also used to obtain a size distribution of Ni nanoparticles (Figure 2). An average size of 8.7 ± 2.7 nm was found, which is similar to the crystallite size calculated from XRD.

Figure 1. (a) Temperature-programmed reduction (TPR) of as-prepared Ni/Al2O3-HTC; (b) XRD pattern of the Ni/Al2O3 catalyst as prepared and reduced at 500 °C.

Figure 2. Transmission electronic microscopy (TEM) images of Ni/Al2O3-HTC (a) as-prepared; (b,c) reduced at 500 °C under H2; (d) histogram size distribution of Ni nanoparticles.
Table 1. Rietveld refinement statistics performed on the XRD of the Ni/Al2O3-HTC catalyst.

<table>
<thead>
<tr>
<th>Ni/Al2O3-HTC</th>
<th>As Prepared</th>
<th>Reduced</th>
<th>Spent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite size/nm</td>
<td>3.9</td>
<td>7.6</td>
<td>42.4</td>
</tr>
<tr>
<td>Rp</td>
<td>1.7%</td>
<td>1.7%</td>
<td>0.5%</td>
</tr>
<tr>
<td>X^2</td>
<td>1.13</td>
<td>1.22</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>NiO</td>
<td>1.00</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni metal</td>
<td>-</td>
<td>0.98</td>
<td>0.99</td>
</tr>
</tbody>
</table>

The activity of the CO2 methanation reaction under atmospheric pressure over Ni/Al2O3-HTC, seen in Figure 3, produces CH4 and CO as the side product. The selectivity to CH4, calculated as mols of CH4 divided by mols of converted CO2, reached its maximum value of 90% around 450 °C, at which point the CO2 conversion rate was of 37%. The CO2 conversion rate maximized at 79% at the highest temperature studied, 800 °C, but at this point the selectivity to CH4 was close to zero and the reaction yielded mostly CO. The high selectivity to methane at low temperatures was expected since it is an exothermic reaction. The rate of methane production, shown in Figure 3b, was calculated based on the initial flow of CO2, the conversion, and methane selectivity. The maximum methane production at atmospheric pressure, obtained at 487 °C, was of 0.12 molCH4·gcat−1·h−1, which corresponds to 2.7 LCH4·gcat−1·h−1, and a 45% yield.

![Figure 3](image.jpg)

Figure 3. Effect of temperature on CO2 hydrogenation at atmospheric pressure over Ni/Al2O3-HTC. Reaction conditions: Ni/Al2O3-HTC pre-reduced at 500 °C, atmospheric pressure, CO2:H2 = 1:4, GHSV = 30,000 mL·gcat−1·h−1. (a) CO2 conversion and CH4 selectivity; (b) CH4 production rate.

The performance of the high-pressure CO2 methanation is shown in Figure 4. A positive correlation between pressure and CO2 hydrogenation to methane is observed, as expected due to the thermodynamic equilibrium of this reaction (Figure 4a). The selectivity to CH4 was 100% in all high-pressure conditions tested, which means CO2 conversion equals CH4 yield. The high-pressure process also allows for a large quantity of reactants to be processed at a given time rate. For instance, in this process, at the optimal conditions of 450 °C and 80 bar, with a selectivity of 100% and conversion of 84%, given the space velocity of 30,000 mL·gcat−1·h−1 with a CO2:H2 ratio of 1:4, 6 L·gcat−1·h−1 of CO2 can be processed and yield 5.04 L·gcat−1·h−1 of CH4. In an extrapolation to a potential scale up, 5.04 cubic meters of CH4 could be produced per kilogram of catalyst per hour.
Figure 4. (a) Effect of pressure at 450 °C and (b) effect of temperature at 40 bar on CO2 methanation over Ni/Al2O3-HTC. Reaction conditions: fixed-bed reactor packed 200 mg of Ni/Al2O3 pre-reduced at 500 °C, CO2:H2 = 1:4, GHSV = 30,000 mL·gcat⁻¹·h⁻¹.

