# A short review on informetric analysis and recent progress on contribution of ceria in Ni-based catalysts for enhanced catalytic CO methanation.

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## Abstract

Energy demand is rising, and the exhaustion of accessible energy sources is currently the greatest challenge. CO methanation has become a crucial reaction for the substituted natural gas production, necessitating a catalyst. Ceria is amongst the most extensively utilized metal oxides owing to its abundance of oxygen vacancies. Despite substantial study on CO methanation, no paper evaluates the impact of ceria in Ni-based catalysts for CO methanation. Hence, we have provided a bibliographic analysis and recent progress on contribution of ceria in Ni-based catalysts for enhanced catalytic CO methanation. This article shows the findings of an informetric investigation of CO methanation conducted between year 1970 and 2022 by examining data from 156 sources and 585 publications. Information regarding the relationships amongst keywords, countries, and journals, an intercountry co-authorship network analysis, and a conception of the co-occurrence network were supplied. Our review concludes with technical challenges and suggestions for future research.

***Keywords:*** CO methanation; Ceria; $CeO_2$; Informetric Analysis.

## 1.0 Introduction

The need for energy on a global scale is growing rapidly. The exhaustion of available energy sources is currently the most difficult challenge facing the world. Methane, which makes up the majority of natural gas, has a significant amount of potential for use in industrial settings as a result of its high heat of combustion (55.70 kJ/g), which is significantly superior to that of coal (39.30 kJ/g) and fossil oil (43.60 kJ/g). Since the ratio of hydrogen to carbon in methane is large, its combustion results in reduced emissions of $CO_2$; 50% less than those produced by coal and 30% less than those produced by fossil oil. As a result, natural gas will serve as the primary energy source of the future, displacing coal and oil.

Carbon monoxide (CO) methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$) is a reaction concerning the generation of substituted natural gas (SNG), and the removal of trace carbon monoxide from a hydrogen stream for fuel cells, has piqued the scientific and industrial interests of many researchers. The majority of the temperatures that have been documented for CO methanation fall somewhere between 300 and 450 °C. High temperatures cause the fast sintering of metal particles and the deposition of carbon. At a low reaction temperature, however, the aggregation of the active species and the byproducts of the side reaction can be reduced. Therefore, it is vital to create catalysts for the hydrogenation of CO that are very efficient, stable and can perform at low temperature.

Rare earth oxide ceria, also known as $CeO_2$, is one of the most broadly used metal oxides and finds widespread application in a variety of industries. These fields include fuel cells, the dry reforming of methane, and photocatalytic reaction. $CeO_2$ is recognized as a promising catalyst in CO methanation, according to recent reports written by a large number of researchers. This is because $CeO_2$ has high oxygen storage capacities and abundant oxygen vacancies, both of which are caused by reversible $Ce^{3+}/Ce^{4+}$ pairs. These vacancies can significantly upsurge the rate of reaction by adsorbing carbon oxides and activate the carbon-oxygen bond. $CeO_2$ by itself, however, is not enough because it merely assists the CO adsorption. Because of this, there are limitations placed on the use of $CeO_2$. The usage of $CeO_2$ could be improved through the application of several approaches, such as the deposition of noble or transition metals, the coupling of $CeO_2$ with other supports, or the use of transition metals.

Few review papers have been issued on CO methanation [1-7] but regardless of much research on CO methanation, there is no study that specifies a full evaluation on contribution of ceria in Ni-based catalysts for enhanced catalytic CO methanation. Motivated by these, herein, we summarized the recent progress on contribution of ceria in Ni-based catalysts for enhanced catalytic CO methanation. Moreover, a concise informetric analysis of the research that has been done in the field has been offered. An overview of the most significant CO methanation-related points of importance discovered in the search findings is presented in Table 1. Nevertheless, despite the fact that formerly available articles on the subject have consciously addressed several trending topics, this article offers a comprehensive analysis of the state-of-the-art informetric investigation together with the recent advancements in ceria-based catalysts for the generation of $CH_4$ through CO methanation. Web of Science, which is currently regarded as the most dependable search resource, was used to compile a summary of the subject's search results, and informetric studies were performed based on the gathered information.

Findings of an informetric study between year 1970 and 2022 using the VOSviewer and Biblioshiny in Rstudio to analyze a Web of Science for keywords, countries, and publications along with inter-country, co-author associations and co-occurrence visualizations are presented. Search results for "CO methanation" in the title of a research publication were summarized in Table 1 based on the most frequently cited research articles.

Table 1. Summary of the most cited articles in the field.

| **Article highlight** | **Year** | **Refs.** |
|---|---|---|
| • Density functional theory computations; extreme-high vacuum experiments; CO dissociation mechanisms on nickel exteriors. | 2008 | [8] |
| • Associative and dissociative methanation mechanisms. Catalyst deactivation; sulphur poisoning, deposition of carbon and sintering of metal. | 2016 | [7] |
| • Modifying a number of factors, such as the different commercial $Al_2O_3$ supports, the loading of NiO and MgO, the calcine temperature, the gas hourly space velocity, the ratio of $H_2$:CO, the pressure, and the duration of the process. | 2012 | [9] |
| • Extensive research is being conducted with the goal of improving the efficiency of the catalyst. Both 25Fe75Ni and 50Fe50Ni exhibited much higher levels of activity and selectivity with regard to methane. | 2007 | [10] |
| • The catalytic capability of noble metal (Ru, Rh, Pt, Pd) loaded onto $Al_2O_3$ catalysts for the carbon oxides methanation and their mixture has been investigated. | 2008 | [11] |
| • Ruthenium catalysts have been designed for the selective CO methanation in the existence of abundant $CO_2$. The methane selectivity increases with temperature. Long-standing stability experiments demonstrate that the 5% Ru loaded onto $TiO_2$ catalyst is extremely stable. | 2009 | [12] |
| • CO dissociation rate at the surface of the catalyst was calculated assuming that 5% of the surface nickel atoms were active for dissociation of C-O. | 2005 | [13] |
| • Methanation of carbon dioxide and carbon monoxide using Ru loaded onto zeolite and $Al_2O_3$ catalysts in idealised and carbon dioxide reformate gases was studied. | 2011 | [14] |
| • CO methanation over a $5Ru/TiO_2$ catalyst was investigated. With a rise in temperature from 25 to 200 °C, the total of adsorbed hydrogen rises by a factor of two, primarily due to hydrogen atom migration from metal to support. | 2011 | [15] |

|  |  |  |
|---|---|---|
| • Carbon oxides methanation over Ni-supported ($Al_2O_3$, $SiO_2$, $TiO_2$, $CeO_2$, and $ZrO_2$) catalysts was studied. Most active was $Ni/CeO_2$. $CeO_2$ surface area increases catalytic activity. Significant Ni dispersion and robust CO and $CO_2$ adsorption accounted for high CO and $CO_2$ methanation catalytic activity. | 2017 | [16] |
| • Informetric studies on CO methanation, current developments of ceria-based catalysts, oxygen vacancies, basicity, durability, regeneration, challenges, suggestion, and prospects. | 2022 | Current study |

