

Review

CeO₂-Based and Containing Catalysts for CO₂ Methanation: A Short Review

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Abstract

The great impact of carbon dioxide emissions on climate change motivates the development of technologies for carbon capture and utilization. CO₂ methanation, which transforms CO₂ into methane using renewable hydrogen, is a promising power-to-gas and carbon utilization pathway. Achieving high activity, strong CH₄ selectivity, and long-term stability remains challenging, as well as pushes to tailor catalyst properties for the methanation reaction. Cerium oxide is therefore widely explored as a support or promoter due to its redox behaviour and oxygen vacancy chemistry. This review surveys recent literature on catalysts based and containing CeO₂ applied for CO₂ methanation, covering not only thermal operation but also non-conventional catalytic routes as photothermal, electrocatalytic, and plasma-assisted, with emphasis on how synthesis and role of Ce tune physicochemical properties and catalytic activity. Across reported systems, dispersing active metals (notably Ni and Ru, Cu for electrochemical systems) on ceria frequently yields to high CH₄ selectivity. Redox properties of ceria enable optimal metal–support interactions and surface basicity to achieve effective CO₂ activation in thermo-catalytic route. Further enhancement of oxygen mobility is associated with doped CeO₂ and solid solutions such as Ce–Zr. The high oxygen storage capacity of CeO₂ promotes photogenerated charge separation for light-driven performance and optimal plasma–catalyst interactions.

Keywords: cerium oxide; CO₂ methanation; catalysis

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1. Introduction

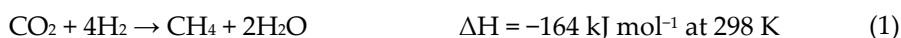
1.1. CO₂ Methanation

The accumulation of long-lived greenhouse gases has increased the global mean surface temperature by ~1.1 °C in the 2011–2020 period relative to 1850–1900 [1], with 2023 recorded as approximately 1.45 °C above pre-industrial levels [2]. Scientific assessments consistently conclude that every increment of additional warming leads to more severe climatic impacts. However, a broad portfolio of mitigation scenarios, covering hundreds to thousands of integrated assessment model pathways, demonstrates that limiting warming to 1.5–2 °C is still technically feasible but requires immediate action and robust enabling conditions. Meeting these goals requires deep and sustained decarbonization

across all major emitting sectors—electricity generation, transportation, buildings/heating, and especially industry, including chemicals, cement, steel, and refining—through electrification, energy efficiency, low-carbon fuels, renewable integration, and carbon capture, storage, and utilization (CCSU) [1,3].

An interesting perspective on CCSU is the possible valorisation of this “waste” molecule as a reservoir of carbon to be exploited as a C1 building block for more complex and added-value compounds such as fuels [4,5], introducing the concept of Circular economy [6]. Carbon capture and utilization (CCU) would revolutionize the petrochemical and chemical industries and allow the closure of the carbon loop. These are motivations for further scientific and technological advancement on CCU and valorisation technologies, which are attracting interest from policymakers, industry, and investors, with global funding over 10 years close to USD 1 billion [7]. Furthermore, CCU requires a source of hydrogen (H₂) to react with carbon dioxide (CO₂) for the formation of added-value molecules. H₂ production via water electrolysis or fuel cells requires electricity, that, if generated from renewable energy sources (RES), turns H₂ into a green energy carrier [7]. However, the storage and transportation of H₂ can be troublesome. Other hydrocarbon molecules are found to be more efficient carriers, such as methane and methanol, which can be supplied via the existing grid and using the current infrastructures for storage [8]. Therefore, with the development of CCU, CO₂ can be seen as a vector for harvest of energy in the Power-to-gas technology [9], which allows the production of synthetic and recycled fuels. The power-to-gas concept is beneficial for the development of electricity generation from RES, which is characterized by a seasonality and fluctuations, and therefore needs an energy carrier or buffer.

In this picture, Sabatier’s reaction of CO₂ methanation (in the equation below (1)), first reported in 1902 by Sabatier and Sendersen [10], is experiencing a renaissance for the development of Power-to-Methane technology. Initially deployed only for CO₂ removal in ammonia and urea synthesis, since the 1980s, it has come back to research and industrial relevance for the progress of Power-to-Methane plants [11,12]. Until now, several CO₂ methanation pilot plants have been established around the world (Japan, USA, and Germany), as well as two commercial operations: in 2013 in Werlte (Germany) and in 2016 in Denmark [11–13]. In a 2022 review, Barbaresi et al. [14] collected 87 Power-to-Methane projects worldwide; most of them started in the 2010s and are located in Germany. In their analysis, they highlighted the importance of the choice of electrolyser technology and heat management for efficient output [14].



The CO₂ methanation reaction (1) is exothermic, releasing 164 kJ per mole. It typically operates between 200 °C and 450 °C, at pressures between atmospheric and 100 bar [13,15]. The selectivity toward methane (CH₄) decreases at high temperature above 500–600 °C, shifting to the reaction of reverse water–gas shift and, therefore, the production of undesired CO [16]. In addition, the problem of catalyst deactivation by sintering arises with temperatures >500 °C [13]. According to le Chatelier’s principle, Sabatier’s reaction is favoured at higher pressure, with an increase of CO₂ conversion [17]. Despite its thermodynamical favourability, CO₂ reduction is an eight-electrons process, therefore highly kinetically limited, which requires a metal-based catalyst for the electron transfer [13,18]. Furthermore, CO₂ is a thermodynamically stable molecule, with a standard formation enthalpy of −393.5 kJ mol^{−1}. Hence, it requires a suitable catalyst to supply the correct energy for its activation and selective conversion [19,20]. In addition to thermal heterogeneous catalysis, novel methods for CO₂ hydrogenation have been recently investigated: photo-thermal, as well as electro- and plasma-assisted catalysis [13,19,21–25].

Sabatier's reaction, despite the large amount of research and development, still consists of a challenging process due to the many factors that influence the reaction. Efforts have been made to determine the impact of different parameters on the reaction selectivity and mechanism, e.g., temperature, pressure, gas hourly space velocity, and reactor type, as well as the catalyst sensitivity [11,13,17,18]. The catalyst must be active and selective toward methane, but of course stable as well; this is the focus of several studies from lab to industrial scale [14]. In the standard thermochemical Sabatier's process, the goal is to limit the coke deposition and other kinds of activity degradation of the catalyst material. The metals used for CO₂ methanation are part of groups 8–11; for instance Ni, Ru, Co, Pd, Pt, Rh, and Au, with the addition of Mo [13,16,17], among which nickel stands out for its good selectivity and relative low cost. The metal phases are characterized by different activity and selectivity, proving that the two are separate phenomena in methanation process [13]. In case of CO₂ methanation, the support does not only have the role to disperse the active phase particles but also plays an important part in the molecules' adsorption, reducibility, dispersion, interaction, stability, and reaction, tuning the mechanism and rate [11,14,17,21]. The most common supports include metal oxides [25], or mixtures of several oxides, hydrotalcite, and zeolites. The supports are expected to have high surface area, and they are studied with the purpose of improving reducibility, active metal dispersion and interaction, and stability [17,18,21]. Promoters can also enhance their performance: they have been investigated in addition to the Ni active phase and mixed within the support [17,18,21]. Among the materials that are found in the literature, cerium dioxide (CeO₂), commonly known as ceria, has been proved to be suitable both as catalyst support and promoter in processes of CO₂ methanation, both conventional and advanced (see Figure 1).

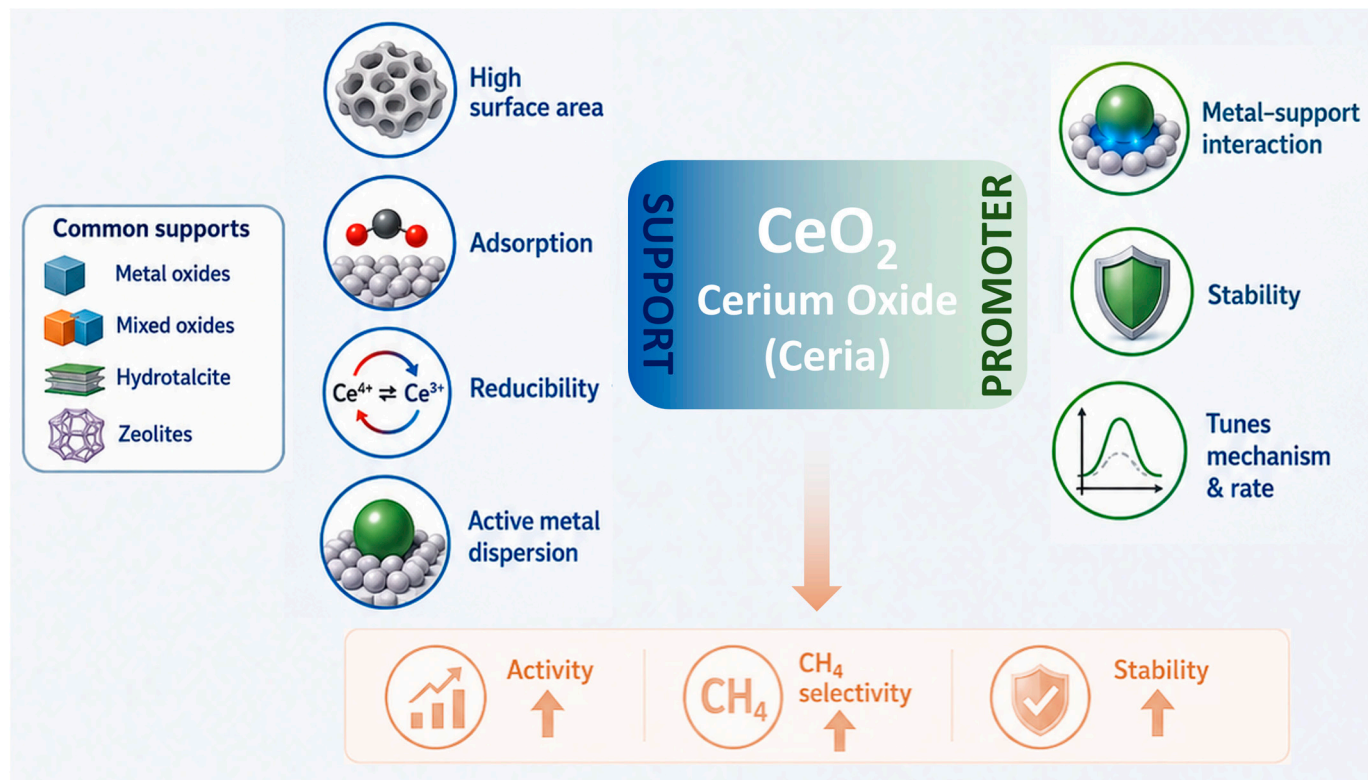


Figure 1. Schematic of CeO₂ application as support and promoter of catalysts.

1.2. Why Cerium Oxide

Despite being a rare earth element, cerium is the most abundant of the rare earth family, with a higher concentration (66.5 ppm) in the Earth's crust than copper (60 ppm)

and tin (2.3 ppm), and it has a low supply risk and a decreasing price over the last years [26,27]. Cerium has two possible oxidation states, +4 and +3, and it spontaneously oxidizes to two possible extreme compositions: CeO_2 and Ce_2O_3 , with fluorite and sesquioxide structure, respectively. The fluorite structure of CeO_2 has $\text{Fm}\bar{3}\text{m}$ space group and face-centered cubic (fcc) unit cell of cerium cations with O^{2-} anions occupying the octahedral interstitial sites with the lattice parameter a is 5.411 Å (schematics shown on Figure 2). The facile modification from the stoichiometric CeO_2 structure to a non-stoichiometric one $\text{CeO}_{2-\delta}$ (with $0 < \delta < 0.5$) makes it possible even to convert CeO_2 to Ce_2O_3 [27]. The formation of oxygen vacancies inside the CeO_2 crystalline structure can be expressed with Kröger-Vink notation (Equation (2)) as



where Ce_Ce represents a Ce(IV) ion on a Ce lattice site, O_O is an ion on an O lattice site, Ce'_Ce represents a Ce(III) ion on a Ce lattice site, and V''_O represents a neutral oxygen vacancy (OV) site. Therefore, the change of valence of two cerium cations is the consequence of each OV that has its electrons in Ce 4f energy states. Furthermore, the presence of an OV in the crystalline structure of cerium oxide will cause the Ce cations to repel each other because of coulombic interactions [27].

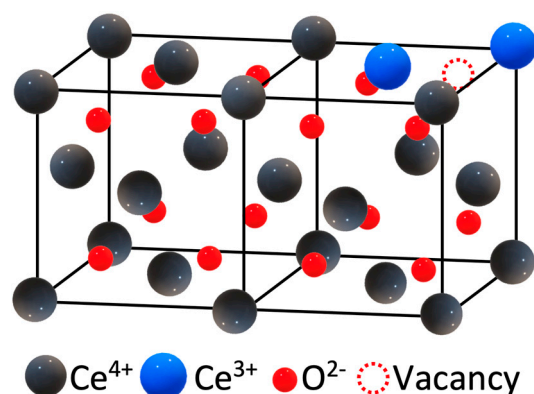


Figure 2. Crystal structure of cerium oxide with presence of an oxygen vacancy.

The structure of CeO_2 allows the exposure of different crystal facets according to the morphology and properties of the particles. A selection of the different possible facets (see Figure 3) has been investigated via density functional theory and the relative surface energies have been calculated. The general consensus ranks the facets as $(111) < (100) < (110) < (200) < (011)$, with (111) being the most stable [28].

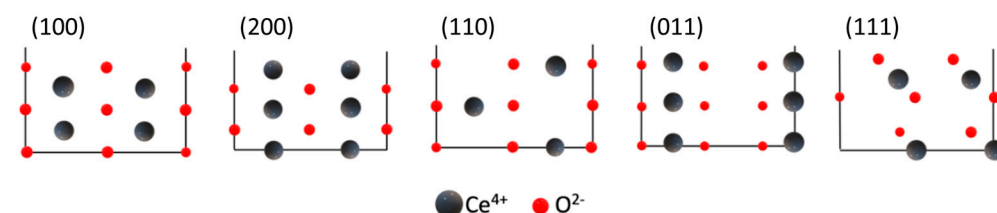


Figure 3. Side view of selected facets of CeO_2 crystal structure.

The OV formation energy on these surfaces has also been calculated theoretically for (100), (110), and (111); the order is opposite as the surface energy with $(110) < (100) < (111)$ [28]. Compared to the stable (111) facet, the other two are more reducible and active, and the high-energy surface (110) requires the lowest energy for OV. Both (200) and (011) are energetic surfaces; therefore it is expected that the defect and OV will form easily on them [28].

Oxygen storage capacity (OSC) is one of the most well-known properties of ceria, which makes it a good material for catalytic system development. The OSC has been linked to the fast change of oxidation state of the cerium ions (from IV to III) inside the fluorite $Fm\bar{3}m$ crystalline structure and formation of oxygen vacancies; therefore, the release of oxygen. Furthermore, in the fluorite structure, the oxygen atoms are all in a plane with one another, which allows for rapid diffusion as a function of the number of oxygen vacancies [29]. Oxygen vacancies are enhanced at the nanoscale, at defective surfaces, and when dopant atoms are inserted in the crystalline structure of the oxide [27,30]. Several synthesis techniques have been tested for ceria to produce nanostructured materials possessing different morphologies and sizes [27,30]. The possibility to synthesize ceria-based nanomaterials allows to increase the surface area and the active phase dispersion.

Ceria is an ionic oxide with basic sites on its surface, and the O^{2-} anion acts as a base and Ce^{4+} as Lewis acid site. Surface basicity is important for interaction with CO_2 , as it is known to be a mildly acidic molecule, so it is attracted by the basic sites [19]. The adsorption and desorption kinetics of CO_2 on ceria surface have an important effect on methanation performance and it is influenced by the strength of the basicity [31]. The strength and the number of basic sites have been reported to increase with decreasing particle size and therefore with larger area and more defects [31].

Another relevant property of ceria as catalyst support that has been reported is the unique metal–support interaction (MSI) [15]. MSI regards reducible oxide supports, and it can have different origins, e.g., reduction or oxidation [32]. A strong metal–support interaction (SMSI) causes structural modifications, as encapsulation by a layer of support material, restructuring of metal nanoparticles, formation of specific metal support interfaces, and charge transfer from/to metal nanoparticles. Consequently, it could promote metal dispersion, which is beneficial for catalytic applications [15,32]. However, SMSI might also have a negative influence on the catalytic performance due to a decreased active metal surface area for the encapsulation of metal particles. MSI should be tuned and controlled with ceria support preparation methods and thermal pre-treatments. The interface of metal oxide support and metal particles can also influence the oxide reducibility and, therefore, the OSC [33]. The OSC increases with metal/support interface perimeter, and it has been proved by experiments and theoretical calculations that O spillover occurs at room temperature between ceria and metal nanoparticles on its surface [33].

CeO_2 is technologically relevant for green energy as a catalyst and has other industrial applications that include magnetics, phosphors, and alloys [26]. First known application of ceria in catalysis is an oxygen storage component in the three-way catalysts for the elimination of toxic gases in automotive exhaust [26,27,30,34]. CeO_2 has been investigated as a catalyst support for CO_2 methanation since the 1990s [35]. As introduced previously, several reports released in the past decades regard the use of such material as support, additive to other metal oxides, and promoter, as Figure 4 shows with increasing number of papers regarding ceria in catalysis in the last 40 years [26]. In addition, previous reports established the good activity of such catalysts for Sabatier's reaction [35,36].