In terms of methane space time yield (STY), at 450 °C the production rate of CH4 increased from 2.05 LCH4·gcat⁻¹·h⁻¹ at atmospheric pressure to 4.50 and 4.80 LCH4·gcat⁻¹·h⁻¹ when the pressure was elevated from 1 to 20 bar and 40 respectively. A maximum of methane yield was achieved at 80 bar and 450 °C, with a STY of 5.04 LCH4·gcat⁻¹·h⁻¹. This is an increase in methane STY of 2.5 times when the pressure increased from 1 to 80 bar.

The effect of reaction temperature on the high-pressure methanation of CO2 can be viewed in Figure 4b. The hydrogenation of CO2 to CH4 is an exothermic reaction, and is therefore thermodynamically hindered by higher temperatures [6]. Despite this thermodynamic effect, the increase in temperature from 350 °C to 450 °C was observed to be beneficial for the conversion of CO2 to CH4, since it helps the CO2 gas phase reaction to overcome its kinetic limitations. Moreover, at high pressure, the negative effect of temperature increases on the thermodynamic equilibrium of CO2 methanation is less pronounced [15]. At the lower reaction temperature of 350 °C and high pressure of 40 bar, a CO2 conversion of 51% was obtained with 100% selectivity to CH4, whereas at atmospheric pressure and the same temperature of 350 °C, a CO2 conversion of only 4% was observed with a 58% selectivity to CH4.

The reaction over Ni/Al2O3-HTC was 100% selective to methane over the range of temperatures and high pressures tested, with no formation of CO through the reverse water-gas shift reaction and no other hydrocarbon or alcohol observed. The absence of CO and maximized CH4 selectivity in the high-pressure reactions is related to a thermodynamic effect. As seen in Equations (1) and (2), CO2 hydrogenation to CH4 occurs with a volume contraction, unlike CO2 hydrogenation to CO. Therefore, high pressure is remarkably favorable for CO2 methanation, since it shifts the equilibrium towards the volume contraction.

\[
CO_2 + 4 H_2 \rightleftharpoons CH_4 + 2 H_2O \tag{1}
\]
\[
CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{2}
\]

The methane yield of the high-pressure CO2 methanation catalyzed by Ni/Al2O3-HTC at 40 bar was 51% at 350 °C and increased to 80% at 400 °C, with no significant changes at 450 °C. Therefore, the high pressure allows the CO2 methanation reaction to maintain high yields at higher temperatures, which is advantageous since this is an exothermic reaction and temperature control can be an issue when reactor hot spots lead to decreased activity [14]. The CO2 methanation reaction has been reported in the literature over a variety of Ni-based catalysts at atmospheric pressure, in which case the CH4 yield starts to decrease
as temperatures increase [7,17,21]. Yi et al. reported a CO\textsubscript{2} conversion of around 60% for the temperature range of 350–450 °C at atmospheric pressure over a similar catalyst Ni/γ-Al\textsubscript{2}O\textsubscript{3} of 45 wt% Ni and CH\textsubscript{4} selectivity of 95% for the temperatures of 350–400 °C [21], noticing a decrease in selectivity to 80% when the temperature reached 450 °C. Kowalik et al. found a CO\textsubscript{2} conversion of 40% for these conditions over Ni/α-Al\textsubscript{2}O\textsubscript{3}, in which case the CH\textsubscript{4} selectivity also decreased at temperatures higher than 400 °C [22]. These similar findings reinforce that, at ambient pressure, even with effective catalysts, the selectivity to CH\textsubscript{4} is hindered at higher temperatures.

As seen in Table 2, CHN elemental analyses performed on the NiAl\textsubscript{2}O\textsubscript{3}-HTC catalyst as prepared and spent after 6 h of reaction at 400 °C reveal that the carbon content did not significantly change after the reaction, indicating that carbon deposition would not be an issue either under 40 bar of pressure or atmospheric pressure. In addition, a time-on-stream plot of the reaction at 400 °C and 40 bar (Figure S7 in Supplementary Materials) showed that the reaction was stable for 7 h at 80% CO\textsubscript{2} conversion and 100% CH\textsubscript{4} selectivity.