## 2.0 Informetric Analysis

An informetric assessment is a methodical investigation of a considerable quantity of journals published in a particular study area. This type of investigation yields information that is as up-to-date and provide knowledge regarding bibliographic link, co-citation analysis, co-authorship networks, scientific movements, and the evolution of developing areas over the course of time, in addition to knowledge regarding the growth of new fields. This study scrutinizes the furthermost frequently mentioned articles, the furthermost recurrently utilized keywords, the progression of articles published over time, and the co-authorship association using the software VOSviewer and Rstudio. It is a data analytic evaluation of available publications and quantitatively illustrates the interconnections amongst papers that relate to a specific scientific subject or area by analyzing the number of occasions they have been co-cited by other released articles, especially with regard to the similar topic or area. The search methodology and strategy involved screening and analyzing the findings of the most-cited articles, significant institutions, and referenced journals.

Since the CO methanation process is currently an important focal area in environmental, energy, and fuel research, the fact that there are a lot of publications devoted to it should not come as much of a surprise. Figure 1 depicts, on average, the terms retrieved from CO methanation with the highest frequency of occurrence. The most pertinent clumps (where the visualization of density is centered) are the red, green, blue, and yellow clumps.

The furthermost relevant keyword has occurrences (links strength) as follows; hydrogenation 144 (817), carbon-monoxide 136 (787), performance 120 (699), carbon-dioxide 95 (525), nickel 76 (456), Ni/$Al_2O_3$ catalysts 59 (386), gas 63 (357), oxidation 59 (356), adsorption 53 (330), and synthetic natural gas 56 (323). All of these keywords in the figure indicated that the research on the CO methanation reaction was appropriately developed. Particularly, significant effort has been devoted (and continues to be devoted) to the production of synthetic natural gas due to its enormous energy generation potential.

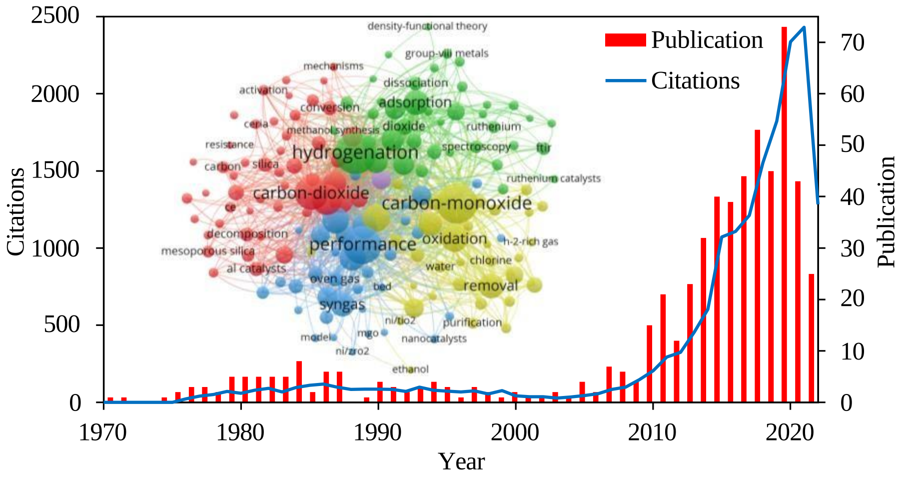

Figure 1 Citation and publication report on CO methanation from 1970 to 2022, scrutinized from Web of Science with the keywords “CO methanation”.

Figure 1 also illustrates the amount of citations and publications on CO methanation reported to the Web of Science data repository. As demonstrated by the rise in the amount of publications produced annually in the field, the trend implies that the issue is becoming increasingly popular for this specific scientific study. Consequently, the quantity of citations climbed at a rate of 7.26% per year. More than 2,300 publications in 2020; as of July 2022, there have been more than 1,200 publications. The absence of correlation in terms of publications and citations between the early 1900s and the 2000s implies that the study field was not adequately explored until around 2010. Consequently, the annual number of publications and citations increased by several hundreds. CO methanation has arisen as a realistic option as the global need to investigate alternate energy sources, such as synthetic natural gas, has become more pressing due to the exhaustion of fossil fuel resources. The data were extracted from 156 sources (journals, books, etc.) and 585 publications, 502 of which were published research papers (average of 29.37 citations per papers), 5 review articles, and 34 proceedings. Figure 2 show the three-field plot analysis of the authors linkage to their country and keywords. It can be comprehended that the country with the utmost amount of collaborations is China, followed by Germany, Korea and Japan. There is ample mention of keywords such like CO methanation, methanation, $CO_2$ methanation, CO, nickel, selective CO methanation, selective methanation, carbon monoxide, and CO removal when analyzing the keywords (right side of the figure).

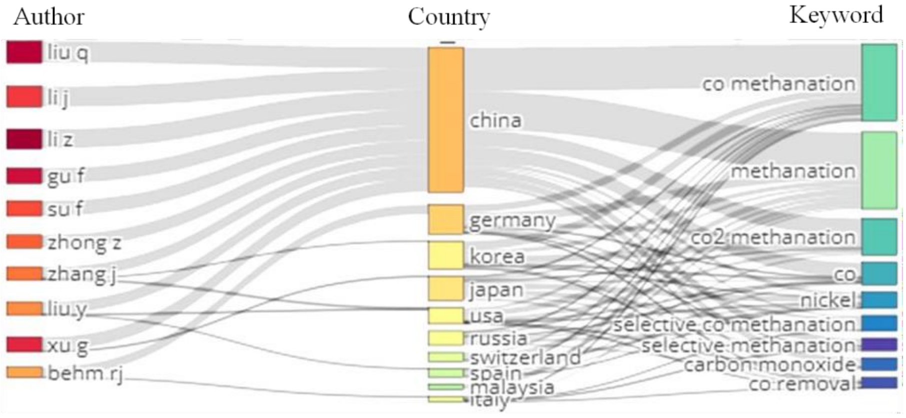

Figure 2 A three-field plot scrutinized from the Web of Science database displaying the authors (left), author's countries (middle), and the keywords (right).

To visualize research collaborations and the potential synergies between countries, we created the collaboration network figure as shown on Figure 3. China has the biggest total strength, and its main partners are the United Kingdom followed by Switzerland and

Singapore in collaboration. In another cluster, three countries with almost have the same strength intensity which are Germany, Denmark and Slovenia collaborate with each other frequently as they have closest distance between each other.