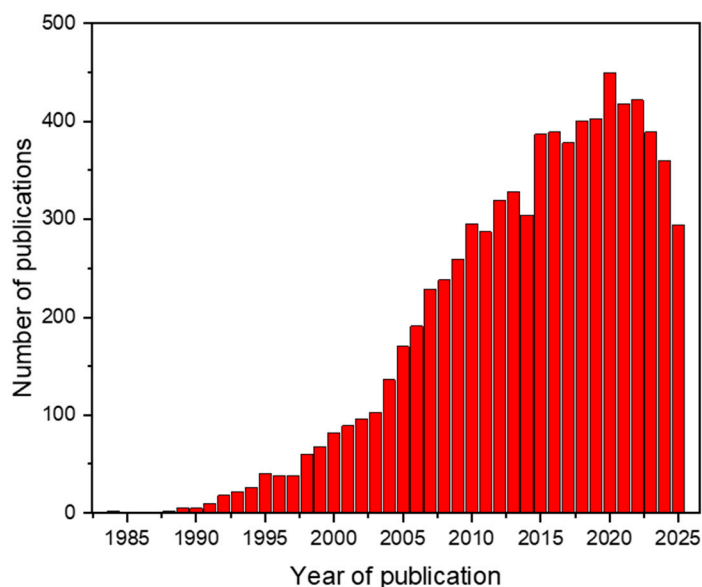


Figure 4. Number of publications about ceria utilized as catalyst per year (source: Web of Science search “ceria + catalysis” [37]).

The aim of this review is to present and discuss the latest advances concerning the use of CeO_2 as catalyst’s support for CO_2 methanation. The role of ceria as support and dopant in the preparation of catalysts is examined. The following section focuses on non-conventional catalytic processes for CO_2 reduction, namely photothermal, electrocatalytic, and plasma-assisted.

2. Ceria as Catalyst Support for Thermal CO_2 Methanation

2.1. Pure Ceria as Support

The results found in the literature regarding catalysts obtained with dispersion of a metal phase (Ni, Ru...) on pure CeO_2 show overall a good activity and remarkable yield for methane with a high selectivity >80% when both commercial and synthesized ceria are evaluated.

The use of CeO_2 supports for catalytic CO_2 methanation was firstly described in the 1990s by Trovarelli and co-workers [35,38–40]. This group published various papers reporting the use of 1%wt. Rh catalysts supported on ceria were synthesized via ammonia precipitation [35,38,40]. Two different reaction conditions at atmospheric pressure were used in their experiments, transient and steady state, to report the positive effect of Ce^{4+} reduction to Ce^{3+} as adsorption sites for CO_2 that favors the breaking of C-O bond [35]. Furthermore, for Rh/ CeO_2 materials, Trovarelli et al. demonstrated the importance of metal-support interactions in achieving an efficient rate of CO_2 hydrogenation. It is proposed that the Rh-Ce interaction is enhanced by several factors, including the formation of oxygen vacancies at the interface with the metal and the reduction of CeO_2 at lower temperatures facilitated by the presence of Rh and the phenomenon of spillover [35,38]. Different geometric and electronic interfaces between metal and oxide at the Rh/ CeO_2 boundary may cause changes in catalytic activity as well [35]. The interaction of ceria with noble metals has been further investigated by the same group [40] by varying the metal phase (1%wt. Rh, Ru, Pt, Pd, Ir) impregnated on ceria. The reaction on Ru and Rh produces exclusively CH_4 , whereas on Pt, Pd, and Ir, it results also in CO formation [40]. A different ceria–metal interaction and modification of the support surface must occur in the different samples. Sintering of metal particles or partial coverage by ceria is one possible surface alteration that takes place at high temperatures. Hydrogen spillover is particularly

favorable by Rh and Ru interacting with the support, hence the improvement of hydrogenation activity [40]. In this publication, the authors also concluded that the metal phase precursor used, in this case of $\text{Rh}(\text{NO}_3)_3$ and RhCl_3 , does not play a relevant role on the catalyst activity [40]. However, a different conclusion is reached in the case of Ni impregnated on ceria using nitrate or chloride salt in another publication [41]. The activity of the catalyst obtained with Ni chloride is considerably lower than the other case due to the chlorine blocking ceria sites [41]. According to Tada et al. [42], Ni dispersion over CeO_2 is influenced by Ni loading. Low Ni charges produce oxygen vacancies of Ni-Ce mixed oxides, while higher Ni loading produce such defects also on CeO_2 and metallic Ni surface. In comparison to oxygen vacancies formed within the CeO_2 structure, the formation of oxygen vacancies related to Ni ($\text{Ni-V}_{\text{ox}}\text{-Ce}$) are highly active in CO_2 conversion and promote CO production via the reverse water gas shift (RWGS), and the exposure of metallic Ni sites improve CO methanation, being both active sites essential for CO_2 methanation (see Figure 5) [42].

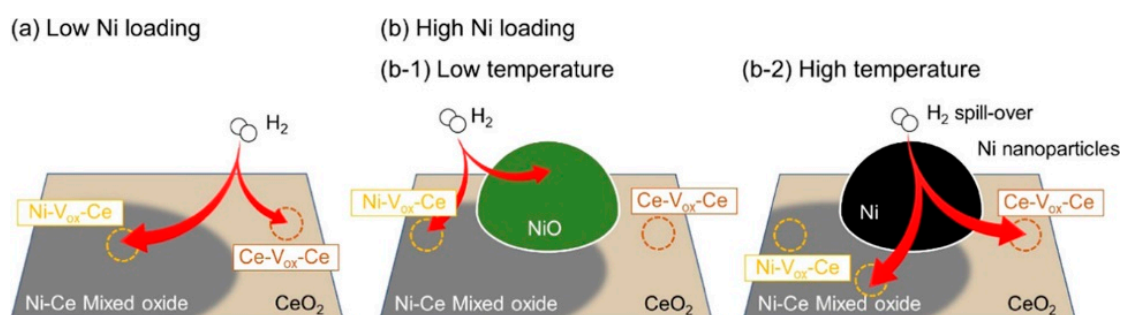


Figure 5. Active site formation of (a) low and (b) high loading Ni/ CeO_2 at (b-1) low and (b-2) high temperature. Reprinted with permission from [42]. Copyright 2021 American Chemical Society.

Additionally, the interaction between metal phase and CeO_2 has been assessed by changing the metal loading (0.7–20%wt.) in one-step ligand-free adsorption–precipitation synthesis method of well-dispersed Ir nanoparticles (1 nm to 2.2 nm) on CeO_2 nanorods [43]. The catalytic reaction of CO_2 methanation at 1 MPa and 300 °C occurs only on the 20 and 15%wt. Ir/ CeO_2 with satisfactory selectivity, while the catalysts with lower loadings in very small clusters mostly produce CO. X-ray photoelectron spectroscopy (XPS) and Extended X-ray Absorption Fine Structure (EXAFS) characterization are used to show that lower size, hence loading, produce more oxygen atoms from the CeO_2 to incorporate in the metal sites due to SMSI, leading to lower hydrogenation. Therefore, the authors claim that the decreased methane selectivity is not caused by the insufficient metal sites. Instead, it is due to the varying chemical nature of Ir and the interaction with ceria [43]. Finally, it has also been demonstrated that a mixture of Ni and CeO_2 powders does not result in an active catalyst [44]. Instead, the catalyst obtained by wet impregnation of 5%wt. Ni on commercial ceria reaches at 523 K (250 °C) a high turnover frequency of CO_2 (TOF_{CO_2}) and 100% selectivity [44]. The interface between ceria and metal plays a very important role: the two phases must be physically in contact and sharing a surficial boundary.

Several publications have compared the activity of ceria-based catalysts in CO_2 methanation to that of other metal oxides used as supports. CeO_2 is compared with $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$, TiO_2 , MgO , ZnO , ZrO_2 , SiO_2 , Ta_2O_5 , Nb_2O_5 , and Y_2O_3 [35,44–52]. Fukuhara et al. [51] reported that, under conventional CO_2 methanation conditions (200–300 °C), 10%wt.Ni/ CeO_2 demonstrated the highest catalytic performance among the tested supports. This result showed near-equilibrium CO_2 conversion (~90%) and almost complete methane selectivity at 300 °C. Ni/ CeO_2 best activity was followed by Ni/ ZrO_2 > Ni/ Y_2O_3 > Ni/ Al_2O_3 > Ni/ MgO > Ni/ TiO_2 [51]. The results reported by Lin et al. also showed that CeO_2 had the highest activity towards CO_2 methanation when compared with TiO_2 and ZrO_2 ,

all impregnated with 5%wt. Ni [48]. All three materials tested for CO₂ methanation have a high selectivity for CH₄ ($S_{CH_4} > 90\%$). However, Ni/CeO₂ achieves a better CO₂ conversion (X_{CO_2}) than the other two metal oxides at 300 °C. Overall, the activity can be ranked as CeO₂ > TiO₂ > ZrO₂. The cations in the crystalline structure of the reducible supports can partially reduce ($Ti^{4+} \rightarrow Ti^{3+}$ and $Ce^{4+} \rightarrow Ce^{3+}$) and create oxygen vacancies at the surface, therefore allowing for a better interaction with the metal and an improved efficiency compared to the nonreducible ZrO₂ [48]. An analogous conclusion with regard to the non-reducible supports has been already made by Trovarelli et al. [35] in the previously mentioned first studies of CeO₂ application to CO₂ methanation. They compared CeO₂, TiO₂, Ta₂O₅, Nb₂O₅ (reducible), and SiO₂ (non-reducible) supporting Rh to observe that Rh/SiO₂ produces the lowest amount of CH₄ moles. Dreyer et al. not only differentiate the metal oxides according to their reducibility but also according to their basicity [46]. They synthesize via single-step flame spray pyrolysis strongly basic ZnO, amphoteric MnO_x, and CeO₂, as well as Lewis acid (and irreducible) Al₂O₃ with some weak basic sites [46]. Conversion of CO₂ on the pristine supports occurs according to the strength of their basic sites, but it produces only CO. The catalysts become active for methanation with the addition of 5%wt. Ru in the synthesis method. Ru/CeO₂ shows the best activity X_{CO_2} 83%, S_{CH_4} 99% at 300 °C followed by Ru/Al₂O₃ > Ru/MnO_x > Ru/ZnO. The improved activity with ceria support is related both to the basic and reducible properties of the material. The number of basic sites on CeO₂ exceeds the other metal oxides. Moreover, the partial reducibility of CeO₂ helps the hydrogenation reaction thanks to the optimized strength of the C-O bond of adsorbed CO* and to the increased dissociation of hydrogen [46]. Ceria and alumina are further compared in two publications; in both cases, synthesized CeO₂ and commercial γ -Al₂O₃ or α -Al₂O₃ are considered. The Ni/CeO₂ catalyst produced by precipitation converts ten-folds more CO₂ in the range 300–350 °C, with a higher selectivity for methane (100%), despite the superior surface area and porosity of commercial γ -Al₂O₃ [45]. Ceria, unlike alumina, has the ability to contribute to the adsorption and reaction alongside Ni sites, that allows the optimal conversion to CH₄ [45]. A similar explanation is suggested by Wang et al. regarding the different activity of Ru catalysts supported on CeO₂ obtained by hydrothermal method and α -Al₂O₃ from Sigma-Aldrich [50]. Oxygen vacancies on ceria play an important role in the CO₂ dissociation, whereas on irreducible and weakly basic α -Al₂O₃, such interactions are not possible [50].

In addition, commercial cerium oxides have also been evaluated. Tada et al. reported X_{CO_2} around 90% and 100% S_{CH_4} starting at 300 °C up to 450 °C with 10%wt. Ni/CeO₂ catalyst and gas hour space velocity (GHSV) 10,000 h⁻¹ [49]. At the same temperature range, Ni/TiO₂, Ni/ α -Al₂O₃, and Ni/MgO converted less CO₂ ($X_{CO_2} < 30\%$ at 300 °C). The TiO₂-supported catalyst had a similar selectivity compared to the ceria-based one (approx. 100%); instead, the other materials produce CO as well ($S_{CH_4} < 95\%$ for Ni/MgO and <80% for Ni/ α -Al₂O₃) [49]. In agreement with the catalytic experiments, the CO₂-TPD (temperature-programmed desorption) analysis shows a significant decrease in adsorption on alumina compared to ceria [49]. In another publication, 10%wt. Ni dispersed on CeO₂ achieves X_{CO_2} of 60% and S_{CH_4} of 99% at 275 °C in H₂/CO₂/N₂ flow with GHSV 36,000 h⁻¹, whereas on SiO₂, it converts CO₂ hundreds of times less and with a selectivity nine times lower [47]. This proves that oxygen vacancies in ceria interact with nickel and improve the conversion rates toward methane with lower activation energies [47]. Lee et al. [53] investigated the role of CeO₂, Y₂O₃, Al₂O₃, and TiO₂ as supports, with a Ni loading of 10%wt. At 300 °C, Ni/CeO₂ and Ni/Y₂O₃ achieved CO₂ conversions of around 65–70% with methane selectivity close to 100%. This was significantly better than the results for Ni/Al₂O₃ (conversion of around 40–45%) and Ni/TiO₂ (<10% conversion). The superior activity of CeO₂ and Y₂O₃ was attributed to enhanced reducibility and oxygen vacancies and SMSI, resulting in higher Ni dispersion (≈ 1.8 –2.8%) and smaller particle sizes (≈ 12.8 –16.5

nm). In contrast, Ni/Al₂O₃ required higher temperatures to become active. Meanwhile, Ni/TiO₂ performed poorly due to very low Ni dispersion (0.012%), higher mean particle size (21 nm), and limited hydrogen activation. Gac et al. [54] also investigated the influence of commercial supports (Al₂O₃, ZrO₂ and CeO₂) across a wide range of Ni loadings (10–40%wt.). The study revealed that, despite their lower active surface area, ceria-supported catalysts achieved the highest CO₂ conversion at low temperatures ($\approx$ 280 °C) due to oxygen vacancies and strong metal–support interactions that facilitate CO₂ activation. The mean Ni crystallite size for CeO₂ supports ranges from 7.9 nm for a 10%wt. Ni loading, to 34.4 nm for a 40%wt. Ni loading. Zirconia-supported catalysts also exhibited high specific activity; however, their performance deteriorated at higher Ni loadings due to crystallite growth (from 9.5 for 10%wt. Ni load to 83 nm for 40%wt.). While less active than ceria and zirconia in the 200–350 °C range, alumina-supported catalysts exhibited superior thermal stability and resistance to sintering (mean Ni crystallite size 3.8–7 nm). Finally, 5%wt. Ni/CeO₂ resulted full selective to CH₄, converting CO₂ up to 40-fold higher than catalysts supported on TiO₂ and SiO₂, the latter giving CO as a by-product [44]. Nevertheless, lower particle size and higher dispersion (5.3 nm and 19.1%, respectively) were found for SiO₂ compared to CeO₂ (8.7 nm and 11.6%, respectively). Therefore, the influence of the metal–support interface and oxygen vacancies was considered to be more important than the size effect.

Wasnik et al. [55] compared the utilization of CeO₂ and silicon carbide (SiC) supports for Ni-M and Ru-M systems (M=Co, Mn). The Co-promoted catalysts, especially 2Ni–2Co/SiC and 2Ni–2Co/CeO₂, showed excellent performance, achieving CO₂ conversions of 77% and 76% and CH₄ selectivity of 88% and 83%, respectively, at 500 °C. SiC offered superior thermal stability and resistance to sintering compared to CeO₂, while CeO₂ facilitated CO₂ activation through its oxygen vacancies and redox properties. The incorporation of Co improved the dispersion of Ni and Ru, reduced particle size, and promoted the formation of active alloy phases. These combined effects contributed to enhanced catalytic activity and long-term stability, making these materials promising candidates for efficient CO₂ utilization.

The reaction mechanism of thermal CO₂ methanation over CeO₂-based catalysts is strongly governed by the metal–support interaction and the presence of OV. Early studies by Trovarelli, De Leitenburg, and Dolcetti [35] proposed a CO-mediated pathway over Rh/CeO₂, in which CeO₂ vacancies promote CO₂ adsorption and dissociation to CO, while the proximity between defective ceria sites and Rh particles facilitates H₂ spillover and subsequent hydrogenation toward CH₄. More recent work has refined this view by showing that the dominant pathway depends on the defect structure of the ceria surface: on OV-rich Ni/CeO₂, CO₂ preferentially adsorbs on Ce³⁺ sites and undergoes oxygen exchange with the support, favoring a formate route through bi-HCOO and br-HCOO intermediates before hydrogenation to methoxy species; conversely, on less defective ceria with highly dispersed Ni, CO₂ activation shifts toward a carboxyl pathway on Ni sites, increasing CO formation through the RWGS reaction [47]. Isotopic and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies further indicate that water desorption may be the slowest elementary step, although the high oxygen mobility of CeO₂ prevents persistent accumulation of carbonates, water, and surface intermediates, in contrast to less reducible supports such as Al₂O₃ [45]. For Ru/CeO₂ catalysts, the mechanism differs because Ru can simultaneously promote CO₂ dissociation to CO* and H₂ chemisorption, enabling hydrogenation through HCOH* intermediates; in this case, the partially reducible ceria support optimizes the CO/H surface coverage ratio by weakening CO adsorption sufficiently while enhancing H₂ activation [46]. Therefore, CeO₂ does not merely act as a structural support but actively determines the mechanistic route through its redox properties, which can be tuned by the synthesis and formulation (doping, solid

solutions...) of the CeO₂-based metal oxide support, as will be explored in the next sections.

2.1.1. Synthesis Techniques

CeO₂ can be directly produced by heating bastnaesite, a rare earth fluorocarbonate, and subsequently treating it with HCl [56]. However, in order to control the final properties of CeO₂ as support for CO₂ methanation catalysts, there are several synthesis techniques that can be used for preparation. The synthetic methods found in the literature include soft and hard templating, pseudo sol-gel, precipitation, flame spray pyrolysis, hydro- and solvothermal, calcination of a cerium precursor, hydrolysis, and combustion [38–41,43–50,57–66]. In this section, different methods and parameters are considered to identify the most relevant features of synthesized ceria as catalysts support.