Table 2. CHN elemental analyses of Ni/Al\textsubscript{2}O\textsubscript{3}-HTC catalyst as prepared and spent at high pressure or at ambient pressure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%C (±)</th>
<th>%H (±)</th>
<th>%N (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Al\textsubscript{2}O\textsubscript{3}-HTC as prepared</td>
<td>0.44 ± 0.04</td>
<td>1.29 ± 0.04</td>
<td>0.02 ± 0.01</td>
</tr>
<tr>
<td>Ni/Al\textsubscript{2}O\textsubscript{3}-HTC spent (40 bar)</td>
<td>0.40 ± 0.06</td>
<td>0.24 ± 0.06</td>
<td>0.04 ± 0.04</td>
</tr>
<tr>
<td>Ni/Al\textsubscript{2}O\textsubscript{3}-HTC spent (1 bar)</td>
<td>0.40 ± 0.06</td>
<td>0.59 ± 0.08</td>
<td>-</td>
</tr>
</tbody>
</table>

Ni 2p XPS analyses were used to explore the surface composition of the Ni/Al\textsubscript{2}O\textsubscript{3} catalyst as prepared, reduced, and spent after CO\textsubscript{2} methanation at 40 bar and 400 °C (Figure 5 and Table 3). A Shirley baseline was applied to all spectra. Ni 2p components were fitted with a GL(30) line shape. The BE difference due to spin orbit coupling of Ni 2p was fitted as 17.27 eV for Ni\textsuperscript{0}, 17.8 eV for NiO, and 17.6 eV for NiAl\textsubscript{2}O\textsubscript{4}. The surface of the as-prepared catalyst contained 74 At% of NiAl\textsubscript{2}O\textsubscript{4}, interpreted as the peak of binding energy (BE) ~856.04 eV, and 26% of NiO, at 853.84 eV. It is noteworthy that the XRD of the as-prepared Ni/Al\textsubscript{2}O\textsubscript{3} catalyst (Figure 1b) only revealed the diffraction pattern of NiO, which suggests that the NiAl\textsubscript{2}O\textsubscript{4} phase observed by XPS was amorphous, as the originate Al\textsubscript{2}O\textsubscript{3} was also amorphous. This composition was expected from a hydrotalcite-derived nickel-alumina catalyst and is in line with previous reports [21–26].

When reduced at 500 °C under H\textsubscript{2} for 1 h, the surface of the Ni/Al\textsubscript{2}O\textsubscript{3}-HTC catalyst presented a metallic Ni peak of ~852.00 eV, which accounts for 31 At% of nickel contribution on the surface. The increase in metallic Ni surface At% observed after reduction of the catalyst was accompanied by a decrease of NiAl\textsubscript{2}O\textsubscript{4} to 37 At%. NiO was also present on the surface of the reduced catalyst at 32 At%. The spent catalyst, in turn, presented a much lower At% of metallic Ni of only 1%, and increased NiO At% of 54, which could be explained by oxidation during reaction; however, a more probable cause was the oxidation due to prolonged exposition to air previous to XPS analysis, as the XPS analysis was performed ex situ. The Al 2p region of the XPS of the Ni/Al\textsubscript{2}O\textsubscript{3}-HTC catalyst showed peaks of Al 2p at 74.8, 75.6, and 74.8 eV for the catalyst as prepared, reduced, and spent, respectively. These energies are coherent with a Al\textsubscript{2}O\textsubscript{3} species [27]. The slight shift to lower energy observed in the as-prepared sample could be linked to a stronger interaction of Al\textsubscript{2}O\textsubscript{3} with oxidized Ni as a NiAl\textsubscript{2}O\textsubscript{4} species. On the other hand, the reduced catalyst presented a weakened interaction of metallic Ni with the Al\textsubscript{2}O\textsubscript{3} support, therefore the energy of the Al 2p orbital in the reduced catalyst closely matched the energy reported for pure Al\textsubscript{2}O\textsubscript{3} at 75.6 eV [27]. The XPS in the O 1s region of these samples can be found in SI (Figure S5) and corroborates these conclusions.
Ni 2p XPS analyses were used to explore the surface composition of the Ni/Al₂O₃ catalyst as prepared, reduced, and spent after CO₂ methanation at 40 bar and 400 °C (Figure 5 and Table 3). A Shirley baseline was applied to all spectra. Ni 2p components were fitted with a GL(30) line shape. The BE difference due to spin orbit coupling of Ni 2p was fitted as 17.27 eV for Ni₀, 17.8 eV for NiO, and 17.6 eV for NiAl₂O₄. The surface of the as-prepared catalyst contained 74 At% of NiAl₂O₄, interpreted as the peak of binding energy (BE) ~856.04 eV, and 26% of NiO, at 853.84 eV. It is noteworthy that the XRD of the as-prepared Ni/Al₂O₃ catalyst (Figure 1b) only revealed the diffraction pattern of NiO, which suggests that the NiAl₂O₄ phase observed by XPS was amorphous, as the originate Al₂O₃ was also amorphous. This composition was expected from a hydrotalcite-derived nickel-alumina catalyst and is in line with previous reports [21–26].

