

Article

The Development of Ni-Al Aerogel-Based Catalysts via Supercritical CO₂ Drying for Photocatalytic CO₂ Methanation

Daniel Estevez , Haritz Etcheberria and Victoria Laura Barrio * 

School of Engineering of Bilbao, University of the Basque Country (UPV/EHU), Plaza Ingeniero Torres Quevedo 1, 48013 Bilbao, Spain; daniel.estevez@ehu.eus (D.E.); haritz.echeverria@ehu.eus (H.E.)

* Correspondence: laura.barrio@ehu.eus

Abstract

The conversion of CO₂ into CH₄ through the Sabatier reaction is one of the key processes that can reduce CO₂ emissions into the atmosphere. This work aims to develop Ni-Al aerogel-based thermo-photocatalysts with large specific surface areas prepared using a sol-gel method and subsequent supercritical drying in CO₂. Different Al/Ni molar ratios were selected for the development of the catalysts, characterized using ICP-OES, N₂ adsorption-desorption isotherms, XRD, H₂-TPR, TEM, UV-Vis DRS, and XPS techniques. Thermo-photocatalytic activity tests were performed in a photoreactor with two different light sources ($\lambda = 365$ nm, $\lambda = 470$ nm) at a temperature range from 300 °C to 450 °C and a pressure of 10 bar. The catalyst with the highest Ni loading (AG 1/3) produced the best catalytic results, reaching CO₂ conversion and CH₄ selectivity levels of 82% and 100%, respectively, under visible light at 450 °C. In contrast, the catalysts with the lowest nickel loading produced the lowest results, most likely due to their low amounts of active Ni. These results suggest that supercritical drying is an efficient method for developing active thermo-photocatalysts with high Ni dispersion, suitable for Sabatier reactions under mild reaction conditions.

Keywords: CO₂ methanation; Sabatier reaction; nickel; alumina; aerogels; supercritical drying; photocatalysis; greenhouse gas; power-to-gas



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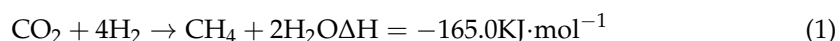
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1. Introduction

Global CO₂ emissions reached a new high in 2023, increasing by 0.1% compared to the previous year [1]. Different carbon capture and utilization (CCU) technologies have been developed with the objective of preventing further growth in emissions and the greenhouse effect. Power-to-X technologies are useful strategies for converting excess electric energy into chemical molecules, such as methane [2], in power-to-gas processes. Moreover, if the hydrogen utilized in the reaction has a renewable origin, the process will be sustainable. Methane is a widely used gas; it is a precursor for a variety of reactions, such as hydrocarbon synthesis [3] (through methane reforming [4]) and halide synthesis [5] and it is used as a rocket propellant [6].

One of the systems included in power-to-gas technologies is the CO₂ methanation reaction. This reaction was first studied by Paul Sabatier in 1902, where methane was generated due to contact between CO₂ and H₂ at high temperatures and in the presence of a catalyst [7]. The Sabatier reaction is an exothermic reaction (1), in which CH₄ and H₂O are the obtained products alongside CO, which can appear as a byproduct.



To achieve a sustainable process, temperatures should be minimized to the lowest value at which methane can still be obtained. To this end, different catalysts have been used. For example, noble metal-based catalysts have been developed, utilizing metals such as Ru [8–10], Rh [11–14], and Pd [15–17]. Ru shows the highest activity and stability [18]; it achieves methane conversion rates close to 90% at 375 °C for 100 h [19], followed by Rh and Pd. Considering the high cost and scarcity of these metals, cheaper alternative solutions have been found. One solution is to use non-noble metals, such as Ni [20–25], Co [26–29], and Fe [30–32], which have been used as catalysts. Nickel is the most widely used due to its low price and high availability. The activity of Ni-based catalysts can vary depending on several conditions, e.g., catalytic support, active metal dispersion, particle size, and the addition of other metals acting as dopants. In some studies, CO₂ conversions of 92% were obtained at 350 °C [33]. Nevertheless, even if these materials present high methanation activity, they deactivate easily via coke deposition, which blocks the active sites of the catalyst. In addition, the Ni particles can suffer from sintering at high temperatures, decreasing the catalyst's activity. Solving this issue requires searching for adequate support, adding other metals to form a co-catalyst, and identifying the proper reaction conditions.

Moreover, the support of each catalyst determines different textural properties, including surface area and pore volume, the acidity or basicity of the catalyst, and the presence of higher or lower active metal dispersion, which yields better conversion and selectivity results. Traditionally, different metal oxides have been used as catalytic supports, and depending on which one is applied, the methanation reaction will follow one reaction path or another. For example, if Al₂O₃ or MgO is used as the support, the reaction will follow a bicarbonate formation route; however, if TiO₂ or ZrO₂ is used as the support, the reaction will occur through the formation of bidentate carbonate species [34].

As stated previously, one of the most important properties when synthesizing a Ni-based catalyst is the surface area; a larger surface area increases the active metal dispersion, and thus, sintering is avoided. In response to the need for higher surface areas, new supports were developed, such as hydrotalcites, zeolites, and aerogels. Hydrotalcites are double-layered hydroxides, the properties of which vary depending on the hydroxides of the compound and the ratios between them. In some cases, hydrotalcite-based catalysts with surface areas as high as 240 m²/g were synthesized [35] in comparison to the 125 m²/g of traditional Ni catalysts [36]. Zeolites are crystalline microporous materials; their activity varies depending on the properties of the materials, which are determined via the synthesis method. CO₂ conversions as high as 70 to 80% were obtained at 400 °C with different zeolite-supported Ni-based catalysts [37–39]. In the case of aerogels, these materials are gelified and supercritically dried so that the original gel structure is preserved; thus, high porosities and surface areas are obtained. While their properties have been widely studied, their potential as catalysts for the CO₂ methanation reaction has not been investigated. Even so, aerogels with surface areas above 300 m²/g have been developed [40], making them adequate candidates for the dispersal of active metals such as nickel. This was tested in a case where a Ni-based graphene aerogel was synthesized, rendering 80% CO₂ conversion at 350 °C in comparison to its graphene oxide counterpart, which reached 68% conversion at the same temperature [41].

Given the high CO₂ emissions and their consequences, global warming, there is a need to develop CO₂ methanation technology for industrial scale-up, reducing the rate of human-generated CO₂ emissions. For this purpose, catalysts with appropriate physical, chemical, and structural properties (such as high specific surface area or high metal dispersion) offering high methanation activity must be studied. Economic and abundant metals like nickel, cobalt, or iron, which are highly active as catalysts for the Sabatier reaction, need to be investigated for this process to become economically affordable. It is also necessary to develop and improve existing catalytic systems with previously validated high CO₂ conversion and selectivity towards CH₄, so that the whole technique can be optimized, either via the search for new catalytic formulations with different metals and supports or using innovative synthesis methods.

In this project, a series of Ni and Al aerogel-based catalysts were prepared. The Al/Ni molar ratio was varied via a sol–gel reaction, followed by subsequent supercritical CO₂ drying. The structural, compositional and physicochemical properties were studied using N₂ adsorption–desorption isotherms, inductively coupled plasma optical emission spectroscopy (ICP-OES), hydrogen temperature-programmed reduction (H₂-TPR), powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), ultraviolet–visible diffuse reflectance spectroscopy (UV-Vis DRS), and transmission electron microscopy (TEM). The thermo-photocatalytic activity of CO₂ methanation was determined in a bench-scale plant with an 8 mm open, removable quartz window, and an LED light source was attached. The reactions were performed at a temperature range of 300 to 450 °C, at a constant pressure of 10 bar, with no light, a 470 nm light source, or a 365 nm light source, and a catalytic mass of 5 mg.

2. Results and Discussion

2.1. Textural Properties

The Al/Ni molar ratio obtained using ICP-OES is displayed in Table 1. The molar fractions of each catalyst were similar to the theoretical values. Regarding the N₂ adsorption and desorption results, the calcined catalysts exhibited large specific surface areas. These values increased with the aluminum content, as expected, owing to alumina's large surface area. The total pore volume and pore diameter increased following the same trend with higher aluminum loading. Notably, the pore diameter values were larger than those typically observed in other large surface area materials, such as hydrotalcites [42].

Table 1. Compositional and textural properties of the prepared catalysts.