Zhou et al. [57] have compared two methods of templating ceria obtained from precipitation. Hard templating, also known as nano-casting, is the process of impregnating cerium oxide on a material used as mold [67], in this case, mesoporous silica KIT-6, that is later removed [57,68]. Soft templating utilizes surfactants (CTAB and ammonium carbonate) for self-assembly of porous materials [69]. Further, 10%wt. nickel is later impregnated on CeO₂-synthesized materials [57,68]. The porous structure of the samples obtained from templating is confirmed by N₂ physisorption and TEM. The hard-templating ceria has a more developed mesoporous structure, and the surface area of porous materials exceeds the one of the ceria synthesized by precipitation. The improved mesoporosity and higher surface area enable a better performance in CO₂ methanation, with a higher conversion as for the ceria catalyst casted on KIT-6 (selectivity is 100% for all samples) [57].

Other synthesis techniques aim to change the morphology of the CeO₂ particles. One example is the hydrothermal method with an NaOH solution (see Figure 6) with variation of the synthesis parameters (precursor, temperature, NaOH concentration, and time) to obtain nanocubes (NCs) [58–60], nanorods (NRs) [58–60], nanooctahedron (NOs) [60], nanopolyhedra (NPs) [58], and nanoplates (NPLs) [61]. NCs are synthesized at a high temperature (180 °C), adding a large NaOH amount (10–14 M). With a decrease of temperature to 100 °C, NRs are formed, whereas at low NaOH concentration, smaller particles (NPs) are obtained [58]. Wang et al. [58] show via TEM that the shape of the particle determines the exposed crystalline facets. Therefore, the coordination of atoms at the surface and the reducibility change for different morphologies. Indeed, the morphology of the cerium oxide particles, and, therefore, the exposed crystal planes on its surface, has been previously linked to enhanced OSC and improved performance in thermal CO₂ methanation [58–61]. The OSC is measured via oxygen pulse injection method and compared to the information regarding vacancies from Raman and positron annihilation spectroscopy. Pristine NPs and NRs should have an improved tendency to OV formation. However, after 3%wt. Ru addition, NCs show the highest oxygen storage capacity and amount of oxygen in defect sites. Therefore, a promoting effect of Ru⁰ for vacancies formation occurs. This property translates to an improved activity as catalyst for methanation, (X_{CO2} 90% and S_{CH4} 99% at 250 °C) [58]. Bian et al. [59] have also compared ceria NC- and NR-based catalysts using as metal phase 5%wt. Ni. The Ni/CeO₂ NRs synthesized in this group possess an improved reducibility shown by temperature-programmed reduction (TPR) analysis and higher Ce³⁺ concentration, as calculated from XPS data. As highlighted before, oxygen vacancies can serve as a cooperative reaction site for CO₂ hydrogenation. Therefore, in this case, NRs have a higher activity than NCs [59]. In agreement with this study, Hashimoto et al. reported improved activity for Ni supported on CeO₂ NRs due to higher concentration of surface OV, lower particle size, and enhanced surface area and reducibility [60]. They have also shown via density functional theory calculations that the CO₂ activation energy on a

NiCeO₂ surface depends on the lattice facet (111), (110), or (100) that is exposed, (110) being the one that characterized the NRs and that facilitates the CO₂ to CO catalytic reaction [60].

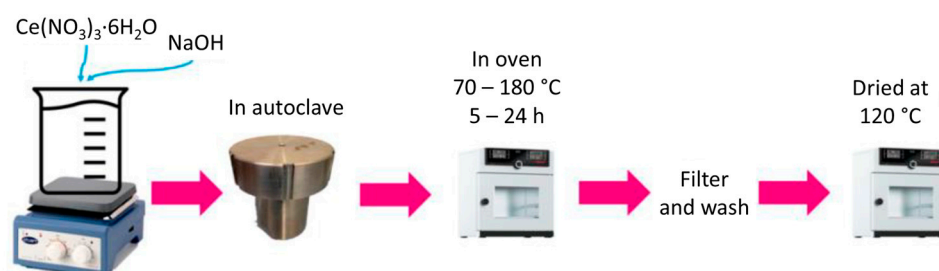


Figure 6. Hydrothermal method with NaOH solution with variation of the synthesis parameters.

Du et al. [61] observed improved activity for Ni supported on CeO₂ NPLs, obtained via hydrothermal method with urea at 90 °C for 6 h, compared to commercial supports due to the OV-rich surface of synthesized ceria. Although some works point to some particular CeO₂ morphologies leading to improved activity towards CO₂ methanation, there is no general agreement concerning the optimal nanoshape and properties of these supports. All these studies agreed, however, on the importance of oxygen vacancy formation ability of these supports. Moreover, OVs close to the metal–support interface are believed to strengthen the interaction between Ni and CeO₂ [61] and to play a role in the CO₂ hydrogenation reaction, providing sites for CO₂ adsorption and activation [60] or contributing to the formation of formate surface intermediates [59].

Sol-gel method with citric acid acting as binding ligand has been used to synthesis CeO₂ and directly the catalysts Ni/CeO₂ [70]. In addition, the sol-gel method with citric/ethylene-glycol-assisted (polyesterification) in H₂O-free media [71,72] or microwave assisted [73] yields highly porous CeO₂ or doped CeO₂ after calcination. The interconnected network supports medium-sized, confined Ni nanoparticles introduced post-synthesis. Ni on sol-gel-derived Pr–CeO₂ exhibits higher dispersion, greater surface defect density, and enhanced basicity, all favorable for CO₂ activation and H₂ dissociation/transfer across the metal–support interface. Experimentally, this translates to marked activity gains and validated reactor-scale predictions via CFD and process simulation, underscoring that pore architecture and defect chemistry can be co-optimized [72].

Flame spray pyrolysis (FSP) combusts organometallic solutions in a methane/oxygen flame to produce CeO₂ nanoparticles, highly Ni-loaded catalysts [74], or mixed oxide composites (e.g., Co–CeO₂) in a single step without subsequent calcination [75]. Particle size and composition are tuned via precursor concentration and flame parameters. In Co–CeO₂ prepared by FSP, Co content and reducibility control product slate: low Co favors CO (RWGS) on Co²⁺–O–Ce interfaces with minimal metallic Co, whereas ≥5–10 mol% Co forms 4–5 nm Co⁰ nanoparticles that selectively produce CH₄ at 200–300 °C with high CH₄ selectivity (≥85%). Partial reduction of ceria during activation increases surface V_{ox}, strengthening metal–support synergy at the Co–O–Ce perimeter. Although these results center on Co systems, the general advantages of FSP—defect-rich nanocrystals, intimate mixing, and scalability—are transferable to CeO₂ supports for Ni used for methanation.

The use of metal–organic frameworks (MOFs) as sacrificial templates for the synthesis of CeO₂-based supports has emerged as a promising strategy to design catalysts with high surface area, tunable porosity, and abundant oxygen vacancies. MOFs provide a well-defined structure that, upon thermal decomposition, yields nanostructured CeO₂ with hierarchical porosity and defect-rich surfaces, which are crucial for CO₂ activation and hydrogenation reactions. Typically, Ce-based MOFs such as Ce-BTC (BTC = benzene-

1,3,5-tricarboxylate) are employed as precursors. Ce salts (e.g., $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) are combined with organic linkers under solvothermal conditions to form the MOF structure [65,76,77]. Active metals (Ni, Cu, Ru) can be introduced either by impregnation onto the MOF or via one-pot synthesis during MOF assembly [70,78]. Thermal treatment (400–600 °C) under air or inert atmosphere decomposes the organic framework, forming CeO_2 nanoparticles while preserving porosity and generating oxygen vacancies [30,77].

2.1.2. Pre-Treatment

A few thermal treatment methods have been already mentioned in Section 2.1. Thermal pre-treatment of catalysts found in literature can be divided in three general categories: reduction, oxidation, and stabilization in inert atmosphere. Broad reviews on CeO_2 -based CO_2 hydrogenation catalysts confirm that tuning ceria's reducibility through controlled H_2 reduction is central to designing high-performance catalysts for CO_2 methanation processes [65,79]. Reductive pre-treatment (H_2/Ar or H_2/N_2) is most commonly applied because partially reduces $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$, generating oxygen vacancies (V_O) that (i) enhance CO_2 uptake/activation via formation of polydentate carbonate and formate species at cation–vacancy sites, (ii) promote H-spillover from the metal to the support, and (iii) strengthen and expand the population of interfacial metal– CeO_2 perimeter sites generally regarded as supporting low-temperature methanation activity [80–83]. The reduction can also restore the metallic phase, improve metal dispersion, and tune SMSI. However, overly harsh reduction can induce particle sintering or excessive SMSI/encapsulation that partially masks active metal facets [84–86]. Reported reduction protocols span a wide range from 5–50 vol% H_2 at 300–750 °C (0.5–4 h) [58,73,76,78,87–92] to pure H_2 at ≥500–700 °C [65,93–95], reflecting the need to reduce different oxide precursors and tune vacancy populations while avoiding sintering. Milder conditions favor high vacancy densities without severe sintering, and higher temperatures are used to fully reduce robust oxide precursors [82,83,96,97]. In the following paragraph, the effect of different pre-treatment techniques on ceria will be discussed in relation to the catalytic activity.

These effects were considered from the first studies on CeO_2 with the variation of the reduction temperature and time. Trovarelli and co-workers compare the effect on catalyst activity in the case of reduction at high (500 °C) and low (227 °C) temperature [35]. There is no benefit of reduction at high temperature under continuous mode (in continuous CO_2/H_2 flow), but in transient conditions (by injecting CO_2 pulses into an H_2 stream), Rh/CeO_2 reduced at 500 °C produced a substantially larger amount of CH_4 during the first pulse [35,38]. They also compared reduction time from 1 to 10 h for treatment at 500 °C [38]. A longer pre-treatment has a slightly negative impact on the reduction at steady-state. Instead, the CH_4 formation during the first pulse increases with reduction time and peaks at 6 h [38]. Similarly, Lin et al. compared reduction temperatures from 400 to 550 °C for Ni/CeO_2 [48]. They confirm that, with higher temperature, the activity of the catalyst decreases probably due to a surface modification that induced a SMSI that decreases the availability of active sites. In their work, they also varied the atmosphere for the pre-treatment at 550 °C with 80 mL/min N_2 or H_2 , and in air under static conditions [48]. The H_2 -treated catalyst displays the better structure with well-dispersed Ni particles that enhance the hydrogen spillover for Ce^{4+} reduction. These characteristics result in a higher conversion of CO_2 . The air calcined Ni/CeO_2 exhibits partial incorporation of Ni inside ceria and too strong interaction. The N_2 pre-treatment leads to agglomeration of Ni particles. Both N_2 and air-treated materials show less oxygen vacancies formation. Furthermore, this group investigated reduction–oxidation–reduction treatments to optimize the SMI. Ni/CeO_2 was reduced at 600 °C, then exposed to an oxidative treatment at temperatures between 250 °C and 550 °C, and then reduced again at 550 °C. This strategy enhances the CO_2 conversion compared to the reduced catalyst. Nikolaraki et al. [98] demonstrate that

the H₂-reduction treatment at two different temperatures (400 °C for 2 h and 750 °C for 30 min) significantly influences the physicochemical properties of the Ir/CeO₂ and Ir/Gd-doped CeO₂ catalysts, thereby affecting their CO₂ methanation performance. Reduction at higher temperature enhances metal–support interactions and promotes the formation of smaller, well-dispersed Ir nanoparticles on nanorod-shaped supports, which exhibit superior reducibility and oxygen vacancy concentration compared to irregularly shaped counterparts. These structural and electronic modifications translate into markedly improved catalytic behaviour: nanorod-based catalysts achieve CO₂ conversions up to ~70% with CH₄ selectivity approaching 95% at 500 °C, while irregularly shaped supports show lower conversions and selectivity due to weaker Ir–support interactions and larger particle sizes. The findings underscore the critical role of reduction conditions in tailoring active sites and optimizing both activity and selectivity for CO₂ hydrogenation.

Proper choice of calcination temperature optimizes defect structures that enable a balance between defect density and metal dispersion after tailored H₂ reduction. In this regard, Barreau et al. [69] observed that Ni-doped ceria catalysts exhibit strong dependence of CO₂ methanation activity on calcination temperature (450–750 °C). After H₂ activation at 400 °C, the catalyst calcined at 600 °C achieved the highest performance, with X_{CO₂} reaching ~76% at 375 °C and S_{CH₄} exceeding 99% above 300 °C. In comparison, the catalyst calcined at low temperature showed lower overall conversion (~56% at 375 °C) but similar high CH₄ selectivity (>95%). Conversely, after calcination at high temperature, the catalyst displayed markedly reduced activity and selectivity, with X_{CO₂} dropping to ~45% and S_{CH₄} falling below 90%, accompanied by increased CO formation. These trends correlate with structural changes induced by calcination: moderate pre-treatment (600 °C) optimizes Ni surface enrichment and maintains active Ni^{δ+}–Ce³⁺ sites, while excessive calcination (750 °C) promotes Ni sintering and reduces ceria reducibility, leading to performance deterioration and carbon deposition. In another publication, Ni/CeO₂ catalysts obtained via wet impregnation of Ni nitrate precursor were stabilized in an inert He atmosphere at 170 °C and reduced in H₂ at 360 °C to prevent Ni(CO)₄ formation and ensure active metallic Ni sites before methanation reaction [41]. This pre-treatment promotes strong metal–support interaction and hydrogen spillover, enabling CO₂ activation on CeO₂ and stepwise hydrogenation to CH₄. Consequently, Ni/CeO₂ achieves nearly 100% CO₂ conversion and CH₄ selectivity at 250 °C. Thus, stabilization and reduction are critical for maximizing Ni dispersion and methanation performance [41].

Recently, plasma pre-treatment has been considered as an alternative to thermal methods. It regards the use of plasma for treatment of catalysts before thermal methanation. Plasma, or ionized gas, in non-local thermodynamic equilibrium is called non-thermal plasma (NTP), or cold plasma. This non-equilibrium is owed to an imbalance between electron temperature and gas temperature, the first being much higher (1 eV) than the latter, which might remain at room temperature. The high electron temperature is due to its small mass compared to the larger atoms that form the gas. Therefore, electrons can be easily accelerated by the electric field and do not lose notable energy during elastic collisions. There are several ignition mechanisms for NTP, but the easiest example is by applying a potential difference between two electrodes in a gas tube establishing an electric field. Above a certain voltage threshold, which depends on the gas composition, pressure, and distance between electrodes, the breakdown of the gas occurs and accelerated free electrons collide with gas molecules to produce new ions and electrons via ionization, excitation, or dissociation. Due to this avalanche effect, known as Townsend mechanism, the plasma can self-sustain. Plasmas consist not only of positively and negatively charged ions and electrons, but also of neutral species, as atoms, molecules, and radicals. Types of cold plasmas used in catalysts studies are dielectric barrier discharge (DBD), corona, and glow discharge. The reactive property and complex chemistry of NTPs are beneficial for

the pre-treatment of the catalyst surface, in addition to being an activation method of CO₂ methanation, that will be later developed in Section 3.3 regarding plasma-assisted catalysis.

Plasma pre-treatment of catalysts summarized in Table 1 has generally the effect of improvement of the physicochemical properties such as metal dispersion, reducibility, metal–support interaction, surface basicity, and oxygen vacancies formation, which are all relevant for a catalyst utilized for CO₂ methanation [99–101,102]. In the works by Bian et al., they applied on ceria-containing catalysts, the pre-treatment process developed by Li et al. with Argon corona discharge for Ni catalysts [103] that leads to the reduction of the Ni particle size, resulting in the decrease of the catalyst coking during thermal methanation [99,100]. The plasma-reduction treatment also improved the surface basic sites of an Ni-Ce/Al₂O₃ catalyst, leading to improved conversion at low temperature, shifting the activation from 310 °C to 260 °C [104]. Metal particle size reduction and higher dispersion are reported also for Ru/CeO₂ catalysts pre-treated in a DBD reactor with Ar plasma [102]. The authors also reported a relevant and beneficial effect of plasma treatment on the ceria support related to a higher concentration of Ce³⁺ species associated with defects such as oxygen vacancies. These structural features play a key role for such support in the activity of the catalyst in thermal methanation [102]. At 350 °C, a higher CO₂ conversion is reported for the plasma-treated catalyst (83% against 65% with untreated Ru/CeO₂) and exhibits excellent CH₄ selectivity of 100% [102]. A similar effect of DBD Argon plasma pre-treatment was reported by Rui et al. for a Ni/CeO₂ catalyst [101]. The plasma pre-treatment leads to more dispersed Ni nanoparticles, which binds to CeO₂ support forming strong metal–support interaction [101]. Interfacial Ni-CeO₂ are active sites for H₂ splitting, which are easily reducible at lower temperature during the H₂-TPR test. Additionally, they facilitate more mobile oxygen atoms and the formation of oxygen vacancies in the plasma pre-treated sample [101]. Such features of the plasma-treated Ni/CeO₂ catalyst allow the methanation reaction temperature to decrease and achieve CO₂ conversion of 84.2% at 275 °C, which is maintained over 24 h in a time-on-stream test [101].

Table 1. Performance of CeO₂-Supported Catalysts for CO₂ Methanation Pre-treated using Non-Thermal Plasma.