Table 3. Surface composition of the Ni/Al₂O₃-HTC catalyst obtained from Ni 2p XPS data.

<table>
<thead>
<tr>
<th>Ni/Al₂O₃-HTC</th>
<th>%At of Surface Elements</th>
<th>%At of Surface Ni Species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Al</td>
</tr>
<tr>
<td>As prepared</td>
<td>21</td>
<td>36</td>
</tr>
<tr>
<td>Reduced</td>
<td>13</td>
<td>36</td>
</tr>
<tr>
<td>Spent</td>
<td>11</td>
<td>33</td>
</tr>
</tbody>
</table>

The XRD of the spent catalyst (Figure 6a) shows well-defined peaks attributed to metallic Ni, whereas the XPS indicates that the surface of the catalyst after reaction was composed mostly of NiO. This discrepancy in XRD and XPS data indicates that the bulk structures of both the reduced and the spent catalyst were mostly metallic nanoparticles, even if their surfaces may have contained NiO. Although metallic Ni is essential for H₂ activation, this residual content of NiO on the catalytic surface may play a role in the reactivity of this material. Residual NiO has been suggested to hinder the agglomeration of metallic Ni nanoparticles [28]. Moreover, the presence of NiO can facilitate the activation of CO₂ and the hydrogenation of oxygenated and CO intermediates to CH₄ on a metal/oxide interface, as previously reported for similar materials [29–31]. As seen in Table 1, the nickel nanoparticles on the catalyst Ni/Al₂O₃-HTC appeared to grow from 7.6 nm to 42.4 nm after exposure to the CO₂ hydrogenation reaction conditions, which is a considerable increase in size, although they still maintained their nanometric dimensions.
A CO2-TPD profile of Ni/Al2O3-HTC pre-reduced at 500 °C (Figure S6) revealed a peak of CO2 desorption at 127 °C, which indicates that this catalyst has basic sites of weak interaction with CO2. The CO2 desorption peak at temperatures between 100–150 °C may be attributed to the interaction of CO2 with surface hydroxyls, and is often found in nickel-hydrotalcite materials [32,33]. The presence of surface hydroxyls on Ni materials has also been linked to their catalytic activity in CO2 methanation, as CO2 adsorbed on -OH groups facilitates the formation of reactive carbonate species, which, under reaction conditions, are hydrogenated to formate, and subsequently to methane [34]. In order to shed light on the reaction intermediates that may be adsorbed on the catalytic surface and help explain the high CH4 selectivity obtained, diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) analysis of the CO2 methanation reaction over the catalyst Ni/Al2O3-HTC was performed over a range of reaction temperatures, as seen in Figure 6b. At the lower temperatures of 50–100 °C, the bands seen around 1650 cm⁻¹ and 1445 cm⁻¹ can be denoted as adsorbed carbonate species [35]. Bands around 1590 cm⁻¹ and 1385 cm⁻¹ can be attributed to formate species adsorbed on the surface of the Ni/Al2O3-HTC catalyst [35]. These adsorbed formate species appeared at 200 °C and grew in intensity up to 300 °C, then started to desorb at 350 °C and could no longer be detected at 500 °C. As observed by CO2 hydrogenation at atmospheric pressure (Figure 3a), for temperatures higher than 400 °C, the CO2 conversion was higher than 20%, which can explain the lack of adsorbed formate species on the DRIFTS experiment, since at high conversion, the species adsorb and desorb quickly. No bands are observed in the 2000–2100 cm⁻¹ range, which indicates the absence of adsorbed CO. These findings may suggest that the reaction mechanism of the methanation of CO2 over Ni/Al2O3-HTC occurred via a formate pathway, which is in agreement with the literature on similar catalysts [11,35]. In this mechanistic route, CO2 adsorbed on the catalytic surface was hydrogenated to adsorbed formate species, which were observed by DRIFTS, then subsequently hydrogenated and desorbed as the final product methane.