Sample	Nominal Al/Ni Molar Ratio	Al/Ni Molar Ratio	Al/Pt Molar Ratio (wt %)	S _{BET} (m ² /g)	V _{t, pore} (cm ³ /g)	D _{BJH} (nm)
AG 1/3	0.33	0.30	---	156 ± 13	0.56	7.5
AG 1/2	0.50	0.41	---	207 ± 18	0.98	17.8
AG 1/1	1.00	0.98	---	215 ± 19	2.28	24.6
AG-Pt	1.00	0.97	1863 (0.1%)	209 ± 19	0.84	6.8
AG 2/1	2.00	1.93	---	270 ± 25	3.26	66.6
AG 3/1	3.00	2.94	---	492 ± 50	5.50	67.0
AG 4/1	4.00	3.79	---	358 ± 35	3.63	11.5

The formation of large pores in the Al/Ni aerogels can be attributed to the synthesis method used, which maintains the gel's structure throughout the supercritical drying process. In all cases, the shape of the isotherms corresponded to Type IV isotherms, which is characteristic of mesoporous materials. These are shown in Figure S1 of the Supplementary Material.

Table 1 shows the complete results of the prepared catalysts, where S_{BET} , $V_{\text{t, pore}}$, and D_{BJH} refer to the surface area calculated using the Brunauer–Emmett–Teller (BET) method, the total pore volume, and the pore diameter obtained using the Barrett–Joyner–Halenda (BJH) model, respectively.

2.2. X-Ray Diffraction

The X-ray diffraction results shown in Figure 1 provide insight into the crystalline structure of the catalysts. As highlighted, the different peaks present in all samples correspond to NiO (PDF 00-001-1239), along with a minor presence of NiAl_2O_4 spinel (PDF 00-001-1299). No peaks were detected for Al_2O_3 ; thus, the support was amorphous. Moreover, the sample with the highest Ni content (AG 1/3) exhibited the highest degree of crystallinity.

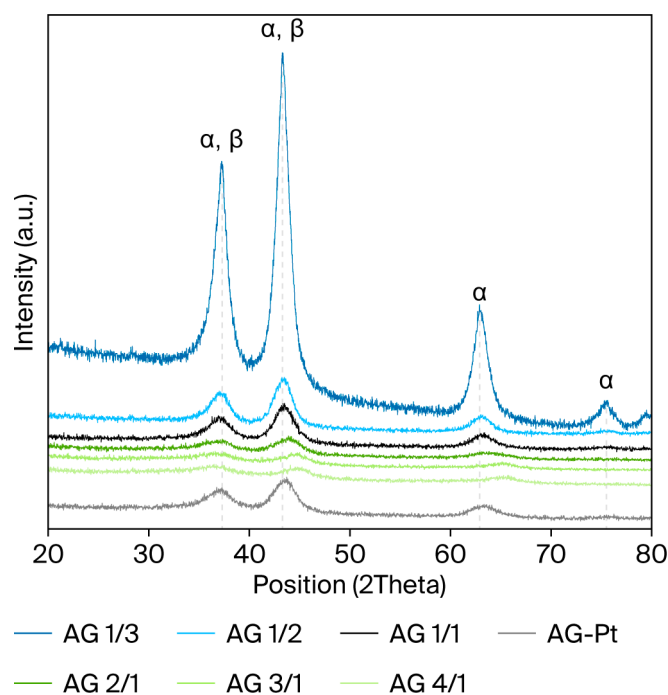


Figure 1. XRD profiles of calcined AGs. α signals correspond to NiO, while β signals correspond to NiAl_2O_4 spinel.

2.3. H_2 Temperature-Programmed Reduction (H_2 -TPR)

The H_2 -TPR profiles of the calcined AGs are shown in Figure 2. In every catalyst, similar behavior was observed—one peak with three different observable regions. The first section, up to 530 °C, was attributed to the interaction between the NiO and the alumina [43,44]. The intermediate peak (from 530 to approximately 640 °C) corresponded to the same species with stronger interactions. Finally, the H_2 consumption from 640 to 680 °C was ascribed to the reduction in the NiAl_2O_4 spinel [45,46], which became apparent in the calcination step of the synthesis. The presence of these species was confirmed by the XRD results. Figure 2 shows how AG 2/1, AG 3/1, and AG 4/1 presented a lower amount of NiO than the rest of the catalysts. In the case of AG 1/2 and AG 1/3 with higher nickel contents, Ni was more extensively reduced, and the formation of aluminates was observed.

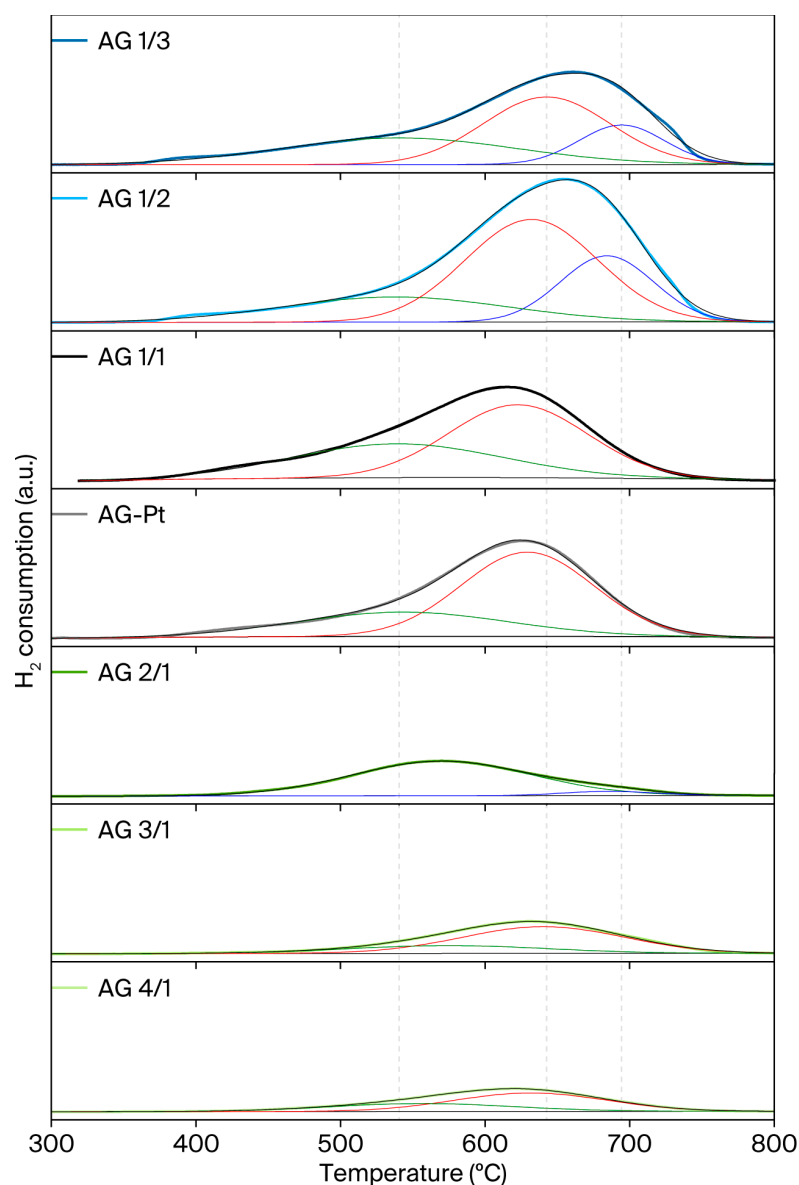


Figure 2. H_2 -TPR profiles of calcined AGs. The different lines are attributed to the contribution of different species: the green line corresponds to the weak $NiO-Al_2O_3$ interaction; the red line corresponds to the strong interaction between NiO and Al_2O_3 and the dark blue line corresponds to the contribution of the $NiAl_2O_4$ spinel.

2.4. Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) measurements revealed that the nanoparticles in all the samples presented an oval morphology, except for AG 1/3, where hexagonal-shaped nanoparticles were observed. This was supported by the XRD results, where the crystallinity of the AG 1/3 sample was superior. Particle size distributions were relatively uniform for each sample, with diameters ranging between 2.0 and 5.0 nm in most cases. However, a shift to larger particle sizes was noted in samples with a higher nickel content from 3.0 to 6.0 nm for AG 1/2 and 3.0 to 8.0 nm for AG 1/3. To evaluate the effect of thermal treatment on the morphology of the materials, the non-calcined sample AG 1/1 (named AG 1/1 V) was also examined. Notably, the virgin aerogel presented larger Ni particles than its calcined counterpart, indicating that the calcination process enhanced the dispersion of the active metal phase. Moreover, EDX mapping confirmed the homogeneous distribution of both Ni and Al samples, with no significant evidence of particle agglomeration. A comparison of the morphological differences for the prepared catalysts is shown in Figure 3,

while the TEM micrographs of the remaining catalysts are provided in Figure S2 of the Supplementary Material.