Catalyst	Plasma Pre-Treatment			Thermal CO ₂ Methanation				Ref.
	Type	Conditions (V, f, P, T)	Gas Flow, Duration	Gas Composition, GHSV	T (°C)	S _{CH₄} (%)	X _{CO₂} (%)	
Ni/CeO ₂ -Al ₂ O ₃	Corona	40 kV	Ar 20 mL/min, 4 min	CO ₂ /H ₂ 1:4 30 L g ⁻¹ h ⁻¹	300	>99	>80	[99]
Ni/Ce/SBA-15	Corona	40 kV	Ar 20 mL/min, 4 min	N ₂ /H ₂ /CO ₂ 1:7.2:1.8	450	>99	80	[100]
10% Ni/CeO ₂	DBD	14 kV, 22 kHz	Ar, 1 h	CO ₂ /H ₂ /N ₂ 4:16:5 56,000 h ⁻¹	275	100	84	[101]
Ni-Ce/Al ₂ O ₃ LDH	Plasma jet	0.6 kV, 20 kHz, 400 °C	H ₂ /Ar 1:9 0.6 m ³ /h	CO ₂ /H ₂ 1:4 60 L g ⁻¹ h ⁻¹	260	100	>70%	[104]
Ru/CeO ₂	DBD	12 kV, 20 kHz, 50 W	Ar 50 mL/min, 1 h	CO ₂ /H ₂ 1:4	350	100	83	[102]

2.2. Doped Ceria

CeO₂ support modification through doping offers a versatile toolkit for tailoring catalyst durability and stability of the active site. The thermal stability of Ni-based catalysts is a critical factor in their long-term performance during CO₂ methanation, particularly when high Ni loadings are employed to maximize active site density. However, excessive Ni content often leads to particle sintering, reducing surface area and catalytic activity. To address this, various support modification strategies have been explored; an example shown in this sub-section is the doping of the cerium oxide support, where CeO₂ serves as the primary support and another metal or metal oxide is incorporated into its lattice.

CeO₂ can incorporate aliovalent dopants that tailor oxygen vacancy concentration, redox properties, and metal–support interactions. Tsitsias et al. [105] showed that incorporating ~10 mol% Pr³⁺ increases extrinsic oxygen vacancies and enhances Ni reducibility, especially when Pr–CeO₂ supports are synthesized under mildly basic NH₃-buffered conditions. These materials exhibit high surface areas and moderately strong basic sites, enabling 75% CO₂ conversion with 99% CH₄ selectivity at 350 °C. Doping CeO₂ with Yttrium, Choudhary et al. [106] demonstrated that isolated Y³⁺ single-atom dopants generate uniformly dispersed defects that further strengthen spill-over pathways and stabilize highly dispersed Ni nanoparticles. Their optimized Ni–Y₁/CeO₂ catalyst reaches 83% CO₂ conversion with full CH₄ selectivity and excellent stability, highlighting dopant engineering as a powerful strategy for optimizing Ni/CeO₂ catalysts.

Fujiwara et al. [74] demonstrated that doping CeO₂ supports with a controlled fraction of SiO₂ ($x = 0.05$) in 60%wt.% Ni/CeO₂ catalysts synthesized via flame spray pyrolysis significantly enhanced both activity and thermal stability. The optimal SiO₂ content increased the Ni surface area from 16 to 20 m²/g and prevented sintering during reduction at 500 °C. Catalytic tests showed a reaction rate of 86 mmol·h^{−1}·g_{cat}^{−1} at 225 °C, outperforming comparable Ru-based systems. Moreover, the catalyst maintained high CO₂ conversion (up to 91%) over 110 h of continuous operation, with minimal degradation after thermal cycling. These improvements were attributed to the dispersion of amorphous SiO₂ between Ni particles, which acted as a physical barrier against agglomeration.

Barreau et al. [69] investigated the performance of Ni-doped ceria catalysts for CO₂ methanation, consisting of CeO₂ nanoparticles doped with nickel (NiCeO_x) in a specific square–planar configuration. In particular, the effects of thermal activation were assessed. Obtained results demonstrated that calcination under oxidizing conditions at 600 °C facilitates partial exsolution of nickel to the surface and the formation of highly active Ni^{δ+}–Ce³⁺ interfacial sites, which enhance both CO₂ conversion (up to 76% in methanation at 350–400 °C) and selectivity (almost 100% CH₄ selectivity in methanation at 300–400 °C); in contrast, higher temperatures lead to nickel sintering, loss of active sites, and catalytic deactivation.

2.3. Ceria Mixed Oxides

Mixed oxide solid solutions based on ceria have emerged as highly promising supports for CO₂ methanation catalysts due to their tunable redox properties, enhanced oxygen mobility, and structural stability. These materials typically involve the substitution of Ce⁴⁺ with other cations, forming homogeneous solid solutions that preserve the fluorite-type structure while introducing oxygen vacancies and improving thermal resistance. Recent systems exemplify the effectiveness of this approach: Ru/CeZrO₂ [107], Ni/Ce_xSm_yZr_{1−x−y}O_{2−δ} [108], Ni–CeO₂–Y₂O₃ [109], or by adding Ni to the Ce–Zr lattice to improve the oxygen storage capacity [110] (See Figure 7).

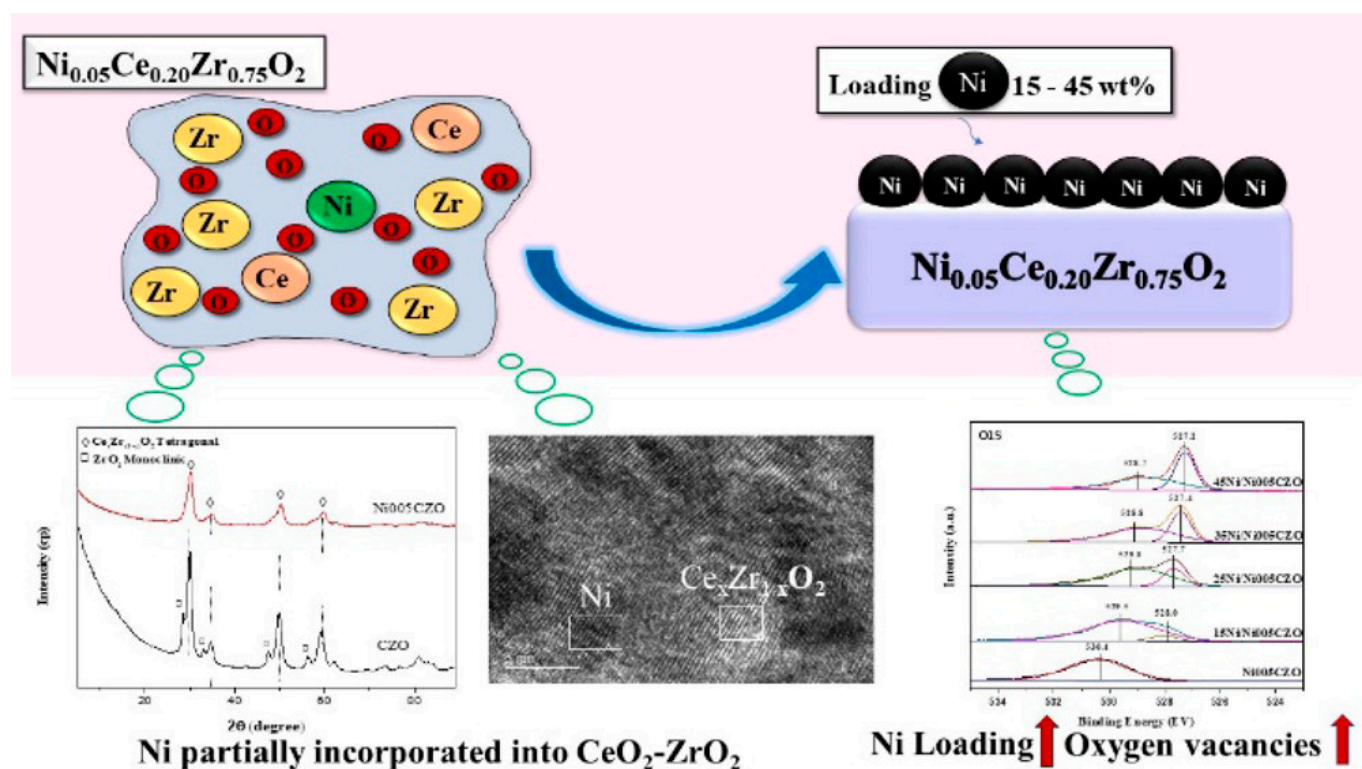


Figure 7. Ni-modified ceria-zirconia support, with Ni impregnation at different Ni-loading catalysis. XRD patterns of CZO and Ni005CZO. HRTEM image of Ni005CZO and XPS spectra of O1s for catalysts. Reprinted with permission from [110]. Copyright 2020 American Chemical Society.

CeZrO_2 , a binary solid solution synthesized via co-precipitation, exhibits superior oxygen mobility and thermal stability compared to pure ceria. In the Ru/CeZrO_2 system, the incorporation of Zr^{4+} helps preserve the fluorite-type structure, while the use of DBD plasma for Ru precursor decomposition leads to the formation of highly dispersed Ru nanoparticles (~ 0.8 nm) [107]. This promotes strong electronic metal–support interactions (EMSI) and a high density of oxygen vacancies. As a result, the catalyst achieves 86.2% CO_2 conversion and 100% CH_4 selectivity at just 275 °C, along with excellent stability over 100 h of continuous operation [107]. In contrast, the $\text{Ni/Ce}_x\text{Sm}_y\text{Zr}_{1-x-y}\text{O}_{2-\delta}$ system introduces Sm^{3+} as an additional dopant, which increases the concentration of oxygen vacancies and improves the thermal stability of the support. Although its low-temperature activity is limited, the catalyst reaches 72.5% CO_2 conversion and 100% CH_4 selectivity at 400 °C, demonstrating robustness under demanding thermal conditions [108]. Soft-templated NiO-CeO_2 mixed oxides, synthesized with varying Ni/Ce molar ratios (0.3–4.0), exhibit strong metal–support interactions and abundant oxygen vacancies due to partial incorporation of Ni^{2+} into the ceria lattice. Raman and XPS analyses confirm the formation of a defective solid solution, particularly at low Ni loadings, enhancing CO_2 adsorption and activation. Despite limited low-temperature activity, the catalyst achieves >99% CH_4 selectivity and up to 81% CO_2 conversion at 300 °C [111].

Makolkin et al. [109] demonstrated that nickel-based catalysts supported on yttria (Y_2O_3), ceria (CeO_2), and ceria-doped yttria exhibit enhanced performance in CO_2 methanation. Of these materials, the $\text{Ni-CeO}_2\text{-Y}_2\text{O}_3$ system exhibited the highest activity and thermal stability ($X_{\text{CO}_2} \approx 85\%$ at 300 °C). The study revealed that Y_2O_3 contributes to improved dispersion and stabilization of Ni nanoparticles, while CeO_2 enhances CO_2 activation and hydrogenation through its oxygen storage capacity. Catalytic tests showed that Ni loading positively correlates with reaction rate and CH_4 selectivity, reaching up to $S_{\text{CH}_4} \approx 95\%$ below 330 °C. Notably, the $\text{Ni-CeO}_2\text{-Y}_2\text{O}_3$ catalyst outperformed a commercial

Ni/Al₂O₃ benchmark, achieving higher mass-specific activity and maintaining structural integrity after thermal aging at 1000 °C. These results underscore the synergistic effect of combining yttria and ceria as supports for Ni-based catalysts in CO₂ methanation applications.

2.4. Cerium as Promoter

CeO₂ is widely recognized as a multifunctional promoter in heterogeneous catalysis, particularly for CO₂ methanation, due to its ability to enhance metal dispersion, provide oxygen storage capacity, and facilitate redox processes at the metal-support interface. Adding CeO₂ to Ni/Al₂O₃ catalysts significantly boosts CO₂ methanation by improving Ni dispersion, reducibility, and creating oxygen vacancies, which enhance CO₂ activation and lead to higher activity, CH₄ selectivity, and stability while suppressing Ni sintering and coking [112]. The strong Ni-CeO₂ interaction and formation of Ni-O-Ce solid solutions are key, often resulting in superior performance compared to unpromoted catalysts or even just Ni/CeO₂, particularly with optimal CeO₂ content (e.g., ~2–15%wt.). A significant advancement in this area was reported by Alkhoori et al. [113], who conducted a systematic study on Ni/CeO₂/Al₂O₃ systems. Their work examined the impact of alumina porosity, ceria loading (5 and 20%wt.), and synthesis method (sequential vs. co-impregnation) on catalytic performance. The most active catalyst, Ni-20Ce/mpAl, was synthesized via co-impregnation using 10%wt. Ni and 20%wt. CeO₂ on medium-porosity alumina, achieving 70% CO₂ conversion and over 98% CH₄ selectivity at 350 °C. In this configuration, CeO₂ serves both as a structural promoter and an oxygen carrier, contributing to enhanced Ni dispersion, increasing oxygen vacancy concentration, and SMSI, all of which are critical for efficient CO₂ activation and hydrogenation. Similarly, Rahmani et al. [114] demonstrated that Ni supported on mesoporous γ -Al₂O₃ and promoted with CeO₂ outperform those modified with MnO₂, ZrO₂, or La₂O₃. Their best formulation, containing 20%wt.% Ni and 2%wt. CeO₂, reached 80.3% CO₂ conversion at 350 °C with full CH₄ selectivity, attributing this improvement to increased Ni reducibility and electronic modifications induced by Ce, which facilitate CO₂ dissociation and hydrogenation. CeO₂ as a promoter also enhances sulfur tolerance, as demonstrated by Alarcón et al. [115], where the formation of Ce₂O₂S phases effectively limits NiS formation and preserves active sites under H₂S-containing streams. The authors investigated the role of CeO₂ as a promoter in Ni/ γ -Al₂O₃ catalysts for CO₂ methanation under severe conditions (500 °C, 5 bar, GHSV = 40,000 mL·g⁻¹·h⁻¹) and in the presence of H₂S impurities (1–5 ppm) [115]. The CeO₂-promoted catalyst exhibited superior thermal stability, maintaining activity for 138 h compared to rapid deactivation of the non-promoted Ni catalyst. At 500 °C, CO₂ conversion remained at 25% for Ni-CeO₂/ γ -Al₂O₃ versus 10% for Ni/ γ -Al₂O₃, with CH₄ selectivity of 100% throughout.

Cerium plays two distinct roles, depending on whether it acts as a dopant when small amounts of Ce are introduced into the Ni-based active phase. Cerium-doped Ni catalysts have been studied by Lu et al. [116], including also other metals such as La, Fe, and Co, supported on zirconia-modified mesoporous clays for CO₂ and CO methanation. The doped catalysts showed excellent catalytic activity and stability for both CO and CO₂ methanation compared to undoped catalysts. Small amounts of La, Ce, Co, or Fe promoted the high dispersion of nickel oxide nanoparticles, and a synergetic effect between the porous clay support and zirconia contributes to the catalyst high performance. Ce doping (Ni-Ce/ZrO₂) showed higher yield for CO methanation, while Fe doping (Ni-Fe/ZrO₂) improves CO₂ methanation. Ce was also studied as promoter in a Ni-Ce-Zr catalyst designed as a disk. The optimal composition (weight %), 74.08%Ni–18.74%Ce–7.13%Zr, achieved 82% CO₂ conversion at 300 °C with 100% CH₄ selectivity and exhibited remarkable stability over 1000 h [117].

2.5. Ceria-Based Catalysts Deposited on Structured Materials

Recent efforts to improve the mechanical robustness of structured catalysts for CO₂ methanation have explored both ceramic and metallic supports. Structured catalysts have gained increasing attention for CO₂ methanation due to their ability to enhance heat and mass transfer, reduce pressure drop, and improve thermal stability under dynamic operating conditions.

Structured CeO₂ was obtained by casting on mesoporous silica KIT-6, the interaction between the impregnated Ni phase and structured ceria was investigated via TPR and XPS [57]. The creation of both Ni⁰ and oxygen vacancies in CeO₂ during the reduction step allows the formation of a redox circulation and two possible active sites for H₂ and CO₂ activation to favor methanation. The reaction performed with this catalyst at 340 °C with weight hour space velocity (WHSV) 22 L_{g_{cat}}⁻¹h⁻¹ results in a remarkable conversion (>90%) and 100% selectivity towards methane [57]. Wang et al. [118] reported the synthesis and evaluation of a trimetallic Ni–Ce–Y catalyst supported on metakaolin (MK) for low-temperature CO₂ methanation. The co-impregnation of nickel, cerium, and yttrium onto the MK support resulted in enhanced dispersion of Ni nanoparticles, increased oxygen vacancy concentration, and improved surface basicity. These synergistic effects contributed to a significant improvement in catalytic performance, with the optimized catalyst achieving 78.4% CO₂ conversion and 99.8% CH₄ selectivity at 300 °C. Furthermore, the catalyst demonstrated excellent thermal stability over 100 h of continuous operation. Low-rank coal (LRC) was proposed as a novel carbonaceous support for CO₂ methanation catalysts due to its high thermal conductivity, tunable pore structure, and abundance of surface functional groups that facilitate metal dispersion. Kim et al. [119] demonstrated that LRC-supported Ni catalysts, especially when doped with Ce or Mg, achieved CO₂ conversions above 95% and CH₄ selectivity over 98% at 350–400 °C—comparable or superior to commercial oxide-supported catalysts. The LRC support enabled nano-dispersion of Ni particles and eliminated the need for a pre-reduction step, thanks to its intrinsic reducing nature. Long-term stability tests (~200 h) confirmed the robustness of Ni–Ce and Ni–Mg catalysts. Characterization via XRD, TEM, and H₂-TPR revealed that promoter addition influenced Ni dispersion, reducibility, and metal–support interaction, with Ce and Mg enhancing Ni accessibility and oxygen vacancy formation.

Morales et al. [93] investigated CeO₂-based technical catalysts shaped via extrusion and reinforced with inorganic binders, identifying boehmite as the most promising additive due to its minimal impact on catalytic activity and its ability to enhance structural integrity. Under reaction conditions of 5 bar and 200 mL·min⁻¹ flow, Ni–CeO₂–boehmite catalysts achieved CO₂ conversion levels comparable to pure CeO₂-supported systems, maintaining 96% of their initial activity ($X_{\text{CO}_2} \approx 56\%$) after 90 h of continuous operation at 300 °C. In parallel, Martínez-Fuentes et al. [89] demonstrated the feasibility of using fused deposition modelling to fabricate steel honeycomb monoliths loaded with NiO–CeO₂ nanoparticles. These structured catalysts maintained stable performance over 18 h at 325 °C ($X_{\text{CO}_2} \approx 50\text{--}55\%$). The study also revealed electronic interactions between the steel substrate and the active phase, contributing to improved reducibility and catalytic behavior. Recent studies on Ni/CeO₂ catalyst coated on honeycomb cordierite or carbon have shown that monolithic CO₂ methanation reactors may operate under diffusional or kinetic/transport mixed regimes, depending on flow rate and structure [120] and temperature [121]. In addition, when mass transport inside channels becomes limiting, there is a change in the reactant-catalyst interaction [120].