Figure 6. (a) XRD pattern of the Ni/Al2O3-HTC catalyst spent after CO2 hydrogenation to CH4 at 400 °C and 40 bar; (b) DRIFTS of CO2 methanation reaction over Ni/Al2O3-HTC pre-reduced at 500 °C at different temperatures, atmospheric pressure, and CO2:H2 = 1:4. All spectra were baseline-corrected with spectra recorder under Ar at the same temperature.
3. Materials and Methods

The hydrotalcite-derived Ni/Al₂O₃-HTC catalyst was synthesized according to a method previously described by Ramos et al. [32]. Briefly, 1.5 M aqueous solutions of AlCl₃·6H₂O and NiCl₂·6H₂O were added to an aqueous solution of urea. The mixture was refluxed at 95 °C under stirring, aged for 65 h, and filtered. The precipitate was suspended in a solution of NH₄HCO₃ to remove residual Cl, washed with water and dried at 95 °C. Finally, the material was calcined at 500 °C in air for 5 h.

X-ray diffraction (XRD) patterns of the catalysts were obtained with a Rigaku Miniflex diffractometer using Cu Kα radiation, 40 kV tension, and 30 mA current, with a step of 2θ of 0.02° at 2°/min. Elemental percentages of Ni and Al on the Ni/Al₂O₃-HTC catalysts were evaluated by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) in a Spectro Arcos spectrometer. Samples were previously digested by alkaline fusion with lithium tetraborate at 980 °C and then dissolved in nitric acid. Elemental percentages of CHN were obtained from a Perkin Elmer 2400 series ii elemental analyzer.

X-ray photoelectron spectroscopy (XPS) data were obtained with a Specs instrument with monochromatic Al Kα of excitation energy = 1486.71 eV. A constant pass energy of 20 eV and a step of 0.05 eV were applied on all high-resolution spectra. CasaXPS software version 2.3.25 was used for peak fitting, and the C 1 s peak on adventitious carbon was calibrated to 284.8 eV.

The atmospheric pressure hydrogenation of CO₂ was performed in a Hiden Analytical Catlab reactor connected to a mass spectrometer. A fixed bed reactor was packed with 50 mg of catalyst, the pre-reduction was carried out under a hydrogen flow at 500 °C, then the catalyst was cooled down to 100 °C under argon flow and fed with the reactants at 30,000 mL·g⁻¹·h⁻¹ at a ratio of CO₂:H₂ equal to 1:4. For the high-pressure reactions, a fixed-bed flow reactor was packed with 200 mg of the as-prepared catalyst, which was pre-reduced in situ under pure H₂ under atmospheric pressure at 500 °C for 1 h before all reactions. The heating ramp employed was of 10 °C/min in all reactions and pre-reduction steps. A spring-loaded backpressure valve was used to maintain the reaction pressure at the desired value. The exit of the backpressure valve was connected to a GC System (Shimadzu GC-2030) comprised of two thermal conductivity detectors (TCD) and one flame ionization detector (FID) for analysis of the reaction mixture. The chromatographic columns used were Rt-Msieve 5A PLOT for the detection of CO and CH₄, Rt-Q-BOND PLOT for the detection of CO₂ and C₂, Rtx-1 for hydrocarbons and alcohols, and molecular sieve 5A for H₂, CO₂, CH₄, and CO₂ were quantified by TCD-1 with He as reference gas, while H₂ was quantified by TCD-2 with N₂ as reference, and other long chain hydrocarbons or alcohols formed would have been detected by FID. All columns were preceded by Porapak-N pre-columns. The calibration of the GC detectors was performed with a standard mixture cylinder sold by Messer. The reagents CO₂ and H₂ were fed into the reactor by a set of syringe pumps. All catalytic tests were performed in triplicate.