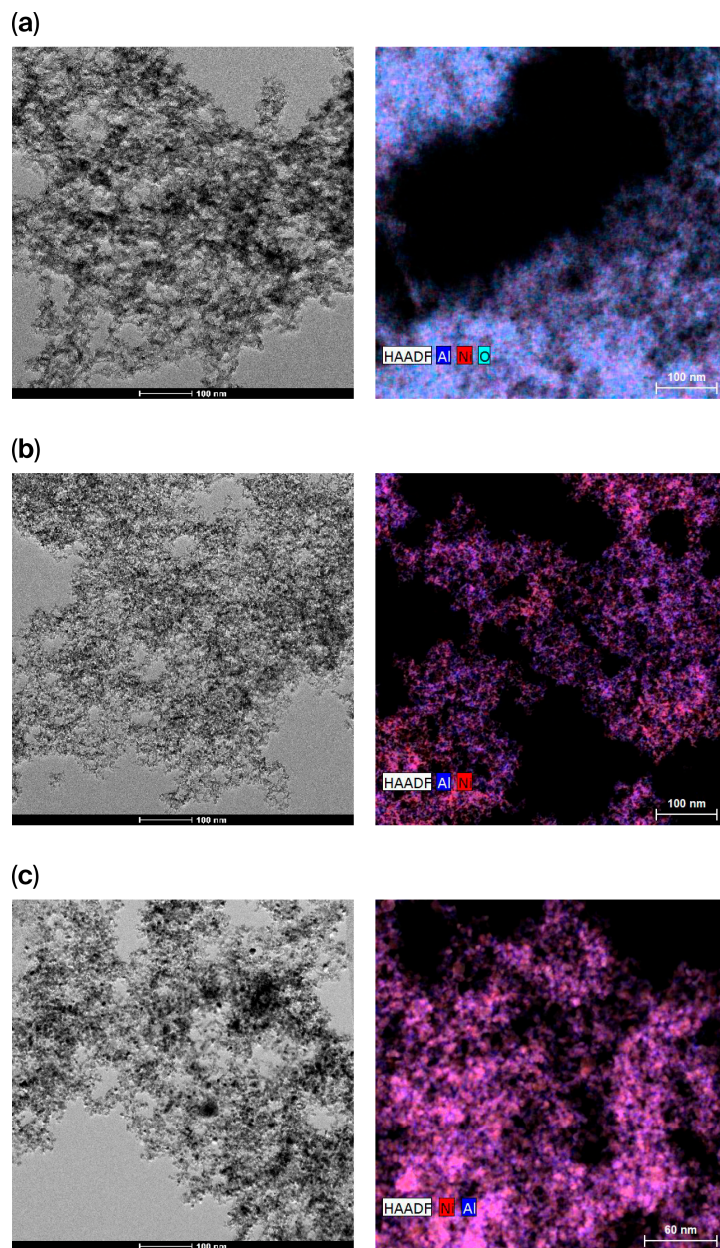


Figure 3. TEM micrographs (left) and EDX mapping (right) of (a) AG 1/1 V, (b) AG 1/1, and (c) AG 1/3.

2.5. UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS)

The bands displayed in the UV-visible diffuse reflectance spectroscopy (UV-vis DRS) spectra (Figure 4) correspond to the different Ni-containing species present in the catalytic samples. The absorption bands in the 250–300 nm region are attributed to NiO species. These bands increase in intensity with metal loading and shift to longer wavelengths (red shift) based on the strong interaction between the Ni^{2+} and the metal support. The bands appearing at these wavelengths have been previously related to the transition of the O^{2-} (2p) $\rightarrow$ Ni^{2+} (3d) charge transfer, which is characteristic of NiO species [47]. The second band, located at the 600–800 nm region, can be attributed to the contributions of the NiAl_2O_4 spinel and NiO species. Catalysts with lower Ni contents (AG 3/1 and AG 4/1) showed a higher absorbance and a flatter shape, which explains the small contribution

of the $d \rightarrow d$ transitions from the tetrahedral Ni^{2+} of the spinel species [48] (as seen in the XRD results). On the other hand, catalysts with higher metal contents (such as AG 1/3 or AG 1/2) showed a profile similar in shape to the typical $d \rightarrow d$ transitions of Ni^{2+} in the NiO [49].

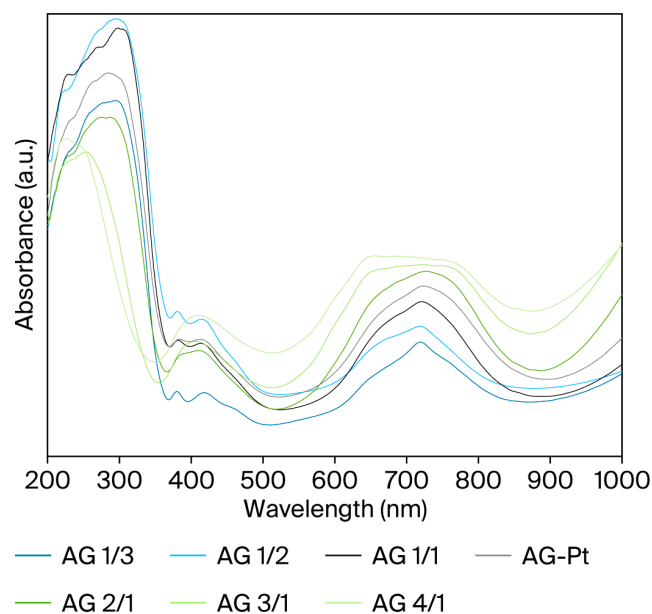


Figure 4. UV-visible DRS absorption spectra of the different Ni aerogels.

Additionally, the direct band gap value was calculated by using the Tauc equation, and by plotting $(\alpha h\nu)^2$ vs. $(h\nu)$. The Tauc plot of every catalyst can be found in Figure S3 of the Supplementary Material, while the resulting band gap energies are shown in Table 2. As can be observed, the band gap energy lowers as the Ni content increases, which could be attributed to the interaction between the Ni 3d and O 2p states in the valence and conduction bands [50].

Table 2. Band gap energy values, calculated by the Tauc equation.

Sample	Band Gap Energy (eV)
AG 1/3	3.38
AG 1/2	3.36
AG 1/1	3.40
AG-Pt	3.39
AG 2/1	3.46
AG 3/1	3.52
AG 4/1	3.87

To summarize, UV-vis DRS was used to confirm the presence of two different species in our samples: NiO, as the principal species in samples with higher metal contents (AG 1/3 and AG 1/2), and NiAl_2O_4 , which appeared in samples with lower loadings (AG 3/1 and AG 4/1) along with the NiO signal.

2.6. X-Ray Photoelectron Microscopy (XPS)

The elemental composition of the surface and oxidation state of the metals were studied via X-ray photoelectron spectroscopy (XPS) and are shown in Table 3. In all cases,

the Al/Ni atomic ratios obtained using XPS were higher than the ratios obtained using ICP-OES, indicating lower nickel loading on the surface than expected, probably due to the defective distribution of the metals during the synthesis or the difference in the general content of each metal, as shown by ICP-OES. In the case of AG-Pt, 0.01% of Pt was detected with the Pt 4d5 signal, which translates into an Al/Pt atomic ratio of 2068.

The Ni 2p XPS spectra of every aerogel catalyst are presented in Figure 5. In all cases, three different peaks were observed for three different species: the first one at 852.8 eV corresponds to metallic Ni on the surface of the catalysts; the second peak at 858.2 eV appears due to the Ni^{2+} coming from the NiO; and the third peak corresponds to its satellite at 864.2 eV [42]. This behavior is apparent in both the Ni 2p_{3/2} and Ni 2p_{1/2} zones. In this regard, no significant differences were spotted when changing the Al/Ni ratio.