Renda et al. [122] introduced a novel approach for preparing structured Ni/CeO₂ catalysts using aluminum open-cell foams coated via chemical conversion coating. This surface treatment technique is used to create a thin, adherent oxide layer, in this case of CeO₂, on metallic substrates. Two nickel deposition techniques were compared: room-

temperature soaking and boiling-water impregnation. The latter resulted in a four-fold increase in Ni loading (up to 18%wt.) and superior catalytic performance, achieving CO₂ conversions up to 70% below 400 °C. Similarly, Italiano et al. [123] investigated a complementary strategy focused on optimizing thermal management in structured catalysts for CO₂ methanation. They explored the impact of support thermal conductivity by comparing SiC and Al₂O₃ open-cell foams coated via in situ solution combustion deposition. SiC, with its higher thermal conductivity, enabled more efficient heat dissipation within the catalytic bed, resulting in a more uniform temperature profile and the suppression of hot spots. This thermal advantage translated into superior catalytic performance under high space velocity conditions, with CO₂ conversions up to 77% and CH₄ productivities reaching 285 NL·h⁻¹ at 2.8 bar. Ho et al. [124] introduced a strategy based on high-cell-density NiCrAl open-cell foams coated via electrodeposition with Ni–Al hydrotalcite precursors modified by cerium. After calcination and reduction, the structured catalysts exhibited stable coatings with highly dispersed Ni nanoparticles and CeO₂ domains, enhancing basicity and promoting CO₂ activation. This configuration achieved superior performance, with CH₄ selectivity above 95% and remarkable CO₂ conversion ($X_{\text{CO}_2} \approx 75\%$) even at low temperatures (275–325 °C), delivering productivity rates up to 6.75 mol CH₄·g_{Ni}⁻¹·h⁻¹ under high space velocity (GHSV $\approx 38,200$ h⁻¹). Furthermore, the metallic foam support provided efficient heat management, mitigating hot spots and outperforming the pelletized counterpart under similar conditions.

Ni–CeO₂@SiO₂ core–shell catalysts, reported by Huang et al. [125], represent a pioneering approach in CO₂ methanation by embedding ultrafine Ni–CeO₂ nanowires (≈ 2.9 nm diameter, up to 102.7 nm length) within a microporous silica shell (see Figure 8). This unique architecture ensures high Ni dispersion and strong Ni–CeO₂ interaction, enriched with oxygen vacancies, while the SiO₂ shell prevents sintering and enhances thermal stability. In gas-phase methanation tests (200–450 °C), Ni–CeO₂@SiO₂ achieved CO₂ conversion above 70% and CH₄ selectivity >95% at 400 °C, maintaining performance during 60 h continuous operation at 400 °C.

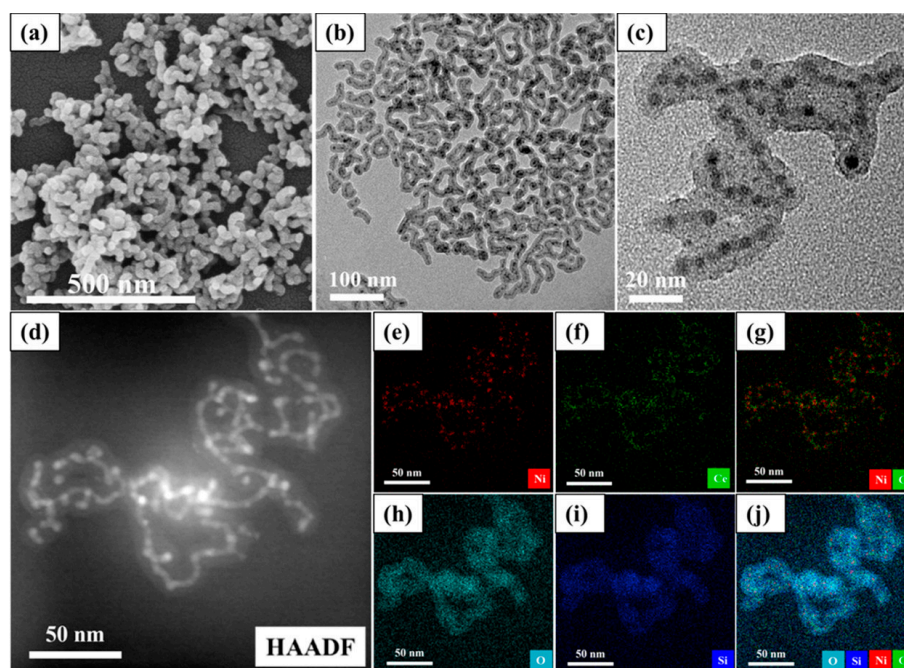


Figure 8. Ni–CeO₂ nanowires embedded in microporous silica. (a) SEM image, (b,c) TEM images, (d) HAADF-STEM image, and (e–j) EDX mapping of Ni–CeO₂@SiO₂ catalyst). Reprinted with permission from [125]. Copyright 2024 American Chemical Society.

In a related approach, García-Moncada et al. [126] combined nanostructured supports with reactor structuring to enhance both activity and stability under fluctuating conditions. Ni was supported on CeO₂ nanorods synthesized via hydrothermal methods and compared to a commercial octahedral CeO₂ counterpart. The nanorod-based catalyst exhibited smaller Ni particles ($\sim 7 \pm 4$ nm), higher dispersion (10.4%), and superior activity and stability. When structured on FeCrAlloy® μ -monoliths, the catalyst achieved enhanced heat transfer and further improved performance, reaching CO₂ conversion rates of $6.2 \text{ mmol}_{\text{CO}_2} \cdot \text{min}^{-1} \cdot \text{g}_{\text{Ni}}^{-1}$ ($X_{\text{CO}_2} \approx 20\text{--}30\%$) at 300 °C and $30 \text{ L} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$. Long-term tests (90 h) under dynamic flow conditions confirmed the resistance of the nanorod-based catalyst to sintering and deactivation.

3. CeO₂-Based and Containing Catalyst in Photothermal and Electro- and Plasma-Catalytic Methanation

Along with thermochemical catalysis, non-conventional catalytic methods and activation mechanisms have been explored and reported in the literature for the valorisation of CO₂, namely photo- and photothermal catalysis, electrocatalysis, and plasma-assisted catalysis [127]. Other non-conventional catalytic methods have been explored in CO₂ valorization such as solar-thermochemical redox cycles for CO₂ splitting with the production of syngas. Ceria has emerged as state-of-the-art material for this solar-driven high temperature reactions as non-volatile redox metal oxide due to the faster kinetics and better stability compared to the ferrite-based oxides [128]. However, the high temperature reached in a concentrating solar thermal reactor exceeds the desired range for CO₂ methanation, which is favored at low temperatures, making this technology not suitable for direct CO₂ hydrogenation.

Photothermal and electro- and plasma-assisted catalysis are suitable routes for CO₂ methanation, as all processes rely on the transfer of charges caused by different mechanisms at mild temperatures. Photocatalysis relies on the absorption of photons by a semiconductor catalyst creating electron-hole pairs [129], and thermal catalysis enhances reaction kinetics and adsorption–desorption dynamics. Electrochemistry relies on the transfer of electrons by a strong electric field established between two electrodes in an electrolyte, while plasma establishes strong electric fields, which have been reported to charge the surface of the catalyst [130,131].

The photoreduction of CO₂ proceeds by the photoexcited electrons in the conduction band of the catalyst moving to CO₂ and the efficiency for the photocatalysis case is influenced by the catalyst, temperature, pH conditions, and, of course, light intensity and spectrum. The reaction pathways and yield of CO₂ conversion via the electrochemical route depend on the electrode/catalyst selection, medium, and temperature. The possible drawbacks of this process are the high potential required and the electrode stability. The photo- and electrochemical processes are normally performed in aqueous media, being water (or aqueous species) oxidized either by the holes generated in photocatalysts or at the anode in electrocatalysis, which could be an issue for CO₂ reduction due to the low CO₂ solubility in water. Photo- and photothermal catalytic processes can be more efficient thanks to direct use of sunlight, while electrocatalytic and plasma-assisted processes make direct use of renewable energy sources. Electrocatalytic and non-thermal plasma reactors are compact, modular, and have easy turn on/off, which makes them flexible technologies, interesting for applications in both industrial and remote environments [132].

3.1. Photothermal CO₂ Methanation

The combination of light and heat signifies a recently developed approach to enhance the efficiency of CO₂ methanation, compared to applying photocatalysis and thermal

catalysis independently [133–136]. Photonic excitation generates charge carriers or induces plasmonic effects, while localized thermal energy accelerates surface reaction kinetics, improves molecular adsorption–desorption dynamics, and facilitates the overcoming of activation barriers. The introduction of light into thermal processes enables milder reaction conditions, improves energy efficiency, and could allow the control of product distribution by adjusting the power density of the irradiation wavelength. Thermal energy could be provided either by catalysts with appropriate light-to-heat conversion properties (such as plasmonic and carbonaceous materials) or by external heaters [25]. Based on the interaction patterns between photons and thermal energy, the following classification of photothermal catalysis pathways is proposed: photo-assisted thermocatalysis (heat is the primary driving force); photo-driven thermocatalysis (thermal effect is introduced by solar energy, without any independent photocatalytic activity); thermal-assisted photocatalysis (light energy is the primary driving force); and photothermal co-catalysis (solar energy and heat energy act synergistically to drive the reaction).

The photothermal approach to CO₂ methanation has garnered significant interest in recent years since the first studies were published [137–141]. In one of the earliest published works, Meng et al. demonstrated the effective application of this photothermal effect using Group VIII metals for CO₂ methanation at 300–400 °C, showing in this case the dominance of the light-induced thermal effect. The photothermal conversion rates observed in their study resulted in values several orders of magnitude larger than those obtained by photocatalytic methods [141]. The study of the application of Ce in the photothermal catalytic process of CO₂ methanation has been initiated in recent years [136,140,142–144]. Table 2 provides an overview of published works on CeO₂-based catalysts for photothermal CO₂ methanation. The use of Ce plays multiple roles in photothermal catalysts: (i) as an active support with high oxygen storage capacity that promote the separation and transfer of photogenerated charge carriers and enhance light absorption and gives thermal stability; (ii) as a dopant in wide-bandgap semiconductors (e.g., TiO₂, ZnO), introducing mid-gap states and enhancing visible-light absorption; and (iii) as a promoter phase in metal-based catalysts, facilitating charge separation and accelerating surface redox cycles. These functions exploit the reversible Ce³⁺/Ce⁴⁺ redox couple and abundant oxygen vacancies to synergistically couple photonic excitation with localized thermal effects, enabling photoinduced electron–hole generation and dynamic defect chemistry. As a result, activation barriers are lowered, alternative reaction pathways (e.g., formate intermediates) become accessible, and methane formation occurs at lower temperatures with higher energy efficiency compared to purely thermal processes [134,135,145]. The highest CH₄ yield summarized in Table 2 of 885.27 mmol g^{−1} h^{−1} has been obtained at 200 °C with 100 mg catalyst, 12 mL min^{−1} of H₂, 4 mL min^{−1} of CO₂, and 4 mL min^{−1} of N₂ using MOFS as a precursor to load well-dispersed metal nanoparticles of Co/CeO₂ [146]. These authors attributed this high yield at such reaction conditions to the intense light absorption, dispersed Co, good gas adsorption performance, and the direct synergistic effect of light and heat. In other work, an Au/Ce_{0.95}Ru_{0.05}O₂ solid-solution catalyst exhibited outstanding photothermal CO₂ methanation performance under visible–near-infrared light without external heating. In a continuous-flow reactor, at a catalyst surface temperature of approximately 340 °C, it was achieved a CH₄ production rate of 473 mmol·g^{−1}·h^{−1} with ~100% CH₄ selectivity and ~75% CO₂ conversion, approaching the thermodynamic limit [147].

The effect of pressure in photothermal CO₂ methanation remains insufficiently explored. The majority of the studies presented in Table 2 were conducted at or in the vicinity of 0.1 MPa. This suggests that the field has focused primarily on mild and easily accessible conditions rather than systematically evaluating pressure as an independent variable. Therefore, the good performance achieved at atmospheric pressure should not be

taken as evidence that pressure is unimportant; rather, it suggests that its specific role has yet to be clearly established.

Table 2. Key Parameters and Performance of CeO₂-Based Catalysts for Photothermal CO₂ Methanation: Insights from Recent Studies.

Catalyst	Active Phase	Radiation Lamp	CH ₄ (mmol·g _{cat} ⁻¹ ·h ⁻¹)	CH ₄ Selectivity (%)	CO ₂ Conversion (%)	Bed T (°C)	P (bar)	Ref.
Continuous flow bed system								
Ru/CeO ₂ -H ₂	Ru (0.97%wt.)	Xe 300 W UV-Vis-IR	2.67 ¹	97.6	*	200	≈1	[148]
Ru/CeO ₂	Ru (2%wt.)	Vis- LED, 2.2 W cm ⁻²	15	99.5	*	220	≈1	[149]
Ru/Mg–CeO ₂ (Single atom)	Ru (0.5%wt.)	Xe 300 W, 2.9 W cm ⁻²	469	93.1	~60	400	≈1	[150]
Ni–CeO ₂	Ni (7.5%wt.)	Xe lamp, 420–780 nm	0.93	*	*	~250	≈1	[151]
Ni/CeO ₂ (SBA-15)	Ni (12%wt.)	Xe 300 W, 0.3–0.5 Wcm ⁻²	62.1 ²	98.6	29.4	282	≈1	[142]
Ni/CeO ₂ -CO ₂	Ni (≈4.3%wt.)	Xe 300 W, 300–2500 nm 4.7 W	92.8 ²	99.3%	≈66% ²	336	≈1	[152]
Ni/CeO ₂	Ni (8.2%wt.)	Xe 300 W	~36 ²	~100	93	285	0.75–1	[143]
La _{0.2} Ce _{0.8} NiO ₃	Ni (exsolved Ni ⁰ , 4.6%wt.)	Xe, XE-300F, 2.9 W cm ⁻²	258.9	97.2	55.4	300	≈1	[153]
Co/CeO ₂ -MOF derived	Co (32.5%wt.)	Xe 300 W	885.27	97.34%	*	200	≈1	[146]
Co/CeO ₂	Co (9.7%wt.)	Blue light, 450–460 nm, 0.44 and 0.5 W cm ⁻²	40.3 ²	94	≈40	300	≈1	[136]
10Co/CeO ₂	Co (9.3%wt.)	LED panel (420 < λ < 710 nm ≈2 W cm ⁻²)	289	90	42	350	≈1	[154]
Au _{0.1} /Ce _{0.95} Ru _{0.05} O ₂	Ru (4.6%wt.)	350–2500 nm, 1.6–5.3 W cm ⁻² CME-303 XE	473	98.6	75	340	≈1	[147]
11 mol%Ni/Ce	CeO ₂ -Ni ⁰ (11%mol Ce)	300 W Xe lamp 300–2500 nm; 1.5 W cm ⁻²	≈ 199	≈ 100	82	220	1.0	[155]
Batch reactor system								
NiCe _{0.8} Ti _{0.2} O ₂	Ni(8%wt.)	Xe 300 W	~21 ²	~100	≈82 ²	~290	0.75–1	[143]
Ni/Ce _x Ti _{1-x} O ₂ Ni/80Ce-20Ti_SG	Ni (10%wt.)	Xe 300 W	~17.0	100	~100	*	0.75	[140]
Au _{0.1} /Ce _{0.95} Ru _{0.05} O ₂	Ru (4.6%wt.)	420–780 nm	327	≈99%	93%	340	6	[147]

* The study does not report an exact value. ¹ 275.1 mmol g_{Ru}⁻¹ h⁻¹. ² Calculated from data reported in the corresponding reference.

Some works have assessed the relative thermal and nonthermal contributions during CO₂ methanation [148,149,152,156]. In some of these studies, it has been observed that high CH₄ yields can be achieved at substantially lower temperatures than those typically

required for purely thermocatalytic methanation. According to Ullah et al., light illumination invoked better catalytic activity in the range of 250–350 °C using Co, Cu, and mixed Co-Cu catalysts loaded on CeO₂ support [136]. At higher temperatures, the benefit of light was lower, likely due to an increase predominance of thermal catalysis. Nevertheless, other studies observed relevant differences between formation rate of CH₄ at higher temperatures. Zhang et al. reported 469 mmol g_{cat}^{−1} h^{−1} with Ru/Mg-CeO₂ catalyst designed on the concept of single atom catalyst at 400 °C with light irradiation (2.9 W cm^{−2}), while in dark conditions CH₄ yield was around 410 mmol g_{cat}^{−1} h^{−1} [150].