Infrared (IR) spectrometry studies were performed in a Shimadzu IR Prestige 21 spectrometer, measuring spectra of 64 scans at a spectral resolution of 4 cm⁻¹. A sample of 20 mg of Ni/Al₂O₃-HTC was placed into a Pike diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) sample cell. The catalyst was pre-treated at 500 °C under a flow of 10 mL·min⁻¹ H₂ and 50 mL·min⁻¹ argon (Ar) prior to measurements. The reaction was studied by flowing 10 mL·min⁻¹ of CO₂ and 40 mL·min⁻¹ of H₂ in 50 mL·min⁻¹ of Ar, at atmospheric pressure and at several temperatures, with a 10 °C/min heating ramp. Each spectrum was baseline corrected with a background spectrum recorder at the same temperature under a flow of pure argon. Surface area and pore volume of the catalyst before and after reduction with H₂ were measured by N₂ adsorption-desorption isotherms with a Nova 1200e surface area analyzer from Quantachrome. Before analyses, the samples were pre-treated under vacuum at 300 °C for 3 h. The surface area was calculated through the multi-point BET method, and pore size distribution was calculated through the BJH method with the adsorption curves. Transmission electron microscopy (TEM) images were acquired using a JEOL JEM 2100 microscope, operating at 200 kV of acceleration voltage.
with a LaB6 filament. The sample was dispersed in isopropanol with sonication, and dripped onto an ultrathin carbon film coated Cu grid. The histogram of nanoparticle size distribution was evaluated through these images by measuring 200 particles with ImageJ and fitting the histogram with a log-normal function. Origin 2019 software was used for data treatment and graphical illustrations of the reactions and characterization techniques.

4. Conclusions

The use of high pressure as tool to enhance the activity of a catalytic process for the production of methane from CO$_2$ hydrogenation was presented over a Ni/Al$_2$O$_3$-HTC catalyst. A selectivity of 100% for CH$_4$ was obtained over the range of temperatures studied of 350 to 450 °C at pressures of 20 to 80 bar. Therefore, the utilization of CO$_2$ for the production of methane, the main component of natural gas, has been demonstrated to be highly effective in the high-pressure catalytic process shown here. Thus, this is an efficient catalytic route to reducing CO$_2$ emissions with readily available non-noble metals with high production rates of 5.1 L·g$_{cat}^{-1}$·h$^{-1}$ of CH$_4$.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/methane3010004/s1, Figure S1: N$_2$ adsorption and desorption isotherm of as-prepared Ni/Al$_2$O$_3$-HTC, Figure S2: N$_2$ adsorption and desorption isotherm of Ni/Al$_2$O$_3$-HTC reduced at 500 °C under H$_2$, Figure S3: BJH pore size distribution performed on the adsorption isotherm of as prepared Ni/Al$_2$O$_3$-HTC, Figure S4: BJH pore size distribution performed on the adsorption isotherm of Ni/Al$_2$O$_3$-HTC reduced at 500 °C under H$_2$, Figure S5: XPS of the O 1s region on Ni/Al$_2$O$_3$-HTC, Figure S6: TPD-CO$_2$ profile of Ni/Al$_2$O$_3$-HTC pre-reduced at 500 °C under H$_2$, Figure S7: Time on stream plot of the CO$_2$ methanation reaction over Ni/Al$_2$O$_3$-HTC. Reaction conditions: 200 mg of catalyst pre-reduced at 500 °C under H$_2$ for 1 h, T = 400 °C, p = 40 bar, GHSV = 30,000 mL·g$_{cat}^{-1}$·h$^{-1}$.

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