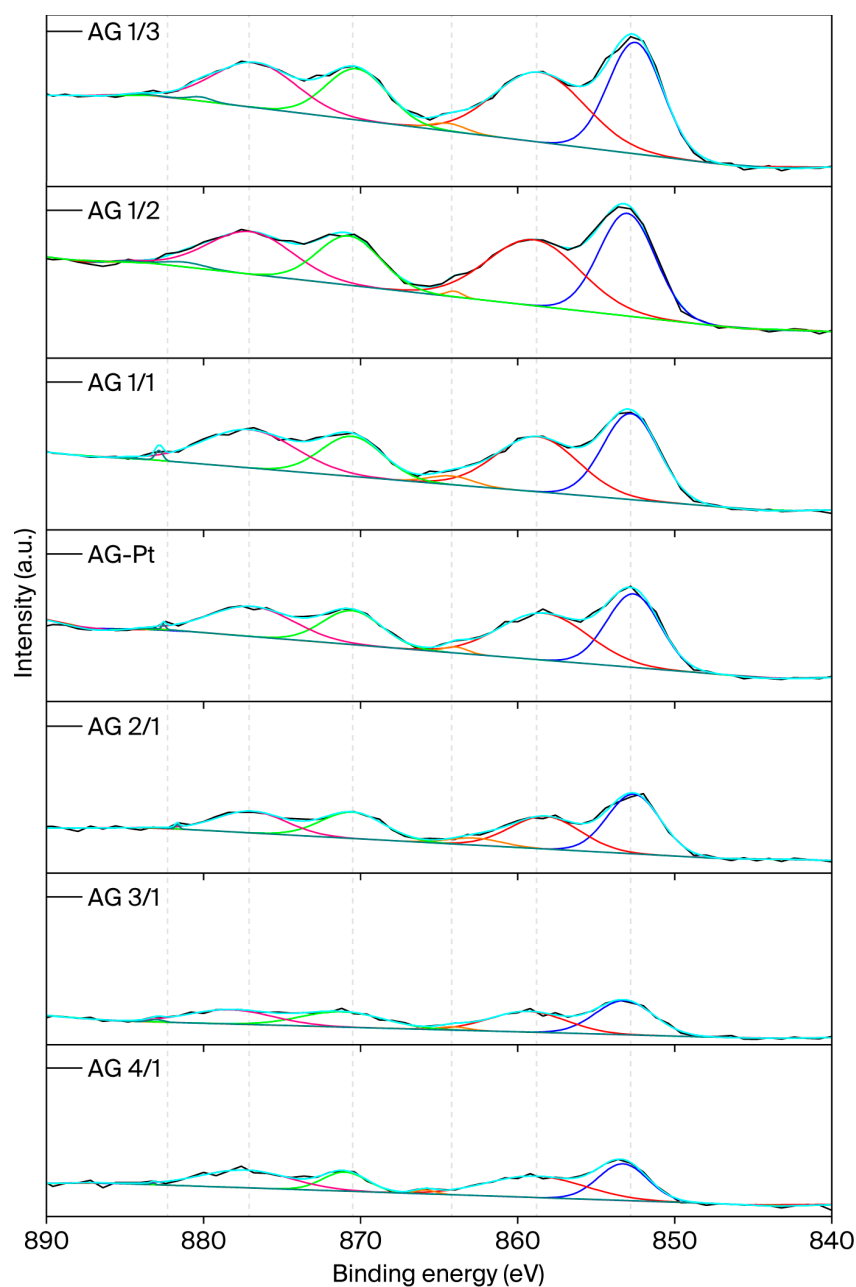


Figure 5. XPS spectra of the different calcined catalysts. The different lines correspond to different signals: dark blue and light green correspond to surface Ni; red and purple correspond to Ni^{2+} coming from NiO; orange and dark green are satellites of the red and purple ones.

Table 3. Al/Ni ratio of the different catalysts obtained by XPS after calcination at 700 °C.

Catalyst	Al/Ni Atomic Ratio	Al/Pt Atomic Ratio
AG 1/3	1.00	---
AG 1/2	1.07	---
AG 1/1	1.67	---
AG-Pt	1.63	2068
AG 2/1	2.04	---
AG 3/1	3.17	---
AG 4/1	3.93	---

In the case of the O 1s spectra, only one peak was found at 528.2 eV, corresponding to the O^{2−} present in the NiO of the catalysts. Moreover, the Al 2p peak of the AG 1/1 sample appeared at 73.8 eV; thus, it was assigned to the Al₂O₃ species in the sample [51]. The position of this peak appeared at a lower binding energy when compared to the rest of the catalysts (e.g., 71.5 eV for AG 4/1 and 70.6 eV for AG 1/3). No peaks were observed for Pt in the AG-Pt sample, probably due to the low loading present in the sample.

2.7. CO₂ Methanation Activity Performance

The performance results of the different materials, in terms of CO₂ conversion, are shown in Figure 6.

For the case under dark conditions, CO₂ conversions of 65–75% were achieved at high temperatures (>400 °C), with the catalytic systems containing higher Ni loadings (AG 1/1, AG 1/2, and AG 1/3). In contrast, the aerogels with a higher aluminum content (AG 2/1 and AG 3/1) only reached 30% conversion at the same temperature. Finally, the catalyst with the highest amount of alumina (AG 4/1) did not produce any methane, probably due to its low content of active nickel, as measured using the H₂-TPR results. Regarding methane selectivity, all catalysts except AG 4/1 exhibited values close to 100%, while AG 4/1 showed a reduced selectivity of 75% at the highest temperature.

When visible light was used as an activity enhancer, CO₂ conversions were generally higher in comparison to those achieved under dark conditions. Additionally, almost all the catalysts presented activity starting at around 400 °C, in contrast to the results achieved under dark conditions. In particular, AG 1/1 and AG-Pt showed catalytic activity starting at 300 and 350 °C, respectively, highlighting their potential to reduce the energy demand of methanation, despite AG-Pt displaying slightly lower overall conversion levels (besides AG 1/3, which showed catalytic activity as low as 250 °C). Furthermore, under visible light conditions, the selectivity towards CH₄ improved with respect to dark conditions, reaching values close to 100% at the highest temperatures in all cases.

Using ultraviolet light, the results were intermediate between those obtained under dark and visible light conditions in terms of both CO₂ conversion and CH₄ selectivity. Regarding CO₂ conversion, a decrease was observed when increasing the aluminum content, and the AG 1/3 catalytic system reached almost 80% conversion at 450 °C. In this case, the catalytic activity became significant at higher temperatures compared to visible light and at lower temperatures compared to dark conditions. Regarding methane selectivity, all the catalysts reached values close to 100%, except AG 4/1, which reached a lower maximum selectivity of 83% at the highest temperature.

Under all three experimental conditions, catalysts with higher nickel contents exhibited higher CO₂ conversion rates, with AG 1/3 obtaining the highest conversion rate under visible light as the catalyst with the largest amount of Ni. This tendency can be attributed

to the high rate of nickel dispersion and low particle size in all the samples, as noted by the TEM results. Additionally, the behavior of the catalysts under both light sources can be explained with the absorbance results, in which absorbance in the UV and the visible regions was noticed for all the catalysts. As can be noticed, the activity results with visible light are enhanced with the drop in the band gap energy, which enables the higher use of the visible-light spectrum [52] and triggers the formation of plasmonic hot electrons that are used by the CO₂ conversion intermediates [53].