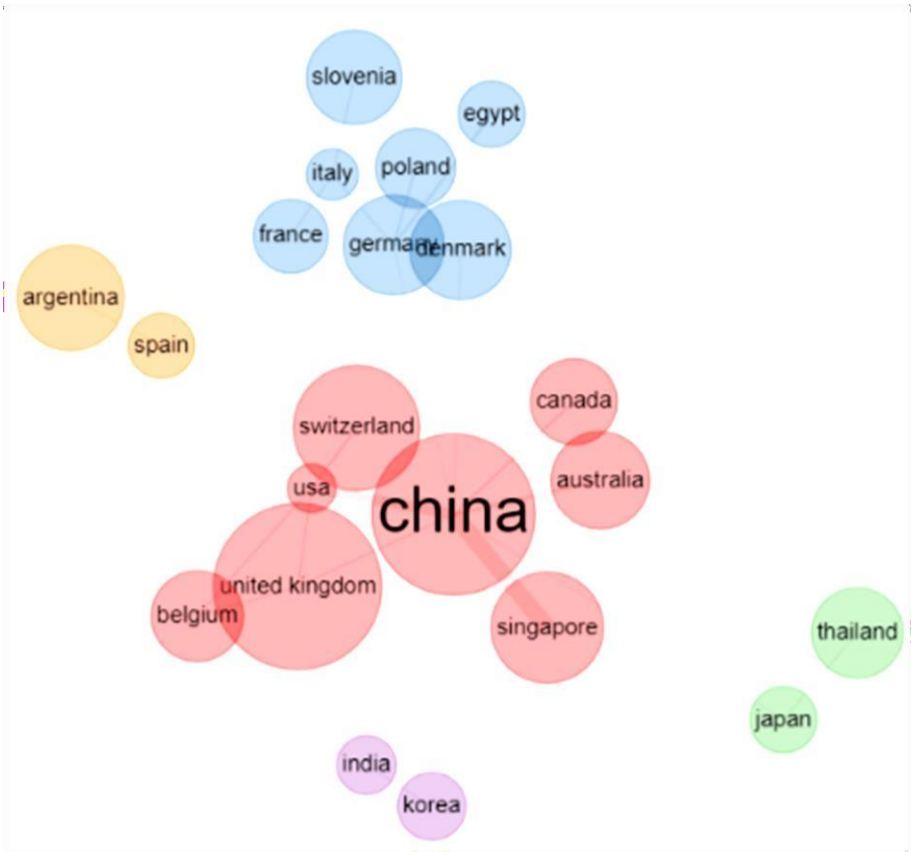

Figure 3 Countries collaboration network dissected from Web of Science databases.

The frequency and strength of CO methanation-related keywords taken from the Web of Science literature to conclude their frequency and connection intensity. Figure 4 is a word cloud displaying the keywords that were determined to be the furthermost important in the CO methanation. The magnitude of each word demonstrates the significance of each term, as well as its frequency in the literature and relevancy to the topic. Performance, nickel, carbon-monoxide, synthetic natural gas, nanoparticles, hydrocarbons are several of the significant catchphrases to be reminisce. A considerable quantity of aspect has been put into the investigation of nickel-based catalyst, alumina-based catalyst, and CO removal from $H_2$-rich stream; however, additional work is needed o the keywords that are not mentioned here such as the usage of other supports such as $CeO_2$, $TiO_2$, $SiO_2$, CO methanation mechanism and the low temperature reaction. The proximity of the keywords indicates the extent to which they are associated and interconnected.

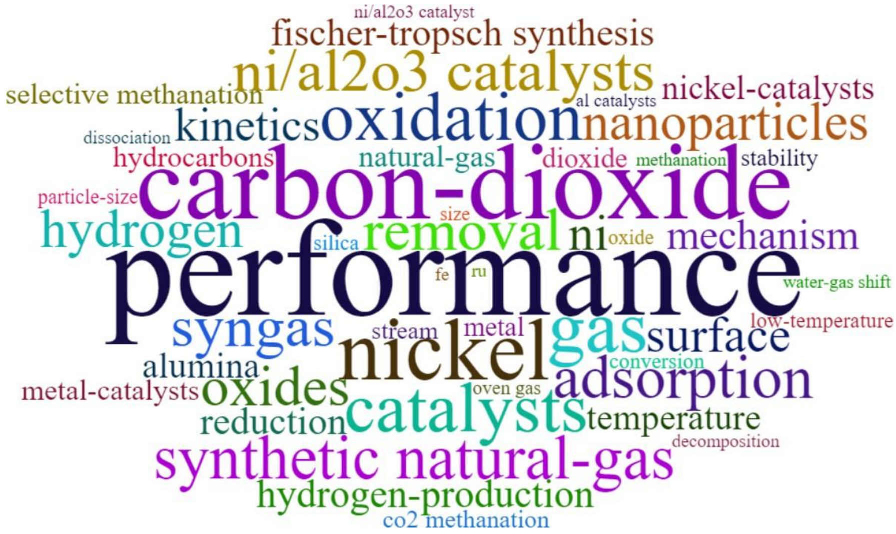

Figure 4 Word cluster presenting the "keywords" that were found to appear the most frequently in the Web of Science database.

The co-occurrence network investigation was then demonstrated in Figure 5 to exemplify the causation model diagram to picture the connection associated between keywords. In this figure, two colors which is blue and red signify the year where the keywords were most used which the blue represent early 2012 while the red represent late 2022 and the color gradiently change from blue to red. The size of word and circle also signify the frequencies of the essential term appears, which if the keyword appears more, the larger the circle develops. Conversely, a reduced gap between them indicates a high frequency of co-occurrences between two terms.