A comparison of photothermal and thermal effect for Ru/CeO₂ and a modified Ru/CeO₂-H₂ system (obtained by pre-reducing the CeO₂ support before Ru deposition, Figure 9) was published by Zhou et al. [148]. The average production rates of the tested catalysts are shown in Figure 10a. Ru/CeO₂ achieved a CH₄ production rate of 69.4 mmol·g_{Ru}^{−1}·h^{−1} under thermal conditions at 200 °C and 111.2 mmol g_{Ru}^{−1} h^{−1} under photothermal operation. For Ru/CeO₂-H₂, the improvement was even greater: from 183.9 mmol·g_{Ru}^{−1}·h^{−1} (thermal) to 275.1 mmol g_{Ru}^{−1} h^{−1} (photothermal). The selectivity to CH₄ for Ru/CeO₂-H₂ was also improved under photothermal conditions, reaching nearly 100% (Figure 10b). Nevertheless, Figure 10b also shows that the improvement in CH₄ selectivity was less pronounced for the Ru/CeO₂ catalyst. As can be observed in Figure 10c, light not only accelerates the reaction by generating localized surface plasmon resonance (LSPR) that induced hot electrons that create oxygen vacancies on CeO₂-H₂ but also lowers the apparent activation energy (from 37.2 to 35.2 kJ mol^{−1} for Ru/CeO₂-H₂). Strong SMSI (in Ru/CeO₂) makes the ruthenium (Ru) electron-rich and partially covers it with CeO₂, which limits hydrogen (H₂) dissociation and reduces the number of active surface sites. Suppressing SMSI (Ru/CeO₂-H₂) left the Ru electron-deficient, thereby facilitating H₂ activation and hydrogen spillover, preventing the migration and encapsulation of CeO₂ over Ru nanoparticles. Meanwhile, LSPR-induced hot electrons migrate to the CeO₂-H₂ interface to create oxygen vacancies for CO₂ activation.

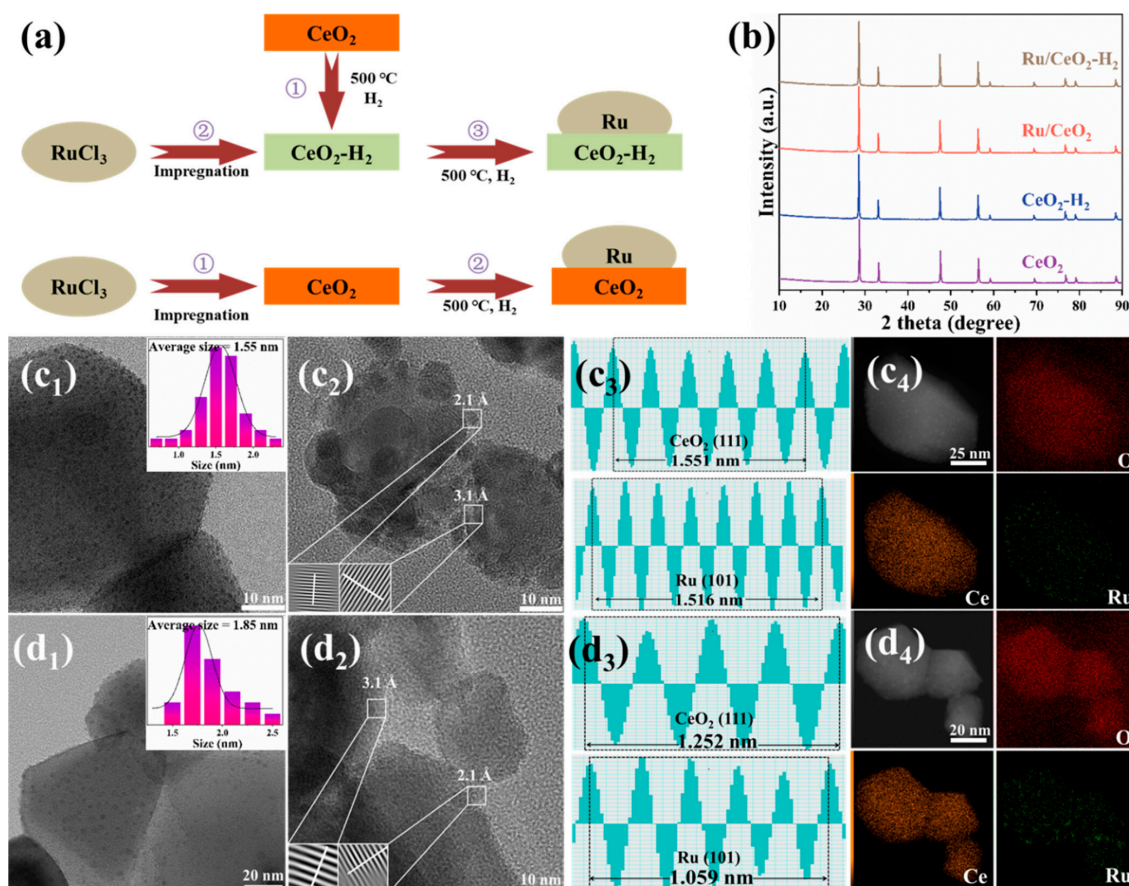


Figure 9. (a) Illustration of the synthesis process of Ru/CeO₂ and Ru/CeO₂–H₂. (b) XRD patterns of CeO₂, CeO₂–H₂, Ru/CeO₂, and Ru/CeO₂–H₂. High-resolution transmission electron microscopy (HRTEM) and element energy dispersive X-ray (EDX) mapping images of Ru/CeO₂–H₂ (c1–c4) and Ru/CeO₂ (d1–d4). The inset plots in the TEM images (c1) and (d1) are the Ru particle size distribution. Reprinted with permission from [148]. Copyright 2024 American Chemical Society.

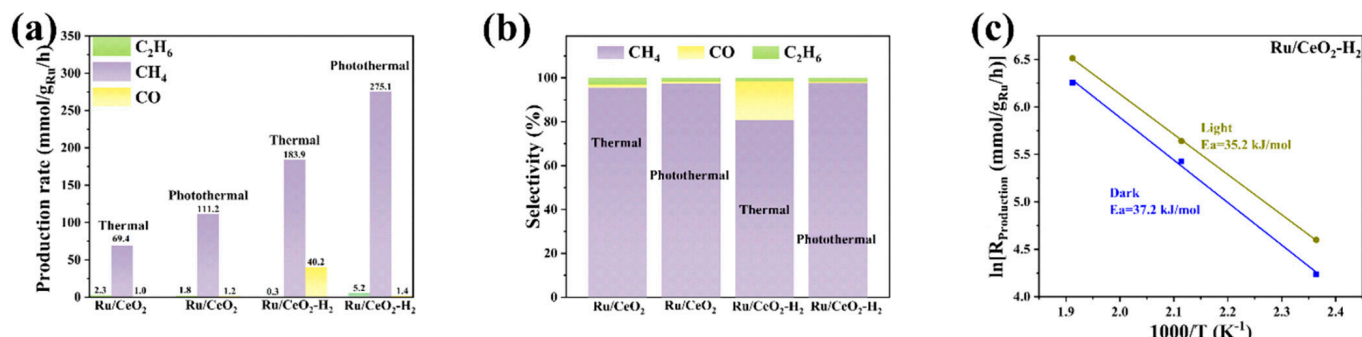


Figure 10. (a) Average production rates, (b) selectivity, and (c) Arrhenius plot of CH₄, CO, and C₂H₆ in Ru/CeO₂–H₂ at different conditions (thermal: 200 °C, dark; photothermal: 200 °C, light). Reprinted in part with permission from [148]. Copyright 2024 American Chemical Society.

Photothermal CO₂ methanation is most often interpreted within a broadly shared mechanistic framework in which H₂ activation takes place on metallic sites, whereas CO₂ adsorption and activation occur on oxide supports or at metal–support interfacial sites, frequently involving oxygen-vacancy-related centers. Across a wide range of catalyst families, the reaction is commonly described as proceeding through formate-mediated pathways, although in several systems a parallel or secondary CO-mediated route has also been proposed [134,136,140,142,146,148,151–155,157]. The role of light appears to span a continuum rather than a set of strictly discrete regimes. In one limiting case, illumination acts predominantly as a photothermal input, increasing the local catalyst temperature and thereby accelerating methanation without fundamentally modifying the overall reaction sequence, although even in such cases, secondary changes in the surface population of adsorbed intermediates may still be detected [140,142,143]. In a second, widely reported mode of operation, light additionally exerts an electronic promotion effect, increasing surface electron density, enhancing the participation of vacancy-related sites, strengthening CO₂ adsorption and activation, and accelerating the hydrogenation of carbonate-, formate-, and CO-derived intermediates while preserving the overall methanation network [146,152–155,157]. Particularly noteworthy is the growing convergence among recent studies around the view that light-enhanced methanation is closely associated with promotion of the formate-mediated reaction network manifold, either through facilitation of adsorbed formate conversion on CeO₂-based surfaces, through sustained vacancy-assisted CO₂ activation, or through electron enrichment in the vicinity of metallic sites that promotes hydrogen activation and subsequent hydrogenation steps. In some catalyst systems, this promotion takes place within a dual-intermediate network involving both HCOO* and CO* without altering the intrinsic reaction pathway [146,152–155,157]. A third, less frequently invoked and more cautiously assigned regime involves non-thermal photochemical contributions, in which nonequilibrium photoexcited charge carriers may participate directly in CO₂ activation or in the transformation of adsorbed intermediates. Within the present body of methanation studies, the work of Jiang et al. provides suggestive evidence consistent with this type of behavior. Taken together, these studies suggest that the fundamental methanation chemistry remains largely conserved across catalyst systems, whereas the role of light ranges from predominantly thermal assistance to electronically mediated enhancement and, in selected cases, to more explicit non-thermal

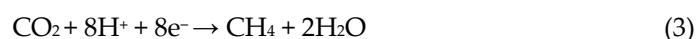
contributions associated with charge-transfer dynamics at the metal–support interface [134,136,140,142,146,148,151–155,157].

Building on these findings, the most promising improvements and future applications involve (i) optimizing power density and wavelength to modulate conversion and selectivity, (ii) engineering CeO₂–metal interfaces that maximize the generation/stability of oxygen vacancies and control SMSI (e.g., pre-reducing the support prior to metal deposition), (iii) employing metals and supports with strong photothermal response (Au, Ru; MOF derived structuring) to increase absorption and non-radiative dissipation, and (iv) rigorously quantifying thermal vs. non-thermal contributions in continuous flow reactors under visible–NIR light without external heating, so that the Ce-based photothermal approach consolidates its efficiency and scalability potential for CO₂ to CH₄ conversion [133,141,147,148,158].

3.2. Electrocatalytic CO₂ Methanation

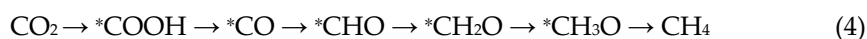
The electrocatalytic reduction of carbon dioxide to methane has emerged as a compelling strategy for sustainable carbon utilization, particularly in the context of the global energy transition. Driven by the rapid expansion of renewable energy and the corresponding decline in electricity costs, this electrochemical approach offers a viable alternative to thermo-catalytic and plasma-assisted CO₂ conversion methods. It enables CH₄ production under ambient conditions using renewable electricity, aligning with decarbonization goals and circular carbon economy principles.

The overall reaction for CO₂ methanation is:



This process (3) occurs in an electrochemical cell, typically comprising an anode where the water oxidation generates O₂, protons, and electrons. There is also a cathode where the CO₂ is reduced to CH₄ via a series of proton-coupled electron transfer (PCET) steps. And finally, an electrolyte, often alkaline to suppress the hydrogen evolution reaction (HER) and improve CH₄ selectivity.

Three main cell configurations are employed named H-cell, which is simple and cost-effective but limited by poor CO₂ solubility and low current density; flow cell that incorporates gas diffusion electrodes (GDEs) to enhance CO₂ mass transfer and current density; and membrane electrode assembly (MEA) that offers a compact design and improved performance, though still challenged by scalability and energy efficiency [159]. Despite its thermodynamic stability, CO₂ can be activated electrocatalytically due to the strong polarity of its C=O bond and the electron-deficient nature of the carbon atom. Upon adsorption onto the catalyst surface, CO₂ undergoes sequential PCET (4) steps leading to CH₄ formation in mechanistic pathways such as [160]:



Therefore, the formation of CH₄ involves multiple intermediates, each with distinct adsorption energies and kinetic barriers. The selectivity toward CH₄ is strongly influenced by the binding strength and reactivity of intermediates such as *CO, *CHO, and *CH₃O [161]. The proximity of redox potentials for competing reactions (e.g., CO formation, HER) further complicates selective CH₄ production. The electrocatalyst plays a pivotal role in mediating the complex PCET steps, facilitating C=O bond cleavage and C–H bond formation [25].

Copper (Cu) is the most extensively studied catalyst due to its unique ability to reduce CO₂ to methane. However, its CH₄ selectivity described by the Faradaic Efficiency to methane (FE_{CH₄}), remains suboptimal, and some strategies are explored such as alloys to tune electronic properties [162], nanostructures to expose active facets [163], or surface

functionalization to stabilize key intermediates [164]. There are, as well, challenges related to high overpotentials due to CO₂ stability, limited energy efficiency at commercially relevant current densities, and catalyst degradation over prolonged operation [165]. Solutions explored are developing advanced catalysts that lower overpotentials and promote CH₄-specific pathways or optimizing cell architectures to improve mass transfer and current density [25]. Works on elucidating reaction mechanisms through in situ and operando techniques are also performed to guide rational catalyst design [166].

Electrocatalytic CO₂ methanation holds significant promise for integrating renewable energy with carbon recycling. However, achieving commercially viable CH₄ production will require breakthroughs in catalyst engineering, system design, and mechanistic understanding. Li et al. [145] reviewed the application of CeO₂-based electrocatalysts for CO₂ reduction and reported that these catalysts show promise for energy conversion due to cerium oxide's unique properties, such as its flexible redox switching between Ce³⁺ and Ce⁴⁺ and abundant oxygen vacancies. These materials are effective in converting CO₂ by optimizing their size, structure, and crystal facets, which can be achieved through strategies like defect engineering and creating composite structures with other materials. Research focuses on improving catalytic performance through advanced synthesis methods and a deeper understanding of the reaction mechanisms to accelerate industrial applications. Cu is the only active metal supported on CeO₂ studied up to now for CO₂ electrochemical reduction catalysts to produce hydrocarbons, methane, or C₂⁺, depending on the interactions established.

Important steps of CO₂ electrocatalytic reduction are CO₂ adsorption and activation, which are enhanced at oxygen vacancies of Cu-CeO₂. These oxygen vacancies were optimised by Xue et al. [167] using specific CeO₂ nanostructures, like nanorods, and high proportions of oxygen vacancies show the highest selectivity and activity. Theoretical calculations show that doping Cu into CeO₂ can lower the energy barrier for CO₂ reduction to COOH and shift the subsequent pathway from CHOH to CH, leading to improved CH₄ production. The Cu oxidation state was related with the selectivity of Cu-CeO₂ catalysts to methane. On the one hand, Zhou et al. [168] concluded that stabilizing Cu²⁺ ions in a solid-solution matrix like ceria CeO₂ promotes the electrochemical CO₂ reduction reaction (CRR) to CH₄ by preventing their reduction to less active forms Cu⁰ or Cu⁺.

By incorporating Cu²⁺ into a matrix as observed in Figure 11, researchers can retain them as active catalytic sites, strengthening the adsorption of *CO intermediates and directing the reaction towards methane production over other products like ethylene (see Figure 12).

However, by carefully controlling the CeO₂ oxygen vacancy concentration (through calcination temperature) and surface termination (via pH), Patra et al. [169] achieved a higher concentration of oxygen vacancies that stabilize the Cu⁺ active sites and boost the reaction, while a more alkaline pH is shown to create surfaces that are more favorable for the competing HER. Moreover, Hong et al. [170] studied how the oxidation state of copper on ceria Cu-CeO₂ nanorods affects the selectivity of the electrochemical reduction of CO₂ toward C₁ versus C₂⁺ products and concluded that a higher oxidation state of copper can promote C₂⁺ products, while a lower one may favor C₁ products. The synthesis of Cu single-atom catalysts (SACs) on CeO₂ nanorods with atmosphere-tuned oxygen vacancies produced high selectivity to CH₄ from CO₂ reduction with a FE_{CH₄} of 70.03% [171] compiled in Table 3. A different approach was followed by Zhang et al. [172] and Chen et al. [162] introducing carbon in the catalyst from metal-organic framework MOF precursors. They used the interaction between copper, cerium oxide, and carbon to improve the selectivity and efficiency of the CO₂ conversion process, the highest FE_{CH₄} reported to date of 80.3% was obtained [172]. This catalyst was synthesised from a MOF to create a carbon-encapsulated, copper-doped cerium oxide material.