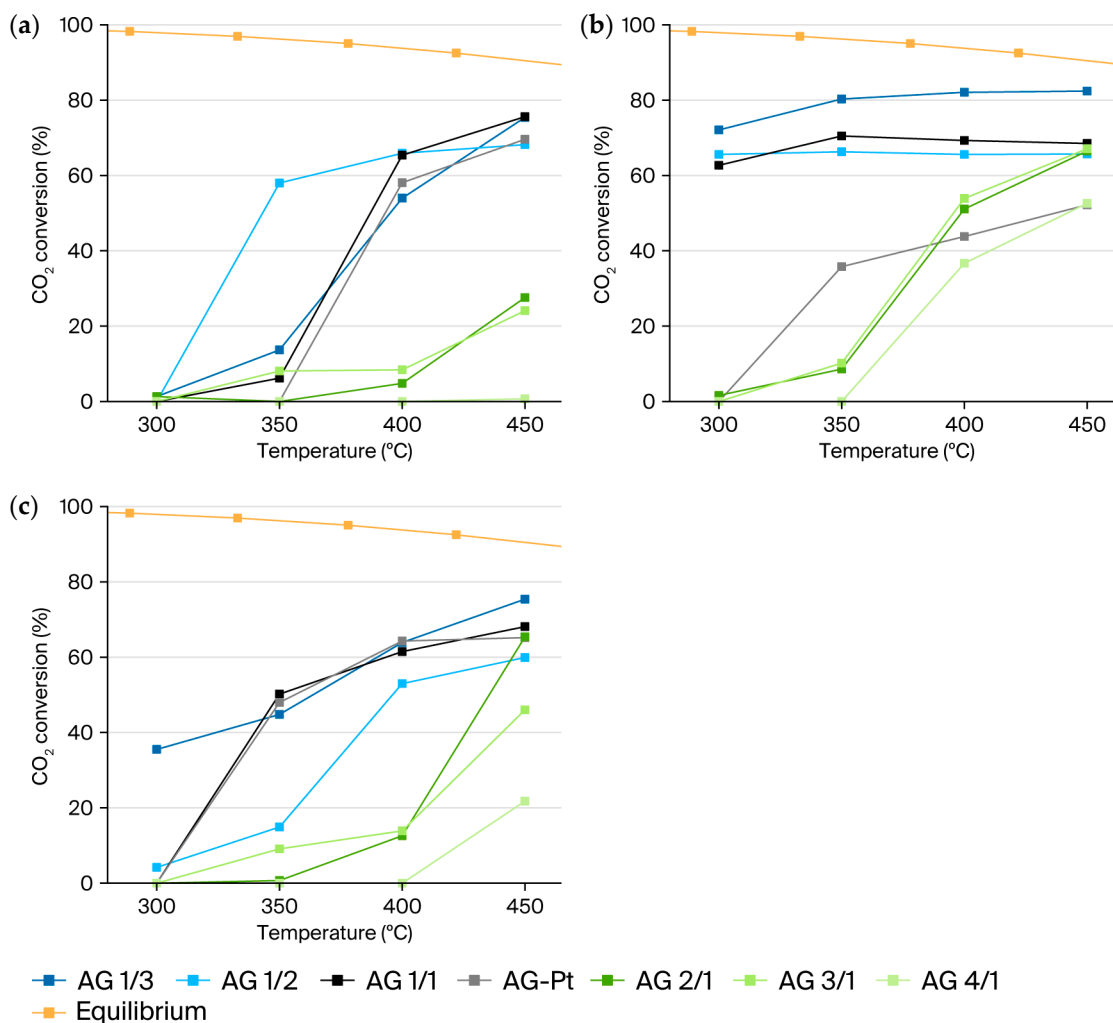


Figure 6. Thermo-photocatalytic activity results of aerogels under different conditions: (a) in the dark; (b) under visible light ($\lambda = 470$ nm); and (c) under UV light ($\lambda = 365$ nm).

It is observed that high conversions are achieved at medium–high temperatures, with visible light enhancing catalytic activity the most in all cases. The use of a visible light source enables higher conversions at 300 °C in comparison to the other conditions. Regarding the AG-Pt catalyst, an improvement in the conversion rate was expected over the original catalyst; however, it did not surpass the conversions obtained by AG 1/1. Therefore, the synthesis and drying method used to obtain the aerogel-based catalysts was successful in synthesizing catalysts with highly dispersed nickel, including those with higher loadings, which were active as thermo-photocatalysts, and those that avoided noble metals.

The use of nickel aerogels as catalysts has yet to be developed in the CO₂ methanation reaction, despite conventional Ni catalysts being widely studied. Lin et al. synthesized Ni-based mesoporous alumina catalysts and tested them in a temperature range between 200 and 500 °C [54]. Their reported conversions are similar to those obtained with our

aerogels under visible light (77% with their catalysts at 360 °C, 80% with AG 1/3 at 350 °C); however, considering that only 1/100 of the catalyst mass (500 vs. 5 mg) was used in our case, the productivity of our catalysts is much higher.

As previously stated, one of the most used metals as a catalyst for CO₂ methanation is the noble metal ruthenium. Garbarino et al. studied the catalytic activity of a pre-reduced commercial 3 wt% Ru/Al₂O₃ catalyst in the temperature range of 250 to 500 °C [19]. They obtained CO₂ conversion values similar to our maximum at 375 °C and reached their highest value (around 80%) at 400 °C. Even if the metal content of their catalyst was significantly lower than our AG 1/3 catalyst, both achieved similar CO₂ conversions. From an economic point of view, nickel is much cheaper than ruthenium, so even if our catalysts have a higher amount of metal, they remain less expensive overall.

In another study, Italiano et al. investigated the CO₂ methanation reaction using Ni-based catalysts, synthesized via solution combustion, and tested in a temperature range from 250 to 500 °C [55]. Their catalyst started to exhibit significant activity when 400 °C was reached (57% of CO₂ conversion); when compared to the results obtained in the present work, this indicates notably lower efficiency. Furthermore, they employed 20 times higher mass for the catalyst compared to ours, emphasizing the high productivity of aerogel-based materials.

3. Materials and Methods

3.1. Catalyst Preparation

The Ni/Al aerogels were prepared following the sol–gel method reported by Gash et al. [56], in which propylene oxide is the gelation agent. Afterward, the supercritical drying of the gels was performed using CO₂ as the solvent. The reagents used in this synthesis were nickel (II) chloride hexahydrate (NiCl₂·6H₂O; 99.9% purity; Sigma-Aldrich, St. Louis, MO, USA) and aluminum nitrate (III) nonahydrate (Al(NO₃)₃·9H₂O; >98% purity; Honeywell, Seelze, Germany) as metal precursors; liquid propylene oxide (PO; >99.5% purity; Sigma-Aldrich, Steinheim, Germany) as the gelation agent; and ethanol (EtOH; pure; PanReac, Darmstadt, Germany) as the solvent. The metal precursors were dissolved and stirred in ethanol with different Al:Ni molar ratios (1:3, 1:2, 1:1, 2:1, 3:1, and 4:1) until the complete dissolution of the salts (total 3.12 mmol in the case of 1:1) was achieved, followed by the slow addition of as received PO, the volume of which varied with the molar proportion of each material (PO mol/precursor mol = 11).

After aging for 24 h and several cleanings with EtOH, supercritical drying was carried out. Small pieces of the as-synthesized gel were placed inside the dryer (10 °C, 1 bar), and it was filled with liquid CO₂ (lCO₂), reaching a pressure of 50 bar. Then, several lCO₂ exchanges were made to remove the remaining EtOH, as well as other impurities. Finally, the temperature of the dryer was raised to 40 °C (70–80 bar), enabling the lCO₂ to reach the supercritical state (scCO₂). These conditions were maintained for 1 h before depressurizing at a slow rate. After performing the supercritical drying, the aerogels were calcined at 700 °C in air [57,58] at a heating rate of 2 °C/min for 4 h. The prepared samples were named AG 1/3, AG 1/2, AG 1/1, AG 2/1, AG 3/1, and AG 4/1.

Considering the previous good performance results of Pt as a catalyst for CO₂ methanation, AG 1/1 with a 0.25 wt% loading of Pt was synthesized. To perform the synthesis, the Pt precursor ([Pt(NH₃)₄][NO₃]₂; 99.9% purity; Thermo Scientific, Kandel, Germany) was added in the dissolution step. The rest of the synthesis and drying methods were followed as described above, and this sample was named AG-Pt.

3.2. Catalyst Characterization

Inductively coupled plasma–optical emission spectroscopy (ICP-OES) experiments were conducted (Optima 2000 DV; Perkin Elmer, Tres Cantos, Spain) to study the metal loading of the samples. They were digested in an acid solution before analysis at a plasma flux of 15 L/min.

The BET surface area (S_{BET}) and the total pore volume (V_p) were calculated with the N_2 adsorption and desorption isotherms (Autosorb iQ3; Quantachrome (Anton Paar), Madrid, Spain) after prior degasification at 250 °C.

X-ray diffraction (XRD) analysis was carried out (X'pert PRO automatic diffractometer; Panalytical, San Sebastián de los Reyes, Spain) at 40 kV to elucidate the crystalline structure of the samples, applying a Cu-K α radiation of $\lambda = 1.5418 \text{ \AA}$, with a scanning 2θ range of 5 to 80°.

The reducibility of the materials was studied through H_2 temperature-programmed reduction (H_2 -TPR) experiments (AutoChem II; Micromeritics, L'Hospitalet de Llobregat, Spain) after the calcination of the catalysts. They were heated up to 850 °C at a rate of 10 °C/min, under a constant 5% H_2/Ar flow, after a previous drying step with He at 200 °C for 30 min.