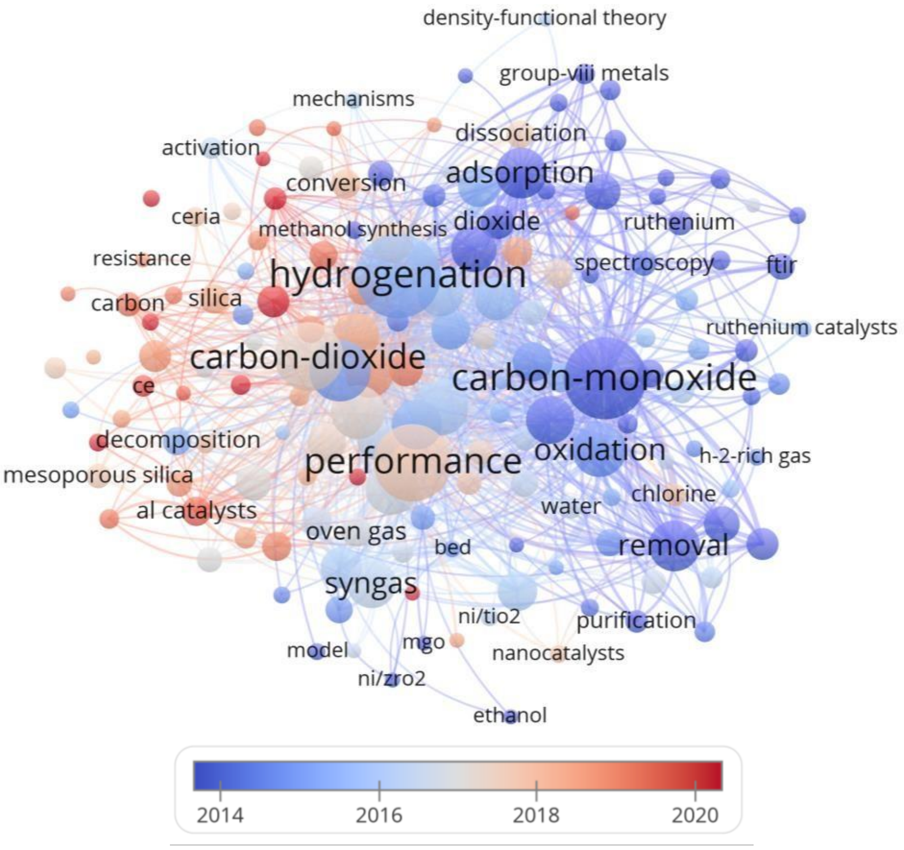

Figure 5 Network visualization of keyword used in publications, scrutinized from the from Web of Science (Blue → Red exemplifies Old → Recent).

Hydrogenation, carbon monoxide, carbon monoxide, and performance are the four major keywords with the highest measured overall connection strengths. Each of these terms is the most closely interrelated keyword in the cluster. The clusters are interrelated, exhibiting the complementary characteristics of distinct CO methanation research subjects. Towards the other hand, density-functional theory, modelling, mesoporous silica, mechanisms, and ceria were found on the peripheral, indicating a inferior frequency and interactivity compared to other clumps. According to the findings of the analysis presented above, ceria is one of the new trend topics nowadays as the color is red and two keyword relating to ceria were there which is “ceria” and “Ce”. While it is a new trend, there is a lack of research in the usage of ceria catalyst. As a result, it is essential to explore and analyzes the prospect of using ceria as a CO methanation catalysts.

## 3.0 Current developments on contribution of ceria in Ni-based catalysts

### *3.1 Ceria as a support and promoter*

Numerous papers attest that much effort has been expended over the past few decades to produce thermally stable methanation catalysts with high activity at low temperatures. Several metal oxides support have been testified for CO methanation reactions, such as $Al_2O_3$, $CeO_2$, $SiO_2$, $ZrO_2$, $TiO_2$, and $La_2O_3$. $CeO_2$ is well-established support owing to its redox characteristics and large oxygen vacancies on its surface. Mainly, two oxidation states of cerium (such as $Ce^{3+}$ and $Ce^{4+}$) are interconvertible between $CeO_2$ and $CeO_{2-x}$ in oxidized and reduced environments to liberate oxygen vacancy. In the dissociative CO methanation mechanisms, this ability is advantageous for dissociating CO into C and O species on the catalyst surface. Another prominent carbon monoxide methanation process is the associative pathway, in which chemisorbed carbon monoxide and chemisorbed $H_2$ are located on the surface of the support and the active sites.

Nickel has long been the most widely utilized transition metal catalyst for $CH_4$ generation due to its high activity, low cost, and access availability. However, carbon monoxide methanation on nickel-based catalysts is frequently hindered by inadequate stability and performance, especially at elevated temperature because of sintering and carbon deposition. Numerous efforts have been made to answer the problems mentioned earlier, including using supports with a substantial surface area and porosity or introducing additional positive attributes, such as high basicity and an extraordinary number of oxygen vacancies.

The incorporation of rare earth elements into nickel-based catalysts might modulate the development of NiO, henceforth regulating the microstructure of the active components. Notably, it is also envisaged that the incorporation of rare earth promoters will increase the rate of reaction of low-temperature CO methanation processes, henceforward preventing the sintering of metal elements and carbon deposition caused by elevated temperatures.

$CeO_2$ has been discovered as viable support and promoter for methanation, particularly for CO conversion, accredited to its oxidation-reduction characteristics and exceptional oxygen retaining capabilities, which limit the likelihood of carbon deposition. For instance, Zeng et al. (2015) [17] designed the Ce-Ni/$Al_2O_3$, in which the exchange of $Ce^{3+}/Ce^{4+}$ redox pair concentrates electrons on active sites and facilitates the C and O separation, resulting in high-temperature carbon deposition resistance.

Significant initiatives have been tried to enhance the substantial characteristics that influence the capabilities of $CeO_2$, such as particle's size, size distribution, and shape. Ni particle sizes also can be tune by the inclusion of $CeO_2$. Atzori et al. (2019) [18] synthesised NiO-$CeO_2$-$ZrO_2$ with narrow mesopores and discovered that NiO was distributed in the form of tiny crystallites on the $CeO_2$-$ZrO_2$ supports and that its reducibility improved with the Ce concentration owing to the anchoring effect of Ce species. Fu et al. (2015) [19] investigated how the presence of Ce affected the characteristics and performance of Ni/$SiO_2$. All Ce-containing catalysts exhibited high durability at elevated temperatures up to 60 hours, ascribed to the existence of well-scattered Ni crystallites due to an intense Ce species anchoring effect and an increase in surface oxygen species. Zyryanova et al. (2014) [20] completed extensive research on selective CO methanation in $H_2$-rich gas and confirmed that tiny nickel-containing ceria-supported particles exhibited excellent activity, limiting the CO concentration in the reformate gas to less than 10 ppm over the broadest temperature range of 250–320 °C.

Figure 6 shows XPS spectra of Ni 2p which were studied by Liu et al. (2018) [21]. Ni0 species are responsible for the Ni $2p_{3/2}$ peak of a reduced catalyst at 853.0 eV, while nickel oxide states ($Ni^{2+}$) are responsible for the Ni $2p_{3/2}$ main peak at 855.8 eV and a shake-up satellite peak at 861.5 eV. $Ni^{2+}$ is made when some of the metal Ni on the surface is partially oxidised. The binding energy of Ni $2p_{3/2}$ was 856.1 eV in $10Ni/Al_2O_3$, which was close to the binding energy of $NiAl_2O_4$ spinel (856.2 eV), showing that the interaction between Ni species and $Al_2O_3$ was extremely strong. In a proposed 7Ce-10Ni/SiC catalyst, the binding energies of $Ni2p^{3/2}$ are a little lower than in 10Ni/SiC. These modifications demonstrate that $CeO_2$ species is an electron promoter in 7Ce-10Ni/SiC for CO methanation and increased the interaction between Ni and SiC, hence boosting the electronic density of nickel active species on the catalyst surface.