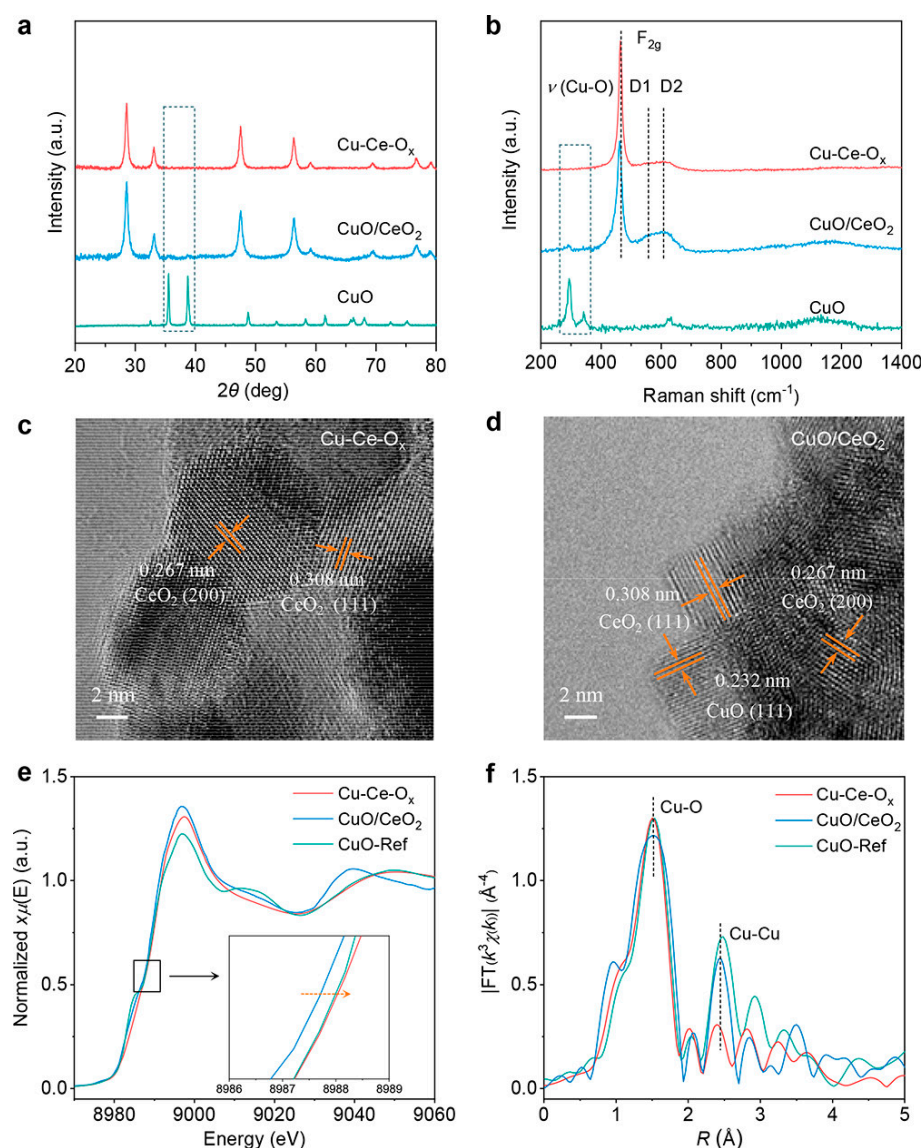


Figure 11. Structural characterizations of CuO/CeO₂, Cu-Ce-O_x, and CuO. (a) XRD patterns. (b) Raman spectra. (c,d) HRTEM images. (e) Cu K-edge XANES spectra. (f) Fourier transformed Cu K-edge EXAFS spectra. Reprinted with permission from [168]. Copyright 2022 American Chemical Society.

Table 3. Composition and Performance of CeO₂-Based Catalysts for Electrocatalytic CO₂ Methanation.

Support Material	Active Metal	Voltage	Electrolyte	FE _{CH₄}	Ref.
CeO ₂ nanorods	Cu (single atom)	−1.8 V vs. RHE	0.1 M KHCO ₃	58%	[173]
CeO ₂	Cu ⁺ ions	−1.1 V vs. RHE	0.1 M KHCO ₃	30%	[174]
CeO ₂ -x nanocrystals	Cu nanoparticles	−1.2 V vs. RHE	0.1 M KHCO ₃	54%	[175]
CeO ₂ nanorods	Cu (Cu ⁰ /Cu ⁺ /Cu ²⁺ mixed)	−1.6 V vs. RHE	0.1 M KHCO ₃	49.3%	[167]
CeO ₂	Cu ²⁺ ions	−0.82 V vs. RHE	1 M KOH	67.8%	[168]
CeO ₂ nanorods	Cu nanoparticles	−1.3 V vs. RHE	0.1 M KHCO ₃	58%	[176]
CeO ₂ nanoparticles	Cu ⁺ (single atom)	−0.89 V vs. RHE	1 M KOH	42%	[169]
CeO ₂ clusters (2.4 nm)	Cu (single atom, Cu ²⁺)	−400 mA/cm ² (current mode)	1 M KOH	67.1%	[177]
CeO ₂ nanorods	Cu ⁰ /Cu ⁺ clusters	−0.9 V vs. RHE	1 M KOH	45.5%	[170]
CeO ₂ + in situ carbon	Cu ²⁺ ions	−1.5 V vs. RHE	0.5 M KHCO ₃	80.3%	[172]
CeO ₂ nanorods	Cu (Cu ⁺ /Cu ²⁺ mixed)	−1.5 V vs. RHE	0.1 M KHCO ₃	49%	[178]

CeO ₂ nanorods (110)	Cu (atomic dispersion)	−1.8 V vs. RHE	1 M KOH	62%	[161]
CeO ₂ nanorods	Cu ⁺ (single atom)	−1.49 V vs. RHE	1 M KOH	70.03%	[171]
CuOx nanoparticles	Cu (atomic with Ce dopant)	−1.6 V vs. RHE	1 M KOH	67.4%	[162]

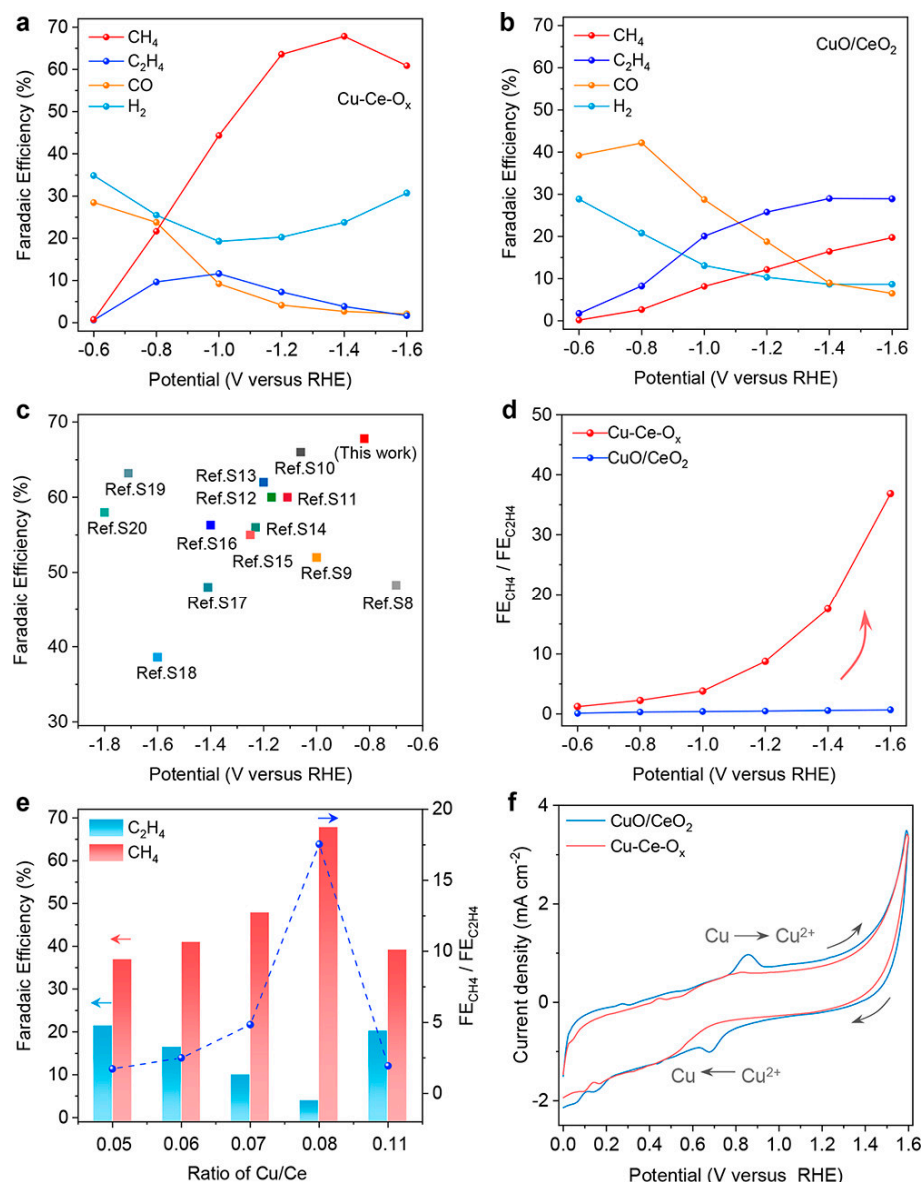


Figure 12. CRR performances of various samples. (a,b) FEs for CRR products at different potentials. CuO/CeO₂ can produce a few liquid products (e.g., formic acid and ethanol) under a more negative potential, which make the total FEs less than 100%. (c) FE_{CH₄} of Cu-Ce-Ox in comparison with other reported Cu-based catalysts. (d) Ratios of FE_{CH₄} to FE_{C₂H₄} for CuO/CeO₂ and Cu-Ce-Ox. (e) FEs for CRR products and ratios of FE_{CH₄} to Ratios of FE_{CH₄} to FE_{C₂H₄} for CuO/CeO₂ and Cu-Ce-Ox. (f) Cyclic voltammograms of Cu-Ce-Ox and CuO/CeO₂ after CRR. Reprinted with permission from [168]. Copyright 2022 American Chemical Society.

A common characteristic of these works on CeO₂ catalysts is that they are carried out at atmospheric pressure, taking advantage of electrochemical reaction being able to be carried out at standard conditions of both temperature and pressure. However, a series of relevant experiments and DFT studies have revealed that high pressure is a simple and effective method to enhance the availability and competitive adsorption of CO₂ [179],

thereby simultaneously activating the CO₂ electroreduction reaction and promoting CH₄ production over catalysts with Cu-N₂ coordination structure [180].

Future work on application of ceria on CO₂ electrolysis to CH₄ should prioritize the rational design of catalysts with tailored properties to overcome current limitations in selectivity, energy efficiency, and durability. Expanding research beyond Cu-based systems—currently the only metal supported on CeO₂ studied for hydrocarbon production—could unlock new catalytic synergies for methane and C₂+ products. Strategies such as optimizing metal–support interactions, controlling particle size, and engineering crystallographic facets will be essential to stabilize key intermediates and lower overpotentials. Advanced synthesis methods combined with computational modeling can accelerate the discovery of catalysts with improved activity.

3.3. Plasma-Assisted CO₂ Methanation

Several publications in the last decade have proved that the coupling of cold plasma with an active and selective catalyst leads to high yield for CO₂ methanation at ambient pressure and lower temperature compared to the thermochemical reaction [181]. Non-thermal plasmas (NTPs) are applied in catalysis as a source of non-equilibrium and highly energetic electrons that enable the reaction by exciting and making the chemical species reactive. These systems operate under mild conditions due to the favorable pressure and temperature required for plasma ignition and to establish the CO₂ conversion reaction. Plasma-assisted catalysis, or plasma catalysis, considers the combination of an NTP with a catalytic material, creating a synergy between the two: the plasma activates the gas molecules, the catalyst controls and selects the yield of the reactions on its surface. Two configurations are found in the literature depending on the plasma temperature and the lifetime of the reactive species: either by packing the reactor with the material (one-stage or in-plasma) or by locating the catalyst downstream of the plasma (two-stage or post-plasma) [181]. The publications described in this section regarding plasma-assisted CO₂ methanation and summarized in Table 4 all report an in-plasma coupling in an atmospheric pressure DBD reactor (with the exception of Debek et al., who used a Ni/CeO₂-ZrO₂ catalyst in a glow discharge [182]). Therefore, the cold plasma can affect both the gas phase and the catalyst surface (and vice versa). Glow discharge requires low pressure for plasma ignition, and in this study, a pressure in the range of 220–270 Pa was measured in the reactor [182]. The efficiency of the process is affected by numerous experimental plasma set-up conditions, such as injected power generator, as well as ignition mechanism, pseudo-adiabatic, adiabatic, or isothermal reactor design, and gas composition, flow and GHSV. The specific energy input (SEI), calculated as the ratio of power over flow rate, describes the average energy per gas molecule and is a popular process parameter to assess the energy consumption and efficiency of a plasma–catalytic reaction [181].

Supports of CeO₂ or ceria mixed oxides are used predominantly for Ni catalysts in these works, as Table 4 reflects, and show good activity and stability for plasma-assisted CO₂ methanation. Ullah et al. showed the synergistic effect of plasma and a Ni catalyst for CO₂ hydrogenation, enhancing CO₂ conversion and CH₄ selectivity at isothermal conditions when both plasma and 15%Ni/CeO₂ material are present [183]. The authors compared Ni catalysts supported on CeO₂, γ -Al₂O₃, and ZSM-5 in a DBD-plasma reactor finding that the ceria-supported catalyst achieved the best conversion and methane selectivity at 300 °C due to high reducibility and CO₂ chemisorption capacity of the catalyst [183]. The effect of the morphology of CeO₂ support on physicochemical properties and plasma-assisted methanation was studied in another publication [184]. Different nanostructures as nanocubes, nanoneedles, and nanorods were synthesized with 15%wt. Ni impregnation was characterized and tested in DBD-assisted CO₂ methanation. Nanorod and nanoneedles showed improved oxygen storage-release capacity and dielectric property, which

influence positively the plasma-assisted reaction and efficiency [184]. CeO₂ nanoneedles were used in another study as support of 5%mol. Ru catalysts and achieved in a DBD reactor enhanced energy efficiency of the CO₂ methanation reaction (40%) compared to the Ni catalyst thanks to increased effective H₂ dissociation and optimal metal-support interaction [185].

Most publications on ceria-containing catalysts for plasma-assisted CO₂ methanation commonly report the use of ceria-zirconia mixed oxides as support for Ni particles. Ce_xZr_(1-x)O₂ (CZ) was considered a promising metal oxide for such application due to the improved redox properties produced by the defects created in the ceria crystalline structure by the CZ solid solution [186–192]. Ceria–zirconia is recognized as an excellent catalyst support for CO₂ methanation due to enhanced formation of oxygen vacancies, which is a key step in the oxygen–electron exchange mechanism activated in the presence of the DBD plasma reported in Figure 13 [191]. The CO₂ conversion obtained in these studies is above 70% with 100% selectivity towards methane, with a remarkably low SEI (0.3–4.56 kJ/L) and temperature conditions more favourable than thermal methanation (120–260 °C) [186–188,191,192].

Mikhail et al. [191] suggest an interesting reduction–oxidation cycle that maintains the CO₂ methanation fed by the non-stoichiometric nature of Ni/CZ catalysts, as reproduced in Figure 13d. The metal/support interaction is compared to a P–N junction, which is the interface of two semiconductors, called N-type (electron rich) and P-type (electron deficient), in a single material. With the superposition of an electric field from plasma, the ceria-containing support behaves as electron acceptor, i.e., N-type semiconductor, that releases oxygen to produce OV, and the metallic Ni behaves as a P-type semiconductor, releasing electrons and accepting oxygen from the OV [191]. The flows of electrons and oxygen are maintained with the effect of the electric field established by the plasma and if the catalyst is characterized by good MSI, therefore making a good interaction boundary at the P–N junction. Furthermore, the reduction–oxidation cycle is preserved thanks to the continuous interaction of the surface sites with CO₂ or H₂ species that provide oxygen to the oxygen-deficient Ce³⁺ sites creating carbonates intermediates on the surface and reduce the Ni sites via H₂ dissociative adsorption [191].

As noted previously, a Ni/CeO₂–ZrO₂ catalyst was also tested in a glow discharge and compared with Al₂O₃ and SiO₂ supports [182]. CH₄ formation is observed in glow discharge plasma with Ni catalysts supported on Al₂O₃ and CZ, but Ni/CeO₂–ZrO₂ reaches lower yield due to the poor physicochemical properties of these catalysts such as low surface area and large metal particle size [182]. Furthermore, the plasma was affected by the dielectric constant of the material establishing a negative linear correlation between CO₂ conversion and dielectric constant. CZ possesses the larger dielectric constant among these supports and results in low conversion [182]. Commercial ceria–zirconia mixed oxide was used as support for Cobalt (Co) in DBD reactors adapted for in situ/operando techniques to assess the plasma–catalyst synergy and the reaction mechanism via temperature-programmed plasma surface reaction and DRIFTS [193,194]. Besides Ni, Co nanoparticles on a CZ support can hydrogenate CO₂ in plasma at ambient conditions involving CO as an intermediate [193,194]. Plasma enhances the electron-induced surface reactions and oxygen vacancies formation on Co/CZ. Nevertheless, gas phase reactions also play a relevant role in the conversion of CO₂. In general, two main pathways of plasma–catalytic CO₂ methanation are proposed in the literature: via CO or via formate [182]. The first mechanism involves dissociation thanks to the energy provided by plasma of CO₂ to CO, which is absorbed as surface carbon species and subsequently hydrogenated to form CH₄. The second one involves direct hydrogenation of adsorbed CO₂ to formate as reaction intermediate that stepwise reacts with absorbed hydrogen to form methane. Mechanistic understanding must be further strengthened through operando plasma diagnostics and

surface spectroscopy, which are quite challenging to design and operate but are fundamental to separate gas-phase activation from vacancy-mediated surface pathways and CO/formate-like intermediates.