Transmission electron microscopy (TEM) was performed (Talos F200X, 200 kV; Thermo Fisher, Alcobendas, Spain) to observe the morphology of the obtained nanoparticles and measure the particle size distribution. Elemental mapping was performed using the HAADF-EDX method.

The binding energies, and thus, the oxidation states of the metals on the samples were measured via X-ray photoelectron spectroscopy (XPS) analyses (5000 VersaProbe II; PHI (Irida), Madrid, Spain), using a monochromatic X-ray source of Al (K α , 1486.6 eV) and a beam diameter of 200.0 μm . The signal corresponding to the C 1s at 284.8 eV was used as an internal standard to correct the binding energy shift.

UV-visible diffuse reflectance spectroscopy (UV-vis DRS) was used to understand the photochemical behavior of the catalysts (V-770; Jasco, Madrid, Spain), measuring their absorbance at different wavelengths. In addition, this technique enabled us to calculate the band gap of each material. The diffuse reflectance of the samples was measured in a range of 2200 to 200 nm, and prior to that, a blank background correction was made.

3.3. Activity Tests

The thermo-photocatalytic activity tests were performed in a photoreactor with an 8 mm open quartz window. Two different light sources can be attached to this reactor for ultraviolet light (365 nm, 3.4 eV) and visible light (470 nm, 2.7 eV). The intensity of the light was analyzed using a GL Optic Spectis 1.0 spectrometer, which was coupled to an Opti Sphere 48 (GL Optic, Puszczkovo, Poland), and a light intensity of 2.4 W/cm² was fixed for both light sources. The bench-scale plant (PID Eng&Tech, Alcobendas, Spain) reached temperatures of up to 450 °C and pressures of 10 bar. In all cases, the total gas flow was 50 mL_N/min with a stoichiometric gas composition ($\text{CO}_2:\text{H}_2 = 1:4$). The composition of the products was analyzed using an online CompactGC 4.0 gas chromatograph (GAS, Breda, The Netherlands), which had both TCD and FID detectors.

Before each activity test, the catalysts were sieved to a particle size of between 0.42 and 0.5 mm and subsequently reduced in a flow of 20% H_2/N_2 . The reduction temperature for each material was determined by considering the H_2 -TPR results. For all catalysts, a common temperature of 600 °C was used to perform the reduction, at a heating rate of 5 °C/min and for 2 h. During the reaction, the temperature varied from 300 to 450 °C, and the pressure was fixed at 10 bar. In each test, a catalyst mass of 5 mg and a ramp of

5 °C /min were used to heat the system to each temperature. The system was maintained for 1.5–2 h while the effluent gas composition was constantly analyzed.

The activity results, in terms of CO₂ conversion and CH₄ selectivity, were calculated using the following equations:

$$\text{CO}_2 \text{ Conversion (\%)} = \frac{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \times 100 \quad (2)$$

$$\text{CH}_4 \text{ Selectivity (\%)} = \frac{[\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{out}} + [\text{CO}]_{\text{out}}} \times 100 \quad (3)$$

4. Conclusions

The objective of this study was to develop aluminum and nickel aerogel-based catalysts for the methanation of CO₂ to decrease emissions and reduce the greenhouse gas effect. Different Al/Ni molar ratios were established, and a sol–gel process followed by supercritical drying with CO₂ was chosen to synthesize the aerogels. Various characterization techniques confirmed the large specific surface areas of these materials, reaching values of almost 500 m²/g in some cases, alongside the presence of reducible NiO. When performing the thermo-photocatalytic activity tests, a trend in the results was observed depending on the light conditions used. In dark conditions, significant CO₂ conversion was reached at temperatures above 400 °C, such as 65.9%, when using the AG 1/2 catalyst. The visible light source helped improve methanation activity in terms of CO₂ conversion. Values as high as 80% were obtained in the case of AG 1/3. UV light provided activity results between dark and visible light conditions, achieving 75% CO₂ conversion with the same catalyst at 450 °C. Regarding metallic loadings, catalysts with higher Ni loadings produced the best results due to the high levels of active metal in the samples. Due to their lightweight nature, large surface area, and high catalytic activity, these materials could provide an alternative for using the Sabatier reaction.

Even if these catalysts provide good thermo-photocatalytic results, some future work should be performed in order to address some of the issues recognized in the present work. For instance, activity tests should be performed at lower temperatures to try to reduce energy consumption and highlight the photocatalytic contribution of the materials. Furthermore, stability tests will be carried out in the future, with the objective of testing out the long-term stability of these materials and evaluating their industrial viability.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal15070686/s1>, Figure S1: N₂ adsorption–desorption isotherms of the different catalysts; Figure S2: TEM micrographs and EDX mapping of AG 2/1, AG 3/1, AG 4/1, AG-Pt, and AG 1/2; Figure S3: Tauc plots for all catalysts, used to calculate the direct band gap energy.

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Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Abbreviations

The following abbreviations are used in this manuscript:

AG	Aerogel
lCO ₂	Liquid CO ₂
ICP-OES	Inductively Coupled Plasma–Optical Emission Spectroscopy
BET	Brunauer, Emmet, and Teller Theory
BJH	Barrett–Joyner–Halenda
XRD	X-Ray Diffraction
H ₂ -TPR	H ₂ Temperature-Programmed Reduction
TEM	Transmission Electron Microscopy
HAADF	High-Angle Annular Dark Field
EDX	Energy-Dispersive X-Ray Spectroscopy
UV-Vis DRS	UV-Visible Diffuse Reflectance Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
TCD	Thermal Conductivity Detector
FID	Flame Ionization Detector

References

1. Liu, Z.; Deng, Z.; Davis, S.J.; Ciais, P. Global Carbon Emissions in 2023. *Nat. Rev. Earth Environ.* **2024**, *5*, 253–254. [\[CrossRef\]](#)
2. Lewandowska-Bernat, A.; Desideri, U. Opportunities of power-to-gas technology in different energy systems architectures. *Appl. Energy* **2018**, *228*, 57–67. [\[CrossRef\]](#)
3. Karakaya, C.; Kee, R.J. Progress in the direct catalytic conversion of methane to fuels and chemicals. *Prog. Energy Combust. Sci.* **2016**, *55*, 60–97. [\[CrossRef\]](#)
4. Sun, L.; Wang, Y.; Guan, N.; Li, L. Methane Activation and Utilization: Current Status and Future Challenges. *Energy Technol.* **2019**, *8*, 1900826. [\[CrossRef\]](#)
5. Ma, J.; Zhu, C.; Mao, K.; Jiang, W.; Low, J.; Duan, D.; Ju, H.; Liu, D.; Wang, K.; Zang, Y.; et al. Sustainable methane utilization technology via photocatalytic halogenation with alkali halides. *Nat. Commun.* **2023**, *14*, 1–8. [\[CrossRef\]](#) [\[PubMed\]](#)
6. van Schyndel, J.; Goos, E.; Naumann, C.; Hardi, J.S.; Oswald, M. Effects of Compounds in Liquefied Methane on Rocket Engine Operation. *Aerospace* **2022**, *9*, 698. [\[CrossRef\]](#)
7. Vogt, C.; Monai, M.; Kramer, G.J.; Weckhuysen, B.M. The renaissance of the Sabatier reaction and its applications on Earth and in space. *Nat. Catal.* **2019**, *2*, 188–197. [\[CrossRef\]](#)
8. Liu, Y.; Zhang, Z.; Tian, J.; Liao, Y.; Zhai, J.; Fang, X.; Xu, X.; Wang, X. Tuning CO adsorption states via enhanced metal-support interaction for boosting CO₂ methanation activity of Ru/rutile-TiO₂. *Fuel* **2023**, *360*, 130600. [\[CrossRef\]](#)
9. Rueda-Navarro, C.M.; González-Fernández, M.; Cabrero-Antonino, M.; Dhakshinamoorthy, A.; Ferrer, B.; Baldoví, H.G.; Navalón, S. Solar-Assisted CO₂ Methanation via Photocatalytic Sabatier Reaction by Calcined Titanium-based Organic Framework Supported RuO_x Nanoparticles. *ChemCatChem* **2024**, *16*, e202400991. [\[CrossRef\]](#)
10. Yang, C.; Wang, W.; Zhuo, H.; Shen, Z.; Zhang, T.; Yang, X.; Huang, Y. Phase engineering of Ru-based nanocatalysts for enhanced activity toward CO₂ methanation. *Chin. J. Catal.* **2024**, *61*, 226–236. [\[CrossRef\]](#)
11. Sun, S.; Higham, M.D.; Zhang, X.; Catlow, C.R.A. Multiscale Investigation of the Mechanism and Selectivity of CO₂ Hydrogenation over Rh(111). *ACS Catal.* **2024**, *14*, 5503–5519. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Gómez-Flores, K.; Solís-García, A.; Lam, S.J.; Cervantes-Gaxiola, M.; Castillo-López, R.; Leyva, J.R.; Gómez, S.; Flores-Aquino, E.; Zepeda, T. Modulating selectivity in CO₂ Methanation through Rhodium catalysts supported on Zirconia-Chemically grafted SBA-15. *Mol. Catal.* **2024**, *558*, 114035. [\[CrossRef\]](#)
13. Dai, X.; Sun, Y. Mechanism of photocatalytic CO₂ methanation on ultrafine Rh nanoparticles. *Nanoscale Horizons* **2024**, *9*, 627–636. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Meloni, E.; Cafiero, L.; Renda, S.; Martino, M.; Pierro, M.; Palma, V. Ru- and Rh-Based Catalysts for CO₂ Methanation Assisted by Non-Thermal Plasma. *Catalysts* **2023**, *13*, 488. [\[CrossRef\]](#)
15. Wu, Y.; Bhalothia, D.; Chou, J.-P.; Lee, G.-W.; Hu, A.; Chen, T.-Y. Electronic metal–support interaction in Pd/CoNi-hydroxides with enhanced CO adsorption for boosting CO₂ methanation. *Sustain. Energy Fuels* **2024**, *9*, 847–854. [\[CrossRef\]](#)