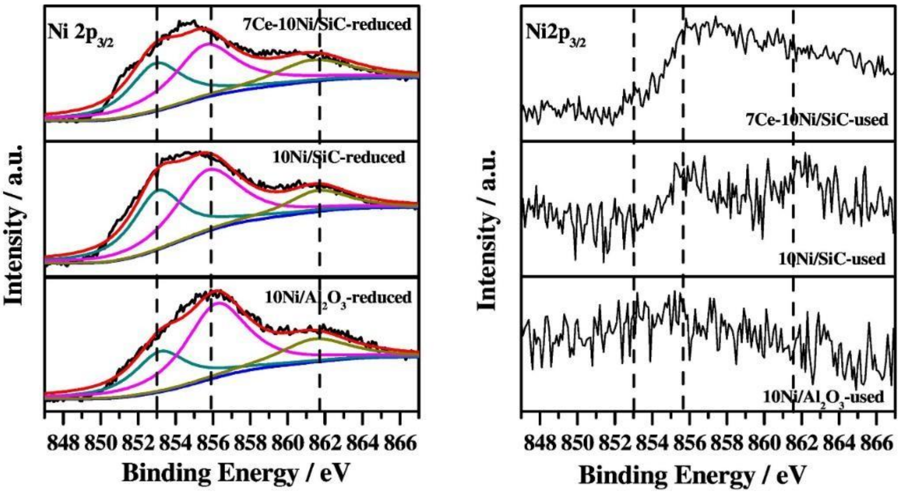

Figure 6 Ni $2p_{3/2}$ XPS spectra for the (a) reduced and (b) used catalyst. Adapted from Liu et al. (2018) [21].

Another study, conducted by Nematoliahi et al. (2015) [22], discovered that the $Ni/CeO_2$ catalyst containing 50% nickel demonstrated exceptional activity in CO methanation. The catalyst's high specific surface area, tiny nickel particle size (below 5 nm), and excellent metal dispersion were attributed to this. This catalyst also demonstrated a high degree of stability when exposed to reaction conditions for 50 hours without seeing any decrease in catalytic activity. The results of the CO-TPD experiment showed that the bulk of the CO was dissociatively adsorbed on the catalyst surface. The capacity of ceria to create oxygen vacancies as a result of changing from $Ce^{3+}$ to $Ce^{4+}$ can hasten the CO adsorption process, which in turn can increase the CO methanation activity.

$CeO_2$ have great stabilizing capabilities resulting from its substantial metallic dispersion and its capacity to hinder the carbon deposition-induced deactivation of the catalyst. For example, no deactivation for $10Ni(Cl_{0.12})/CeO_2$ was experiential throughout 70 hours reaction as investigated by [20]. Zhang et al. (2019) [23] studied $Ni/CeO_2$ and it showed superior stability in which the CO conversion remained constant at 100%. Additionally, $NiO-CeO_2$ studied by Atzori et al. (2021) [24] and Aberkane et al. (2022) [25] was very promising, being highly active for the CO methanation reaction and stable up to 50 hours. Understanding how the CO methanation reaction works helps a lot when trying to figure out how to stop the catalyst from becoming inactive or to understand the whole process of the reaction. The mechanism of the reaction is determined by the kind of catalyst used, specifically the characteristics of the catalyzed active metal and the support. Rombi et al. (2016) [26] organized the Ni-Ce catalyst for carbon monoxide methanation and found out that the enhanced $CH_4$ selectivity is attributed that $CeO_2$ inhibits the side reaction, which then impedes the formation of $CO_2$. The interactivity between Ni atoms and $CeO_2$ (111) surfaces was studied by Senanayake et al. (2011) [27]. The authors noticed that nickel maintains its metallic structure after being adsorbed on $CeO_2$ (111) at a temperature of 300 K. However, when the $CeO_2$ substrate is heated to elevated temperatures (between 500 and 800 K), a partial reduction of the ceria $CeO_2$, resulting $Ni^{2+}$ species creation (NiO and/or $Ce_{1-x}Ni_xO_{2-y}$). Chemisorption of carbon monoxide on nickel results in a more robust interaction, which can be detected when nickel is present. At a temperature of 300 K, the adsorbed CO begins to dissolve when the Ni encounters an incompletely reduced $CeO_{2-x}$ (111) surface. This phenomenon results in the development of $NiC_x$ complexes, which may be participating in the generation of $CH_4$ at elevated temperatures. This finding showed the presence of $CeO_2$ positively helps to enhance the character of Ni.

Different pre-treatment conditions were found to affect the surface structure of the supported $Ni/CeO_2$ catalyst, which was studied by Cao et al. (2021) [28]. The catalyst activation in a combination of CO and $H_2$ rather than the more conventional hydrogen activation method results in the production of polycrystalline Ni nanoparticles. These nanoparticles have plentiful surface defects and a larger CO adsorption capacity, both beneficial to the CO methanation process. There is a possibility that carbon deposition on the surface is related to the creation of polycrystalline nickel nanoparticles.

Zhang et al. (2022) [29] investigated CO methanation using a $10CeO_2$-$20NiO/SiO_2$ catalyst and discovered that both $CH_4$ selectivity and yield are greatly improved. The reductive pre-treatment before to the reaction maximizes oxygen vacancies as mobile reactive sites, which plays a critical role in determining the high selectivity and yield of $CH_4$ by assisting CO adsorption, reducing the C-O binding strength, and breaking the C-O bond. Sub-stoichiometric $CeO_{2-x}$ oxygen vacancies are subsequently filled with oxygen, and carbon is hydrogenated to generate $CH_4$ molecules. During adsorption, $Ni^0$ sites are responsible for CO and $H_2$ dissociation as well as C* hydrogenation. Furthermore, the inclusion of $CeO_2$ significantly improves CO dissociation, explaining the catalyst's improved $CH_4$ selectivity. These results will help figure out how ceria works as a catalyst promoter in heterogeneous catalytic processes. Furthermore, Michalska et al. (2019) [30] synthesized several model Ni–Ce–Al catalysts with varying amounts of cerium oxide. It was found that Ni–Ce–Al catalysts were 2.5 times and 1.5 times more active in $CO_2$ and CO methanation, respectively than the reference catalyst.

Besides, a few fields have not been investigated enough, like the use of plasma during treatment and reaction. Zhang et al. (2019) [23] examined $Ni/CeO_2$ in the presence of plasma during treatment and discovered the development of a highly dispersed $Ni/CeO_2$ catalyst with improved CO adsorption and metal-support interaction. The plasma-decomposed catalyst exhibited significantly improved low-temperature activity with remarkable methane selectivity (up to one hundred percent) and increased carbon resistance for CO methanation. Compared to a thermally decomposed catalyst, the plasma-decomposed catalyst had a CO conversion of 96.8 percent and a methane selectivity of nearly 100 percent at a temperature of 250 °C. In the future, this sort of inquiry should be looked into. Chlorine addition hasn't gotten nearly enough attention. $CO_2$ methanation activity and the reverse water gas shift reaction are two side reactions of CO methanation that are inhibited by chlorine [31]. Konishcheva et al. (2015) [32] noticed that the $Ni(Cl)/CeO_2$ catalyst prepared from $NiCl_2$ precursor showed the best performance and was the most selective. This phenomenon could be explained by ceria surface blocking by chlorine species and appropriate inhibition of $CO_2$ hydrogenation activity.

