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# A review on recent bimetallic catalyst development for synthetic natural gas production via CO methanation



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## HIGHLIGHTS

- Fossil fuels depletion contributed to the growth of alternate energy sources.
- The synergistic interaction of both metals can improve the catalyst's efficiency.
- The metal-support and metal-metal interaction can either be reinforced or weakened.
- Catalyst's particle size, reducibility, basicity, and dispersion were improved.
- Additional metal modifies the mechanism's energy and rate value.

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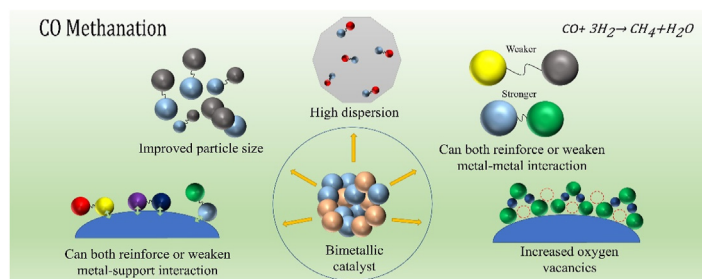
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## GRAPHICAL ABSTRACT



## ABSTRACT

CO methanation has arisen as an attractive research area due to its ability to transform syngas into substituted natural gas. Current monometallic catalysts have a severe problem; quickly deactivated. It is generally known that by introducing another metal to create a bimetallic catalyst, synergistic interaction between both metals considerably enhances catalyst effectiveness. This paper provides a detailed overview of bimetallic catalysts for CO methanation, covering its synthesis method and effect on physicochemical

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characteristics. The bimetallic catalyst can both reinforce or weaken the metal-support and metal-metal interaction, which weakening it favors reducibility while reinforcing it favors stability. Particle size and dispersion also improve, whereas adding lanthanides can increase the basicity. We also present the mechanism of CO methanation over the bimetallic catalyst, which modifies the mechanism's energy and rate value. This review provides insights on how reaction effectiveness is enhanced, enabling catalyst development with the highest possible performance.

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## Introduction

Global demand for energy is thriving. The success of manufacturing civilization, the development of the economy, and the quality of the population's lifestyle are a function of energy consumption. Therefore, the worldwide energy consumption of all fuel sources has increased significantly. Natural gas is among the most cost-effective and substantial sources of energy available in the world today [1]. It remains an attractive choice for the industrial and electric power sectors due to its reasonable capital cost and relatively high fuel efficiency [1].

Furthermore, many country governments have executed national or international plans to reduce CO<sub>2</sub> emissions [2]. As a result, demand for natural gas is increasing since it is regarded as an environmentally favorable clean fuel that provides more significant environmental benefits than other fossil fuels. Natural gas is also becoming more affordable [3]. Natural gas is colorless, odorless, and lighter than air, and because it does not include minerals, it produces no ash residue when burned, making it a cleaner fuel [4]. For this reason, natural gas may surpass the more carbon-concentrated coal and other liquid fuels [4].

However, the oil reserves and natural gas are restricted to the next 40–60 years, and the coal reserves will be available until the next 150 years [5]. Therefore, many researchers and scientists tried to find another alternative sustainable source of energy. They propose a resolution in the form of synthetic natural gas, also known as substitute natural gas (SNG), which is a form of natural gas that has been artificially generated [4,6]. It is attracting increasing attention due to SNG has been considered as an adaptable energy carrier that may replace natural gas due to its extraordinary conversion effectiveness, existing gas distribution structures such as pipelines, well-established and efficient end-use technologies, and power stations [4]. Meanwhile, expenditures involving methane generation using catalytic and biological processes from gases containing significant amounts of carbon oxide gases (CO/CO<sub>2</sub>) are actively researched [7–9]. The SNG production via carbon monoxide and carbon dioxide methanation is widely investigated since both oxides are abundant in the atmosphere. CO<sub>2</sub> can be obtained from the atmosphere, while CO can be obtained from almost all fuel refineries that produce syngas. Both CO methanation and CO<sub>2</sub> methanation is an exothermic process; hence, it needed catalyst to lower down the activation energy [10]. Due to the overwhelming

methanation activity of transition metal catalysts (Ni, Co, Fe, Ru, Rh, Pd, Os, Ir, and Pt), they have been extensively studied in CO methanation [11].

Many researchers looked into the particular reaction rate and selectivity of the various metallic element and discovered that the reaction rate of Ru, Fe, Ni, Co, and Mo decreases in the sequence of the metals, while the selectivity of Ni, Co, Fe, and Ru decreases [11]. Catalysts based on iron have high reaction rate but a low selectivity for methane, which is well recognized in the industry [12]. Ru is well-known for being the most active component in the methanation of CO, CO<sub>2</sub>, and mixtures of these gases [9]. Nevertheless, Ru is approximately one hundred and twenty times more expensive than Ni in term of mass [9]. Owing to the relatively low cost, great catalytic performance, and excellent selectivity of Ni-based catalysts when compared to Ru-based catalysts, Ni-based catalysts have been extensively used in methanation catalytic reactions [13]. The deactivation of catalysts (coking and sintering), on the other hand, limits the usage of metallic catalysts in the future [14–18]. Tao, Meng [18] show that typical nickel-based catalysts were subjected to significant catalyst deactivation as a result of sintering and carbon deposition, respectively. Hou, Gao [19] demonstrated that Ni catalysts deactivate due to the growth of Ni nanoparticles and carbon deposition on the surface of the catalyst during methane auto-thermal reforming with carbon dioxide and oxygen in a fluidized-bed reactor. Yan, Liu [16] revealed that Ni nanoparticles (NPs) increased in size and dispersion significantly decreased in the reaction atmosphere of CO methanation. In a nutshell, whereas other metal-based catalysts are less active than Ni-based catalysts, sintering as well as carbon deposition are the primary issues with Ni-based catalysts. Thus, it can be inferred that monometallic catalysts, in general, have significant disadvantages and disadvantages for CO methanation and that additional research is required to overcome this issue.