16. Yang, T.; Beniwal, A.; Bhalothia, D.; Yan, C.; Wang, C.-H.; Chen, T.-Y. Oxygen vacancies coupled with surface silicide facilitate CO₂ activation at near-room temperature for efficient methane productivity on Ni-oxide supported Pd nanoparticles. *Sustain. Energy Fuels* **2024**, *8*, 3399–3411. [\[CrossRef\]](#)
17. Danielis, M.; Jiménez, J.D.; Rui, N.; Moncada, J.; Betancourt, L.E.; Trovarelli, A.; Rodriguez, J.A.; Senanayake, S.D.; Colussi, S. Tuning the hydrogenation of CO₂ to CH₄ over mechano-chemically prepared palladium supported on ceria. *Appl. Catal. A Gen.* **2023**, *660*, 119185. [\[CrossRef\]](#)
18. Memon, M.A.; Jiang, Y.; Hassan, M.A.; Ajmal, M.; Wang, H.; Liu, Y. Heterogeneous Catalysts for Carbon Dioxide Methanation: A View on Catalytic Performance. *Catalysts* **2023**, *13*, 1514. [\[CrossRef\]](#)
19. Garbarino, G.; Bellotti, D.; Riani, P.; Magistri, L.; Busca, G. Methanation of carbon dioxide on Ru/Al₂O₃ and Ni/Al₂O₃ catalysts at atmospheric pressure: Catalysts activation, behaviour and stability. *Int. J. Hydrogen Energy* **2015**, *40*, 9171–9182. [\[CrossRef\]](#)
20. Spataru, D.; Carvalho, G.; Quindimil, A.; Lopes, J.M.; Henriques, C.; Bacariza, C. CO₂ methanation under more realistic conditions: Influence of O₂ and H₂O on Ni-based catalysts' performance. *Chem. Eng. J.* **2024**, *496*, 153709. [\[CrossRef\]](#)
21. Ma, L.; Ye, R.; Huang, Y.; Reina, T.R.; Wang, X.; Li, C.; Zhang, X.L.; Fan, M.; Zhang, R.; Liu, J. Enhanced low-temperature CO₂ methanation performance of Ni/ZrO₂ catalysts via a phase engineering strategy. *Chem. Eng. J.* **2022**, *446*, 137031. [\[CrossRef\]](#)
22. Zhang, Z.; Yu, Z.; Feng, K.; Yan, B. Eu³⁺ doping-promoted Ni-CeO₂ interaction for efficient low-temperature CO₂ methanation. *Appl. Catal. B Environ.* **2022**, *317*, 121800. [\[CrossRef\]](#)
23. Cañón-Alvarado, M.; Blanco, C.; Daza, C. Exploring dolomite as a promising support for Ni catalysts in CO₂ methanation. *J. Environ. Chem. Eng.* **2024**, *12*, 112224. [\[CrossRef\]](#)
24. Liu, F.; Park, Y.S.; Diercks, D.; Kazempoor, P.; Duan, C. Enhanced CO₂ Methanation Activity of Sm_{0.25}Ce_{0.75}O_{2-δ}-Ni by Modulating the Chelating Agents-to-Metal Cation Ratio and Tuning Metal-Support Interactions. *ACS Appl. Mater. Interfaces* **2022**, *14*, 13295–13304. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Kristiani, A.; Takeishi, K. CO₂ methanation over nickel-based catalyst supported on yttria-stabilized zirconia. *Catal. Commun.* **2022**, *165*, 106435. [\[CrossRef\]](#)
26. Song, W.; Wang, K.; Wang, X.; Ma, Q.; Zhao, T.-S.; Bae, J.W.; Gao, X.; Zhang, J. Boosting low temperature CO₂ methanation by tailoring Co species of CoAlO catalysts. *Chem. Eng. Sci.* **2024**, *298*, 120405. [\[CrossRef\]](#)
27. Fu, W.; Liu, S.; He, Y.; Chen, J.; Ren, J.; Chen, H.; Sun, R.; Tang, Z.; Mebrahtu, C.; Zeng, F. CO₂ hydrogenation over CoAl based catalysts: Effects of cobalt-metal oxide interaction. *Appl. Catal. A Gen.* **2024**, *678*, 119720. [\[CrossRef\]](#)
28. O'Connell, G.E.; Tan, T.H.; Yuwono, J.A.; Wang, Y.; Kheradmand, A.; Jiang, Y.; Kumar, P.V.; Amal, R.; Scott, J.; Lovell, E.C. Seeing the light: The role of cobalt in light-assisted CO₂ methanation. *Appl. Catal. B Environ.* **2023**, *343*, 123507. [\[CrossRef\]](#)
29. Mehrabi, M.; Ashjari, M.; Meshkani, F. Cobalt supported on silica–alumina nanocomposite for use in CO₂ methanation process: Effects of Si/Al molar ratio and Co loading on catalytic activity. *Res. Chem. Intermed.* **2023**, *50*, 219–238. [\[CrossRef\]](#)
30. Prabhakar, J.K.; Apte, P.A.; Deo, G. Exploring optimal total metal loading of Ni₃Fe/Al₂O₃ catalyst for CO₂ methanation and its kinetic model. *Fuel* **2024**, *367*, 131447. [\[CrossRef\]](#)
31. Li, J.; Xu, Q.; Han, Y.; Guo, Z.; Zhao, L.; Cheng, K.; Zhang, Q.; Wang, Y. Efficient photothermal CO₂ methanation over NiFe alloy nanoparticles with enhanced localized surface plasmon resonance effect. *Sci. China Chem.* **2023**, *66*, 3518–3524. [\[CrossRef\]](#)
32. Yan, P.; Peng, H.; Zhang, X.; Rabiee, H.; Ahmed, M.; Weng, Y.; Rozhkovskaya, A.; Vogrin, J.; Konarova, M.; Zhu, Z. Unlocking the role of Ni-Fe species in CO₂ methanation. *Fuel* **2024**, *374*, 132373. [\[CrossRef\]](#)
33. Aziz, M.A.; Jalil, A.A.; Hassan, N.S.; Bin Bahari, M.; Hatta, A.H.; Abdullah, T.A.T.; Jusoh, N.W.C.; Setiabudi, H.D.; Saravanan, R. Kinetic exploration of CO₂ methanation over nickel loaded on fibrous mesoporous silica nanoparticles (CHE-SM). *Process. Saf. Environ. Prot.* **2024**, *186*, 1229–1241. [\[CrossRef\]](#)
34. Ilseemann, J.; Murshed, M.M.; Gesing, T.M.; Kopyscinski, J.; Bäumer, M. On the support dependency of the CO₂ methanation–decoupling size and support effects. *Catal. Sci. Technol.* **2021**, *11*, 4098–4114. [\[CrossRef\]](#)
35. Zhou, L.; Guo, X.; Hu, X.; Zhang, Y.; Cheng, J.; Guo, Q. CO₂ methanation reaction over La-modified NiAl catalysts derived from hydrotalcite-like precursors. *Fuel* **2024**, *362*, 130888. [\[CrossRef\]](#)
36. Abahussain, A.A.M.; Al-Fatesh, A.S.; Rajput, Y.B.; Osman, A.I.; Alreshaidan, S.B.; Ahmed, H.; Fakeeha, A.H.; Al-Awadi, A.S.; El-Salamony, R.A.; Kumar, R. Impact of Sr Addition on Zirconia–Alumina-Supported Ni Catalyst for CO_x-Free CH₄ Production via CO₂ Methanation. *ACS Omega* **2024**, *9*, 9309–9320. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Guo, X.; Traitangwong, A.; Hu, M.; Zuo, C.; Meeyoo, V.; Peng, Z.; Li, C. Carbon Dioxide Methanation over Nickel-Based Catalysts Supported on Various Mesoporous Material. *Energy Fuels* **2018**, *32*, 3681–3689. [\[CrossRef\]](#)
38. Bacariza, M.; Graça, I.; Lopes, J.; Henriques, C. Enhanced activity of CO₂ hydrogenation to CH₄ over Ni based zeolites through the optimization of the Si/Al ratio. *Microporous Mesoporous Mater.* **2018**, *267*, 9–19. [\[CrossRef\]](#)
39. Quindimil, A.; De-La-Torre, U.; Pereda-Ayo, B.; González-Marcos, J.A.; González-Velasco, J.R. Ni catalysts with La as promoter supported over Y- and BETA- zeolites for CO₂ methanation. *Appl. Catal. B Environ.* **2018**, *238*, 393–403. [\[CrossRef\]](#)
40. Gao, B.; Wang, L.-W.; Ren, L.; Haines, T.; Hu, J. Catalytic Performance and Reproducibility of Ni/Al₂O₃ and Co/Al₂O₃ Mesoporous Aerogel Catalysts for Methane Decomposition. *Ind. Eng. Chem. Res.* **2018**, *58*, 798–807. [\[CrossRef\]](#)