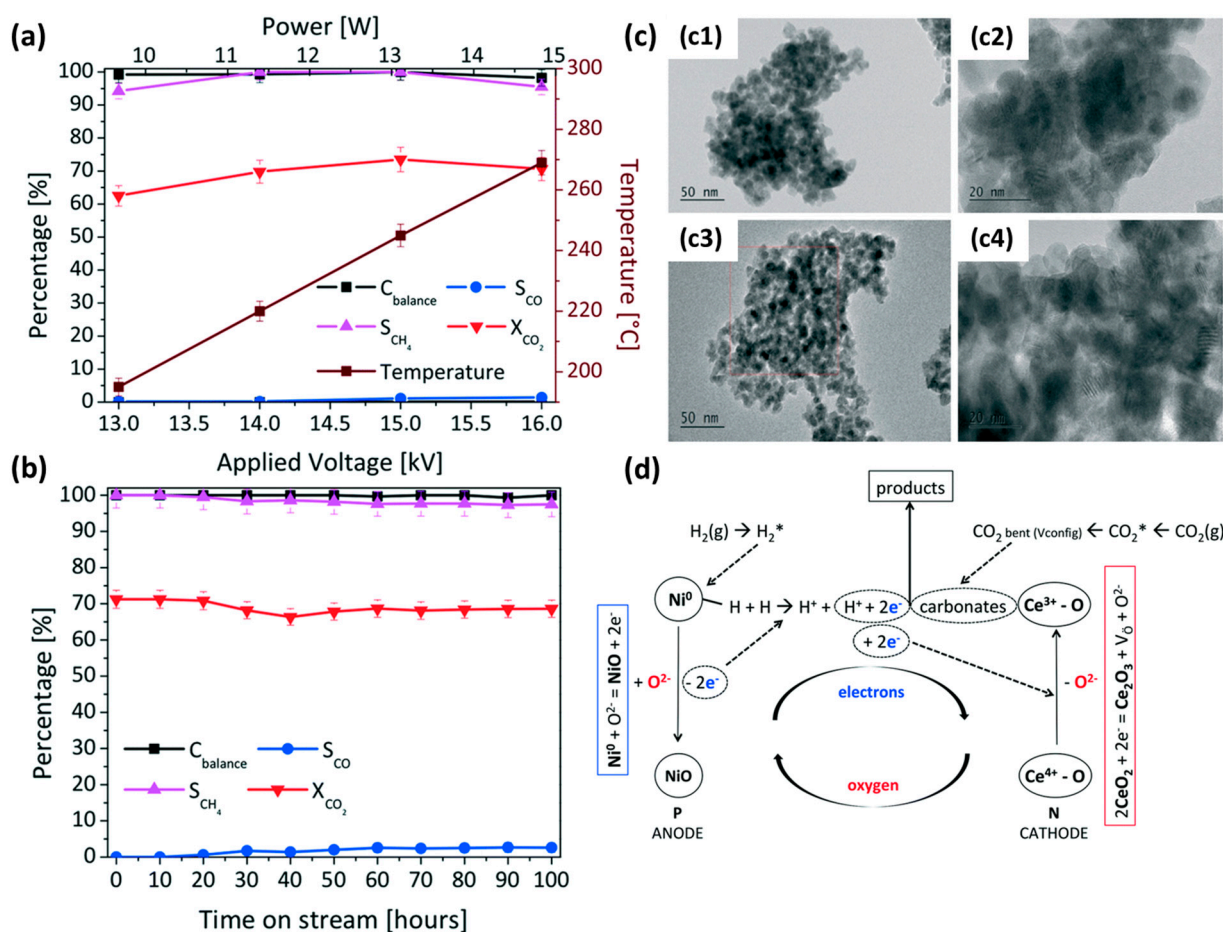


Figure 13. Plasma-catalytic activity of Ni/CZ catalyst (a) at different power and (b) during 100 h time-on-stream. (c) TEM and HR-TEM micrographs of (c1,c2) reduced catalyst and (c3,c4) spent Ni/CZ after plasma-assisted methanation. (d) Proposed plasma-assisted reaction mechanism on ceria-containing Ni catalysts (* refers to plasma excited species). Reproduced from [191] with permission from the Royal Society of Chemistry.

The effect of addition of promoters (Co, Y, Na, Ga...) to Ni catalyst supported on commercial ceria and CZ for plasma-assisted CO_2 methanation has also been investigated [189,190,195,196]. The inclusion of 1%wt. of Co and Y as promoters has positive effects on the activity. The wet impregnation of Co is linked with improved surface basicity, which is promoting the thermal and plasma-assisted CO_2 methanation [195]. Guo et al. obtained the Y-doped Ni/CeO₂ via mechanochemical synthesis and compared different amounts of Ni and Y [196]. The 50% CO_2 conversion reached at SEI 13 kJ/L with the 7.5%Ni/CeO₂ catalyst is improved to 65% with the optimal addition of 1%wt. Y [196]. Y improves the basicity and oxygen vacancy concentration on the surface of the catalyst, which are beneficial for CO_2 activation [196]. Mikhail and co-workers considered the influence of different promoters, namely Cu, La, Y, Mn, Gd, Sr, Co, Na, and K, observing enhanced performance for Gd-containing Ni/Ce_{0.58}Zr_{0.42}O₂ and the detrimental effect of K and Na [189,190]. The dielectric properties of the catalyst were related to the catalytic activity since, together with physicochemical properties, they strongly influence the characteristics of the plasma discharge catalysts [190].

Cerium oxide has been in turn employed as a promoter, resulting in enhanced activity of Ni supported on Al_2O_3 and zeolites in DBD plasma (reported in the last rows of Table 4) [197–199]. The amount of CeO_2 varied from 0 to 50%wt., and it was found that for the plasma-assisted reaction, the optimal amount is 10%wt., while for thermal methanation, a higher quantity (40%wt.) is required for an enhanced methane yield as ceria promotes the CO_2 adsorption and activation on the catalyst surface [198]. The performance of a catalyst with similar Ni-Ce composition (15%Ni/30%Ce) impregnated on a macrostructured Al_2O_3 support has been improved by the plasma reactor design [199]. The authors used a thermally insulated DBD reactor and utilized the plasma to ignite the methanation reaction, which was later self-sustained for up to 8 h by the exothermicity of the reaction [199]. The addition of 20%wt. Ce on Ni/Cs-USY(38) had a decisive positive effect on the performance of the catalyst in thermal and plasma-assisted CO_2 methanation (especially below the maximum power 20–30 W) [197]. Such catalyst enhancement is linked with the favorable activation of CO_2 on the cerium oxide surface sites, improvement of the Ni dispersion and increase of the dielectric constant of zeolite-based catalyst (dielectric constant 1.5–5) with the addition of CeO_2 (dielectric constant 24) [197].

The synergy between NTPs and CeO_2 -based catalysts for efficient CO_2 conversion to methane was shown by the reported publications. Several factors, such as plasma reactor design, GHSV, and presence of promoters, impact the activity of the plasma-catalytic methanation, but the CeO_2 tendency of oxygen vacancies formation, either as pure cerium oxide or in solid solution with Zr, proved beneficial for the efficiency and mechanism of the reaction in plasma.

Table 4. Key Parameters and Performance of CeO₂-Containing Catalysts for Plasma-assisted CO₂ Methanation in DBD * NTP Reactors.

Catalyst	Plasma Conditions		Gas Feed Conditions		Plasma-Catalytic Results				Ref.
	V (kV)	f (kHz)	Composition	GHSV	SEI (kJ/L)	CH ₄ Selectivity (%)	CO ₂ Conversion (%)	Bed Temperature (°C)	
15%wt. Ni/CeO ₂	45–47	7.5	CO ₂ /H ₂ 1:4	45 L g ^{−1} h ^{−1}	18	95	85.7	300	[183]
15%wt. Ni/CeO ₂ nanoneedles	22–25	12.3	CO ₂ /H ₂ 1:4	30 L g ^{−1} h ^{−1}	16.3	99.7	83.3	158	[184]
5%mol.Ru/CeO ₂ nanoneedles	12–24	26	CO ₂ /H ₂ 1:4	30 L g ^{−1} h ^{−1}	10.6	99	69	100	[185]
15%wt. Ni/Ce _{0.58} Zr _{0.42} O ₂	14–18	40	CO ₂ /H ₂ 1:4	42,720 h ^{−1}	3.126	100	71.2	260	[192]
15%wt. Ni/Ce _{0.58} Zr _{0.42} O ₂	13–16	70	CO ₂ /H ₂ 1:4	44,000 h ^{−1}	3.9	100	73	240	[191]
15%wt. Ni/Ce _{0.58} Zr _{0.42} O ₂	10–15	40	CO ₂ /H ₂ 1:4	50,000 h ^{−1}	0.3–0.9	100	80	270	[187]
15%wt. Ni/Ce _{0.58} Zr _{0.42} O ₂	13–18	40	CO ₂ /H ₂ 1:4	20,000 h ^{−1}	1.11	100	73	120–170	[186]
15%wt. Ni/Ce _{0.58} Zr _{0.42} O ₂	19	41	CO ₂ /H ₂ 1:4	46,300 h ^{−1}	4.56	100	79	220	[188]
15%wt. Ni/1%wt. Co/CeO ₂	25–29	12.3	CO ₂ /H ₂ 1:4	52,000 h ^{−1}	4.95	98	75	158	[195]
7.5%wt. Ni/ 1%wt. Y/CeO ₂	10	7.7	CO ₂ /H ₂ 1:4 + 25%vol Ar		18	83	84	<100	[196]
15%wt. Ni/ 2%wt. Na/Ce _{0.58} Zr _{0.42} O ₂	13–16	70	CO ₂ /H ₂ 1:4	44,000 h ^{−1}	6.42	75.9	57.5	272	[189]
15%wt. Ni/ 4%wt.Gd/Ce _{0.58} Zr _{0.42} O ₂	12–15	70	CO ₂ /H ₂ 1:4	44,000 h ^{−1}	2.25	99.8	84.9	249	[190]
4%wt. Ni/CeO ₂ -ZrO ₂	2 *	50 *	CO ₂ /H ₂ 1:4 + 50% Ar	360,000 h ^{−1}			25	RT	[182]
5%wt. Co/CeZrO ₄	20	1	CO ₂ /H ₂ 1:4		30.6	100	80	200	[194]
10%wt. Co/CeZrO ₄	18	1	CO ₂ /H ₂ 1:4		30.6	98	75	150	[193]
15%wt. Ni/ 10%wt. CeO ₂ /Al ₂ O ₃	4–15	54	CO ₂ /H ₂ 1:4	40,000 h ^{−1}	8.1	98	75	150	[198]
15%wt. Ni/ 30%wt. CeO ₂ /Al ₂ O ₃	4–9	52	CO ₂ /H ₂ 1:4	13,333 h ^{−1}	3	100	84	360	[199]
15%wt. Ni/ 20%wt. CeO ₂ /Cs-USY(38)	5–6	42	CO ₂ /H ₂ 1:4	32,000 h ^{−1}	10.5	>95	75	170	[197]

Except * Glow Discharge.

4. Challenges and Future Prospects

CeO₂-based catalysts have attracted considerable attention for CO₂ methanation due to their remarkable oxygen storage capacity, redox flexibility, and ability to stabilize highly dispersed metal nanoparticles. Despite significant progress across thermally driven, photothermal, electrocatalytic, and plasma-assisted processes, several fundamental and technological challenges still hinder their large-scale implementation.

Future developments in CeO₂-based catalysts for CO₂ methanation should focus on translating the excellent low-temperature activity and methane selectivity observed in powder catalysts into robust, scalable, and thermally managed reactor architectures. The most promising strategies include defect-engineered CeO₂ nanostructures, CeO₂-ZrO₂ and multi-doped solid solutions, controlled plasma or thermal pre-treatments, and structured supports such as foams, monoliths, core-shell systems, and thermally conductive substrates that can mitigate hot spots in this highly exothermic reaction. However, several challenges remain unresolved, including the precise quantification of active oxygen vacancies under reaction conditions, the prevention of metal sintering or excessive encapsulation by strong metal-support interaction, the long-term stability of doped or structured materials under dynamic operation, and the development of synthesis methods that are reproducible at scale. Future studies should therefore combine operando spectroscopy, isotopic tracing, transient kinetic analysis, and realistic reactor testing to distinguish true active-site effects from apparent improvements caused by heat and mass transfer. In this context, CeO₂ will remain a strategic platform for CO₂ methanation, but its practical impact will depend on integrating defect chemistry, interfacial catalysis, thermal management, and catalyst shaping into durable systems compatible with fluctuating renewable H₂ and industrial CO₂ utilization.

In photothermal methanation, the key challenge is separating true photocatalytic contributions from purely thermal effects induced by light absorption. The relatively poor visible-light absorption of CeO₂ necessitates coupling with plasmonic or photothermally active components. Moreover, catalytic performance is highly sensitive to the engineering of CeO₂-metal interfaces, where vacancy formation and SMSI must be finely tuned. Future studies should focus on optimizing light power density and wavelength to precisely tune catalytic conversion and selectivity. Advances in engineering CeO₂-metal interfaces are essential, particularly to enhance oxygen vacancy formation, stabilize active sites, and control SMSI through strategies such as pre-reduction treatments. Additionally, selecting metals and supports with strong photothermal responses, including Au and Ru or MOF-derived structures, can boost light absorption and heat generation. Finally, rigorous differentiation between thermal and non-thermal effects under visible-NIR irradiation in continuous flow systems will be critical to validate and scale efficient Ce-based photothermal CO₂ methanation technologies.

Electrocatalytic CO₂ methanation over CeO₂-supported catalysts is presented in a limited number of works and is largely limited to Cu-based systems, which suffer from low CH₄ selectivity and high overpotentials. Critical challenges include stabilizing key intermediates and suppressing competing hydrogen evolution. Future research should expand to alternative metals and bimetallic systems, combined with precise control over particle size and crystallographic facets. Integrating computational modeling with advanced synthesis could accelerate the rational design of efficient catalysts with improved selectivity and durability.

In plasma-catalytic systems, the interaction between CeO₂ surfaces and non-equilibrium plasma species introduces additional complexity. The most critical challenges remain energy efficiency, SEI minimization, and reactor thermal management. Scale-up will require coupling catalyst durability, plasma uniformity, and standardized performance

metrics into reactor designs that can move beyond laboratory demonstrations. Future progress should prioritize rational design of ceria-containing catalytic systems as nanostructure, dielectric behavior, OV formation, and metal and promoter chemistry govern plasma–catalyst synergy.

Overall, the future of CeO₂-based CO₂ methanation relies on integrating defect chemistry, interfacial engineering, and reactor design into robust, scalable systems compatible with dynamic renewable energy inputs.

5. Conclusions

This review has examined the most recent advances in CO₂ methanation using CeO₂ as catalyst support, promoter, and active component. The study of CO₂ methanation is supported on the urgency of efficient CO₂ valorisation and the relevance of methanation in Power-to-Gas schemes, while the distinctive chemical properties of CeO₂ clearly establish it as one of the most adaptable and effective components for CH₄ synthesis from CO₂. As discussed, the combination of high oxygen storage capacity, facile Ce⁴⁺/Ce³⁺ redox cycling, and abundant oxygen vacancy formation provides CeO₂ with an exceptional ability to activate CO₂ and enhance hydrogenation pathways. Moreover, its tuneable defect chemistry and structural robustness under harsh reaction environments further emphasize its technological relevance for large-scale catalytic deployment. The aim of this review—to evaluate CeO₂ across thermal, photothermal, electrochemical, and plasma-assisted reaction environments—has been fulfilled by analysing both conventional and advanced activation strategies.

In thermal methanation, CeO₂-supported metal catalysts (especially Ni- and Ru-based) consistently deliver high CO₂ conversion exceeding 80%, whether commercial or synthesized ceria is used, with a high CH₄ selectivity yield by highly dispersed active metals (notably Ni, Ru, or Cu for electrochemical systems). The wide range of available synthesis methods—including templating, sol–gel, precipitation, hydrothermal/solvothermal routes, flame spray pyrolysis, and combustion—offers fine control over ceria morphology, surface area, and defect density, all of which directly affect catalytic performance. Likewise, the diversity of pre-treatments (oxidative, reductive, inert, or plasma-based) reflects the need to adjust oxygen vacancy concentration, metal dispersion, and reducibility to meet different reaction conditions. Beyond pure ceria, doped CeO₂ formulations have shown that introducing aliovalent elements can substantially enhance stability and vacancy formation, while mixed oxides, including CeO₂–Y₂O₃ systems, display synergistic effects on the performance of Ni-based catalysts. Cerium as a promoter further broadens its applicability by improving dispersion, redox behaviour, and metal–support interactions in catalytic systems. Progress in structured catalysts demonstrates the potential of CeO₂-based coatings on metallic and ceramic substrates to offer superior mass and heat transfer, reduced pressure drop, and improved temperature control under dynamic operation.

In advanced CO₂ methanation, CeO₂ continues to reveal distinctive advantages. In photothermal catalysis, Ce-based materials benefit from charge separation, enhance light absorption, temperature rise through non-radiative dissipation, and dynamic formation of vacancies under illumination. Future work should focus on optimizing power density and wavelength, engineering CeO₂–metal interfaces with enhanced SMSI, and rigorously differentiating thermal from photophysical effects in continuous-flow reactors. In electrocatalytic CO₂ reduction, the field remains underexplored, with most studies limited to Cu/CeO₂ systems; however, ceria’s capacity to tune metal–support interactions and stabilize intermediates indicates considerable potential for designing next-generation catalysts for CH₄ and C₂⁺ products. Broadening the range of supported metals, controlling particle size and exposed facets, and integrating computational modelling will be essential for

advancing the field. In plasma-assisted methanation, existing studies clearly show a beneficial synergy between CeO₂ and non-thermal plasmas, largely due to ceria's capacity to form oxygen vacancies and OSC even under mild energetic conditions. Reactor design, gas hourly space velocity, and promoter selection remain decisive parameters, but across the literature, ceria consistently enhances CO₂ activation and guides plasma-driven reaction pathways.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

The following abbreviations are used in this manuscript:

CCSU	Carbon Capture, Storage and Utilization
CCU	Carbon Capture and Utilization
CRR	CO ₂ reduction reaction
CZ	Ceria-Zirconia
DBD	Dielectric barrier discharge
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
EXAFS	Extended X-ray Absorption Fine Structure
FE _{CH4}	Faradaic efficiency to methane
FSP	Flame spray pyrolysis
GDE	Gas diffusion electrode
GHSV	Gas hour space velocity
HER	Hydrogen evolution reaction
LRC	Low-rank coal
LSPR	Localized surface plasmon resonance
MEA	Membrane electrode assembly
MK	Metakaolin
MOF	Metal–organic framework
MSI	Metal-support interaction
NC	Nanocube
NO	Nanooctahedron
NP	Nanopolyhedra
NPI	Nanoplate
NR	Nanorod
NTP	Non-thermal Plasma
OSC	Oxygen storage capacity
OV	Oxygen vacancy
PCET	Proton-coupled electron transfer

RES	Renewable energy sources
RWGS	Reverse water gas shift
S _{CH4}	CH ₄ Selectivity
SEI	Specific energy input
SMSI	Strong Metal-support interaction
TOF _{CO2}	Turnover frequency of CO ₂
TPD	Temperature-programmed desorption
TPR	Temperature-programmed reduction
WHSV	Weight hour space velocity
X _{CO2}	CO ₂ Conversion
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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