Cobalt, on the other hand, is more stable than nickel at low-temperature reaction circumstances, although being more costly. The cobalt oxides and ceria interactions that were seen for the co-precipitated catalysts were found to be stronger than those reported for the wet-impregnated catalysts. By calcining the substance at a lower temperature, a high catalytically active surface area may be attained. During the calcination process, the number of basic sites in the co-precipitated and impregnated catalysts decreased significantly as temperatures rose from 500 to 700 °C. The activity of CO methanation appears to be linked to the quantity of active surface area. The quantity of catalytically active surface area and the number of strong basic sites both influence the catalytic activity for CO methanation. Based on in-situ results from the DRIFTS experiment, CO methanation occurs largely through the CO associative route. Carbonate, bicarbonate, and formate are found as intermediates in this route. The CO dissociative pathway was also active at the same time, as demonstrated by the presence of adsorbed CO species on the metallic cobalt's surface sites [30]. As temperatures increased from 500 to 700 °C during the calcination process, the quantity of basic sites in the co-precipitated and impregnated catalysts considerably reduced. The amount of active surface area appears to be related to the activity of CO methanation. Strong basic sites and the amount of catalytically active surface area both have an impact on the catalytic activity for CO methanation. Based on the in-situ findings of the DRIFTS experiment, CO methanation happens mostly via the CO associative pathway. In this pathway, the intermediates carbonate, bicarbonate, and formate are present. Adsorbed CO species were found on the surface locations of the metallic cobalt, indicating that the CO dissociative pathway was also active at the same time [33].

In terms of their overall catalytic properties, it was subsequently revealed that bimetallic catalysts are superior to their monometallic correspondents [34, 35, 3]. Research on bimetallic catalysts has recently been the primary area of interest in heterogeneous catalysis. This phenomenon is because these catalysts offer an enormous capability for activity, selectivity, and better stability. For bimetallic $CeO_2$-based catalysts, only a few have experimented with CO methanation. For instance, Razzaq et al. (2013) [36] investigated various supports doped with various added metals using a conventional impregnation and co-precipitation technique. The quantity of added metals was found to affect the supports' properties. At temperatures of approximately 300 °C, the $ZrO_2$–$CeO_2$-supported catalyst produced by co-precipitation can convert CO totally, and it has a $CH_4$ selectivity of approximately 99 %. Ashok et al. (2017) [37] explored the methanation of nickel supported on Ce-$ZrO_2$. They theorized that nickel ions ($Ni^{2+}$) are incorporated into the mixed oxide lattice, resulting in the formation of oxygen vacancies and a consequent increase in the adsorption of oxygenating species.

Table 2 provides an overview of the recent advances in the utilization of $CeO_2$ as support and promoter for CO methanation. It can be proven that ceria has been established as viable additive component whether as a support or promoter due to its stabilizing capabilities, resulting from its substantial metallic dispersion and its capacity to hinder the carbon deposition-induced deactivation of the catalyst. Additionally, several doped metals will improve the capabilities of supported ceria as a preferable catalyst for methane formation.

Table 2. Literatures on $CeO_2$-based catalyst for CO methanation.

| **Catalyst** | **Condition T (°C), P (atm)** | **CO Conversion (%)** | **$CH_4$ Selectivity (%)** | **Year** | **Refs.** |
|---|---|---|---|---|---|
| | | $CeO_2$ as support | | | |
| $50Ni/CeO_2$ | 220, 1 | ~99.9 | ~99.9 | 2015 | [22] |
| $Ni/CeO_2$ | 250, 1 | 96.8 | ~99.9 | 2019 | [23] |
| $30NiO\text{-}CeO_2\text{-}ZrO_2$ | 300, 1 | 98.0 | ~99.0 | 2019 | [18] |
| $Ni\text{-}Co/CeZrO_2$ | 360, 1 | ~90.0 | ~30.0 | 2018 | [38] |
| $NiO\text{-}CeO_2$ | 300, 1 | ~99.9 | 94.0 | 2016 | [26] |
| | | $CeO_2$ as promoter | | | |
| $CeO_2\text{-}Ni/\gamma\text{-}Al_2O_3$ | 350, 1 | ~99.9 | ~82.0 | 2014 | [39] |
| 7Ce-10Ni/SiC | 600, 1 | ~95.0 | ~85.0 | 2018 | [21] |
| $7.7Ni\text{-}La_2O_3\text{-}CeO_2/SiO_2$ | 210, 1 | - | 89.5 | 2018 | [40] |
| 7Ni-2Ce/Si | 230, 1 | ~99.9 | - | 2013 | [41] |

| | | | | | |
|---|---|---|---|---|---|
| $NiCe/Al_2O_3$ | 280, 10 | 95.4 | 90.7 | 2015 | [42] |
| $La_{0.75}Ce_{0.25}NiO_3/SiO_2$ | 350, 1 | ~99.9 | 98.3 | 2018 | [40] |
| $10CeO_2$-$20NiO$/ p-$SiO_2$ | 350, 1 | ~99.9 | 82.0 | 2022 | [29] |
| Ni-6Ce/$\gamma$-$Al_2O_3$ | 260, 1 | ~99.9 | ~99.9 | 2015 | [17] |

### *3.2 Reaction mechanism*

Since hydrogenation processes are typically endowed with an endothermic characteristic, it is recommended that these processes be carried out at comparatively low temperatures. Regardless of this, the mechanism of hydrogenation, specifically CO methanation, is still a topic of discussion among researchers today. Two types of CO methanation mechanisms were proposed; direct dissociation of CO and hydrogen-assisted CO dissociation [4]. Both of these different kinds of mechanisms can take place simultaneously, but the characteristic of the catalyst plays a vital role in selecting the pathways. In general, each catalyst has the same mechanistic routes; however, it can vary depending on the ability to dissociate CO and the stability of the major intermediates, both of which influence the amount of energy and the rate of reaction.