41. Hu, F.; Chen, X.; Tu, Z.; Lu, Z.-H.; Feng, G.; Zhang, R. Graphene Aerogel Supported Ni for CO₂ Hydrogenation to Methane. *Ind. Eng. Chem. Res.* **2021**, *60*, 12235–12243. [[CrossRef](#)]
42. Canales, R.; Barrio, V.L. Photo- and Thermocatalytic CO₂ Methanation: A Comparison of Ni/Al₂O₃ and Ni–Ce Hydrotalcite-Derived Materials under UV and Visible Light. *Materials* **2023**, *16*, 5907. [[CrossRef](#)] [[PubMed](#)]
43. Zhang, B.; Yao, P.; Li, F.; Pan, L.; Xiong, W.; Zhang, Y.; Li, X. Catalytic Pyrolysis of Waste Textiles for Hydrogen-Rich Syngas Production over NiO/Al₂O₃ Catalyst. *Processes* **2024**, *13*, 15. [[CrossRef](#)]
44. Oliveira, G.V.; de Macedo, V.; Urquieta-González, E.A.; Magriotis, Z.M.; Pereira, C.A. Fe₂O₃/γ-Al₂O₃ and NiO/γ-Al₂O₃ catalysts for the selective catalytic oxidation of ammonia. *Catal. Today* **2024**, *444*, 114991. [[CrossRef](#)]
45. Tian, T.; Zhao, Z.-M.; Zhang, Y.; Jing, J.; Li, W.-Y. Insight into the Nature of Nickel Active Sites on the NiAl₂O₄ Catalyst for Phenanthrene Hydrogenation Saturation. *ACS Omega* **2025**, *10*, 8303–8313. [[CrossRef](#)] [[PubMed](#)]
46. Valecillos, J.; Iglesias-Vázquez, S.; Landa, L.; Remiro, A.; Bilbao, J.; Gayubo, A.G. Insights into the Reaction Routes for H₂ Formation in the Ethanol Steam Reforming on a Catalyst Derived from NiAl₂O₄ Spinel. *Energy Fuels* **2021**, *35*, 17197–17211. [[CrossRef](#)] [[PubMed](#)]
47. Garbarino, G.; Chitsazan, S.; Phung, T.K.; Riani, P.; Busca, G. Preparation of supported catalysts: A study of the effect of small amounts of silica on Ni/Al₂O₃ catalysts. *Appl. Catal. A Gen.* **2015**, *505*, 86–97. [[CrossRef](#)]
48. Zhang, L.; Wang, X.; Chen, C.; Zou, X.; Shang, X.; Ding, W.; Lu, X. Investigation of mesoporous NiAl₂O₄/MO_x (M = La, Ce, Ca, Mg)–γ-Al₂O₃ nanocomposites for dry reforming of methane. *RSC Adv.* **2017**, *7*, 33143–33154. [[CrossRef](#)]
49. Garbarino, G.; Campodonico, S.; Perez, A.R.; Carnasciali, M.M.; Riani, P.; Finocchio, E.; Busca, G. Spectroscopic characterization of Ni/Al₂O₃ catalytic materials for the steam reforming of renewables. *Appl. Catal. A Gen.* **2013**, *452*, 163–173. [[CrossRef](#)]
50. Kumar, S.; Ojha, A.K. Ni, Co and Ni–Co codoping induced modification in shape, optical band gap and enhanced photocatalytic activity of CeO₂ nanostructures for photodegradation of methylene blue dye under visible light irradiation. *RSC Adv.* **2015**, *6*, 8651–8660. [[CrossRef](#)]
51. Castillo-Saenz, J.; Nedev, N.; Valdez-Salas, B.; Curiel-Alvarez, M.; Mendivil-Palma, M.I.; Hernandez-Como, N.; Martinez-Puente, M.; Mateos, D.; Perez-Landeros, O.; Martinez-Guerra, E. Properties of Al₂O₃ Thin Films Grown by PE-ALD at Low Temperature Using H₂O and O₂ Plasma Oxidants. *Coatings* **2021**, *11*, 1266. [[CrossRef](#)]
52. Roškarič, M.; Žerjav, G.; Zavašnik, J.; Pintar, A. The influence of synthesis conditions on the visible-light triggered photocatalytic activity of g-C₃N₄/TiO₂ composites used in AOPs. *J. Environ. Chem. Eng.* **2022**, *10*, 107656. [[CrossRef](#)]
53. Canales, R.; Gil-Calvo, M.; Barrio, V.L. UV- and visible-light photocatalysis using Ni–Co bimetallic and monometallic hydrotalcite-like materials for enhanced CO₂ methanation in sabatier reaction. *Heliyon* **2023**, *9*, e18456. [[CrossRef](#)] [[PubMed](#)]
54. Lin, J.; Ma, C.; Luo, J.; Kong, X.; Xu, Y.; Ma, G.; Wang, J.; Zhang, C.; Li, Z.; Ding, M. Preparation of Ni based mesoporous Al₂O₃ catalyst with enhanced CO₂ methanation performance. *RSC Adv.* **2019**, *9*, 8684–8694. [[CrossRef](#)] [[PubMed](#)]
55. Italiano, C.; Llorca, J.; Pino, L.; Ferraro, M.; Antonucci, V.; Vita, A. CO and CO₂ methanation over Ni catalysts supported on CeO₂, Al₂O₃ and Y₂O₃ oxides. *Appl. Catal. B Environ.* **2020**, *264*, 118494. [[CrossRef](#)]
56. Gash, A.E.; Satcher, J.H.; Simpson, R.L. Monolithic nickel(II)-based aerogels using an organic epoxide: The importance of the counterion. *J. Non-Crystalline Solids* **2004**, *350*, 145–151. [[CrossRef](#)]
57. Gil Seo, J.; Youn, M.H.; Bang, Y.; Song, I.K. Effect of Ni/Al atomic ratio of mesoporous Ni–Al₂O₃ aerogel catalysts on their catalytic activity for hydrogen production by steam reforming of liquefied natural gas (LNG). *Int. J. Hydrogen Energy* **2010**, *35*, 12174–12181. [[CrossRef](#)]
58. Hao, Z.; Zhu, Q.; Lei, Z.; Li, H. CH₄–CO₂ reforming over Ni/Al₂O₃ aerogel catalysts in a fluidized bed reactor. *Powder Technol.* **2007**, *182*, 474–479. [[CrossRef](#)]

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