Some researchers have concentrating on the CO methanation reaction mechanism by the ceria-based catalyst to enhance its capabilities. According to experimental data done by Konishcheva et al. (2016) [43], the reaction over $Ni/CeO_2$ progresses via the nickel-carbonyl dissociation, an then the hydrogenation of the linked C and O atoms to $CH_4$ and $H_2O$. Then, they discovered that formates and a substantial quantity of hydrocarbonates were identified on the surface of $Ni/CeO_2$ support during in situ FTIR, indicating that the reaction is influenced by the adsorbed species on the surface of ceria, which can be hydrogenated to $CH_4$ by $H_2$. This discovery is also consistent with Atzori et al. (2021) [24], which discovered that $CeO_2$ could successfully adsorb carbon oxides, generating carbonates and C-H, which are then hydrogenated to create formates and finally methane by hydrogen dissociatively adsorbed on Ni particles. CO methanation was significantly favoured over $CO_2$ methanation in the feed presence of a lower hydrogen concentration. The reaction between the $C_{ads}$ and $H_{ads}$ intermediates is preferred since the nearness of the sites on which both CO and $H_2$ are dissociated and activated.

Calculations using density functional theory (DFT) were carried out by Zhang et al. (2022) [29] on the NiO and $CeO_2$-NiO models depicted in Figure 7 to comprehend the specific evidence regarding carbon monoxide adsorption and the succeeding carbon monoxide methanation. In this instance, the carbon monoxide adsorption energies on the NiO and $CeO_2$-NiO are respectively -0.27 and -0.36 eV. $CeO_2$-NiO displays more negative carbon monoxide adsorption energy than NiO, indicating that carbon monoxide has a greater capacity for adsorption on the $CeO_2$-NiO surfaces. Additionally, the C-O bond on $CeO_2$-NiO is longer than the C-O bond on NiO. This occurrence indicates that the C-O bond on $CeO_2$-NiO is simpler to break during the reaction process, which is favourable for the additional hydrogenation reaction. A DFT simulation results imply that adding $CeO_2$ encourages adsorption and dissociation of CO, which ultimately results in an improvement in $CH_4$ selectivity.

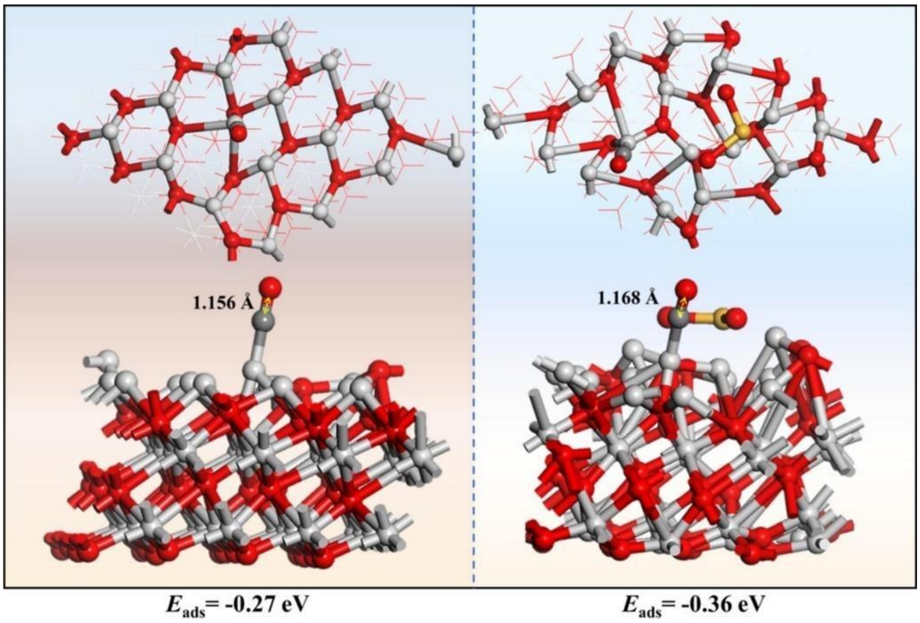

Figure 7 The side and top-down views of CO adsorption on the NiO and $CeO_2$-NiO surface (Ni: White; O: Red; Ce: Yellow). Adapted from Zhang et al. (2022) [29].

It is possible to conclude that adding $CeO_2$ has beneficial effects on the methanation of CO based on many observations. The ceria lattice contains oxygen vacancies, and the readily reducible nature of $CeO_2$ makes it possible to reduce metal phases via a spillover mechanism. $CeO_2$ can effectively adsorb carbon oxides, which results in the formation of carbonates and C-H. These are further hydrogenated to produce formates and, eventually, CH4, produced by $H_2$ dissociatively adsorbing onto Ni particles.

## 4.0 Oxygen vacancies and basicity of ceria-based catalysts

Material parameters, such as basic properties and oxygen storage capacity, significantly impact catalytic behaviour, performance, and coke inhibition in CO methanation. Ceria has been discovered as viable support and promoter for CO methanation due to its redox characteristics and exceptional oxygen retention capabilities, limiting the likelihood of carbon deposition. During the conversion of $Ce^{4+}$ to $Ce^{3+}$, $CeO_2$ can simultaneously release oxygen and replenish it by filling oxygen vacancies.

Zhang et al. (2022) [29] investigated CO methanation on a porous $10CeO_2$-20NiO/p-$SiO_2$ nanosphere catalyst with enhanced $CH_4$ selectivity and yield. The experimental data and DFT calculations indicate that oxygen vacancies in sub-stoichiometric $CeO_{2-x}$ are maximized by pre-treatment, acting as mobile reactive sites and contributing to CO methanation. Oxygen vacancies aid in the absorption of CO molecules, reduce the strength of the C-O bond and break the C-O bond to enhance $CH_4$ production. The oxygen vacancy is then filled by oxygen, and then carbon is hydrogenated to produce $CH_4$. Liu et al. (2014) [44] produced nickel oxide supported on a cerium oxide-lanthanum oxide and discovered that doping $La^{3+}$ into the $CeO_2$ lattice yields a high number of oxygen vacancies aid in removing the carbon deposited on the surface. Similarly, the oxygen deficiency on the surface of $CeO_2$ facilitates carbon oxides reduction and dissociation, hence increasing methanation activities [45].

The existence of a considerable number of oxygen vacancies is strongly linked with the high adsorption capacity of CO and the easily broken C-O bond in a decreasing $H_2$ environment. According to Wang et al. (2015) [46], a high abundance of oxygen vacancy serves as the active site for the activation and conversion of carbon oxides. In this case, oxygen vacancies operate as mobile reactive sites to aid in the adsorption of CO molecules and the breakage of the C-O bond, which is followed by oxygen filling the vacancies and carbon hydrogenation to $CH_4$. The selectivity and yield of $CH_4$ are greatly improved with the help of sub-stoichiometric $CeO_{2-x}$.

In addition, it has been observed that reduction of ceria in $H_2$ can generate oxygen vacancies and that hydrogen spillover can accelerate the formation of $Ce^{3+}$ [47]. The more significant $Ce^{3+}$ concentration is attributable to increased hydrogen spillover from Ni particles to the support, which promotes ceria reduction [48]. Rombi et al. (2016) [26]

postulated that partly reduced $CeO_x$ would help in the dissociation of CO at the nickel-ceria interface by absorbing oxygen, hence reducing the production of $CO_2$ through the interaction of adsorbed oxygen with CO.

TPR analysis was used to examine the reducibility of nickel-ceria catalysts, and the findings are depicted in Figure 8. The TPR profile displays three distinct types of reduction peaks, denoted by the α, β and γ symbols. The α peak, the most significant peak, found between 250 and 350 °C, can be linked to the reduction of oxygen species in oxygen vacancies created by the solid solution of $Ce_xNi_yO$. The solid solution $Ce_xNi_yO$ can be generated when $Ni^{2+}$ cations enter the $CeO_2$ framework and substitute some $Ce^{4+}$ ions. This lattice distortion and charge imbalances in the $CeO_2$ framework result in oxygen vacancies. Therefore, hydrogen could quickly diminish the oxygen species adsorbed in ceria's oxygen vacancies at low temperatures. As the nickel content of catalysts increased, the peak area dropped, which corresponded to a reduction in oxygen vacancies.

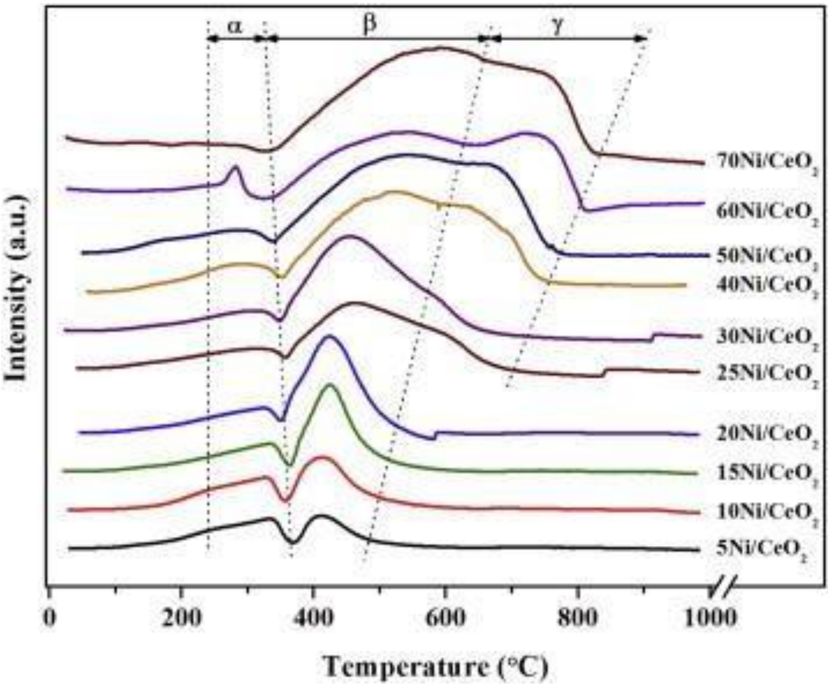

Figure 8 $H_2$-TPR profiles of nickel-ceria catalysts adapted from Nematoliahi et al. (2015) [22].

Literature indicates that the presence of oxygen vacancies can increase the basicity of ceria's surface catalyst [49, 50] and the concentration of such vacancies can be regulated by doping $CeO_2$ with various metal oxides [51] due to a size/charge mismatch between host cerium ions and dopant ions. Li et al. (2015) [51] reported an apparent rise in the quantity of oxygen vacancies in Cu- and La-doped $CeO_2$. According to the literature, it is possible to argue that the inclusion of Ni improves the fundamental properties of Ni-Ce catalysts by intensifying oxygen vacancies, as verified by Raman analysis. Nevertheless, when the amount of Ni grows, the external surface of ceria diminishes, resulting in a decrease in the accessibility and number of sites responsible for carbon dioxide adsorption. In order to prevent the physical obstruction of the support surface, it is vital to identify the optimal metal percentage.

## 5.0 Conclusion and Future Prospects

In conclusion, we discussed the most up-to-date advancements in the field of $CeO_2$-based catalysts for SNG synthesis via CO methanation along with informetric analysis. This article highlights the effect of $CeO_2$-based catalysts' basicity and oxygen vacancies on the CO methanation process. The creation of SNG from the methanation of CO is needed for future energy concerns and to reduce environmental pollution. Nevertheless, the high temperature required for the methanation typically makes the catalysts inactive over time. Ni-based catalysts have been extensively insinuated and shown to be effective for the reaction due to their comparable capability to that of noble metals. The instability, carbon deposition and metal sintering issue cannot be disregarded within CO methanation. As a result, the requirement to improve or substitute them became unavoidable. Dispersion of metal, temperature, $H_2$/CO ratio, duration, coke morphology, catalyst actives sites, calcination temperature, optimum loading, and proper pre-treatment gas and temperature can help solve these problems to a considerable extent.

It has been established that $CeO_2$-based catalysts are an excellent solution for CO methanation. Due to its oxidation-reduction characteristics ($Ce^{3+}/Ce^{4+}$) for carbon deposition resistance and increased possibility for the adsorption of carbon oxides, $CeO_2$ exhibited superior catalytic performance as support. The ceria support's qualities can be modified according to the specific structure of the metal active sites. Ce's importance as a metal is comparable. Three factors have been shown to contribute to high activity and carbon resistance. First, the enhancement of $CeO_2$ surface oxygen mobility and oxygen storage capacity increased carbon gasification effectiveness, which allowed the elimination of deposited coke from the catalyst. Second, the fundamental properties of $CeO_2$ enhanced the adsorption of carbon oxides, hence facilitating the elimination of carbon production. Thirdly, great metal and support interactivities and the anchoring effect of $CeO_2$ decreased the particle size of metal and increased the metal active sites dispersion, hence preventing coke formation and sintering of metal for preventing catalyst deactivation. Large-scale CO methanation reactions and low-temperature systems continue to present difficulties. However, it has been commonly observed that a combination of noble metals and basic promoters such as ceria can considerably extend the catalyst's lifetime without interruption.

For the prospect, it is necessary to investigate the roles that basic and fibrous supports materials associated with $CeO_2$, bi-metallic Ni-based catalyst conformations with noble and non-noble metals supported and promoted by $CeO_2$, and the dimension of pore play in the diminution of coke generation during CO methanation processes. The progress of a low-temperature carbon monoxide methanation process for the effective generation of substituted natural gas is essential and should be considered as future research objectives. In addition, research is recommended to focus on the prevention of side reactions such as $CO_2$ methanation and reverse water-gas shift reactions in CO methanation. Potentials for the future assessment of coke strength, permeability, durability, reusability, and regeneration, of catalytic materials, particularly bi- and tri-metallic CO methanation catalysts, can be examined.

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## 7.0 Conflict of interest

The authors confirm that there are no known conflicts of interest associated with this publication.

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## Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical Abstract