Despite the growing research efforts, overcoming catalyst deactivation and achieving satisfactory catalytic activity at low temperatures continue to be the greatest issues to be solved. Several research groups have recently investigated the use of bimetallic catalysts to increase catalytic activity while simultaneously suppressing catalyst deactivation. As a result, during the last 15 years, there has been a noteworthy upsurge in the amount of research being done on CO methanation over bimetallic catalysts. The formation

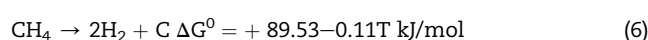
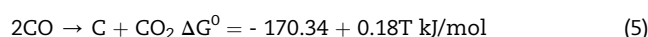
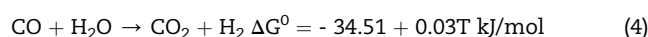
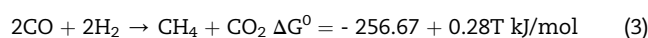
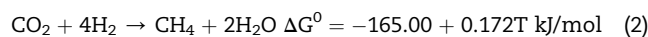
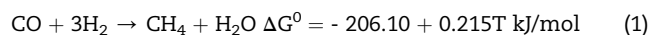
of active and stable catalysts is the essential phase in the CO methanation process. The purpose of this paper is to provide a critical overview of CO methanation catalyst manufacture and research that has taken place over the previous 15 years. The authors of the majority of the review publications on methanation processes [4,9,11,20] have primarily explored the progressive development of methanation technology in general, rather than explicitly discussing bimetallic catalysts for CO methanation processes. To our knowledge, there is no paper that stipulates a comprehensive review of the progress of bimetallic catalysts for CO methanation, which would be beneficial to our readers. For this reason, taking into account current studies on bimetallic CO methanation and in order to gain a well understanding of the CO methanation reaction over a bimetallic catalyst, we are investigating the features of bimetallic catalysts, including their effectiveness in CO methanation. It is crucial to select and comprehend the reference of each bimetallic catalyst correctly. Therefore, in this review, the concepts regarding CO methanation and bimetallic catalyst will be initially discussed, and conclusively, a review of current studies regarding the synthesis method, effect on physicochemical characteristics, and mechanisms modification of CO methanation over bimetallic catalyst will be presented. The objective of this review is to present an overview of the most recent developments in the field of bimetallic catalysts and to investigate the advantages of using bimetallic systems for the CO methanation process.

## CO methanation

CO methanation became significant for SNG production during the late 1970s oil crisis. The purpose was to create the replacement of natural gas utilizing syngas produced by coal gasification, which is abundant and was discarded without any value. Numerous ideas and models of methanation were created at that time, and the most vital application for CO methanation is to remove CO from a stream of product gas, for example, in processes of ammonia manufacture and in membrane cells of proton exchange which CO is a strong poison of their iron catalyst [21]. In addition, carbon oxide methanation is utilized as a secondary step in the purification of synthesis gas following the dry reforming of the methane process [22]. While steam reformation employed methane as the reactant to produce syngas, some used it primarily to generate hydrogen, with carbon monoxide being the undesirable by-product [22]. To enhance the quantity of hydrogen in the produced gas, the gas is delivered through a water-gas shift (WGS) reactor, which also reduces the amount of CO in the gas. After that, a carbon monoxide selective methanation reactor is employed to reduce further the CO content of the produced gas [22]. As a result, carbon monoxide procedures are critical in dry reforming methane for hydrogen purification. Not only can carbon monoxide methanation be used to remove CO from syngas, but it can also be utilized to adjust the syngas ratio [23]. It's important to note that methane steam reforming is the reversal of the methanation reaction in this case. Similarly, a good catalyst for methanation is also a good catalyst for methane steam

reforming and vice versa, resulting in identical deactivation mechanisms for both processes [24].

There are a variety of reasons why the methanation process appears to be fascinating. The aim of the methanation process is to generate CH<sub>4</sub> from H<sub>2</sub> and carbon oxide gases. CO methanation is the term used to describe the process by which carbon monoxide is converted to methane [Eq. (1)], then the process of converting carbon dioxide into methane is referred to as CO<sub>2</sub> methanation, [Eq. (2)].



Both CO methanation and CO<sub>2</sub> methanation is an exothermic process. It takes 206 kJ of heat to decompose a mole of CO, and for every 1 m<sup>3</sup> of methane produced in the STP state, it corresponds to 2.3 kW of heat. CO methanation uses syngas (H<sub>2</sub>+CO) which are generally obtained at plants for the generation of synthetic fuels that use coal or biomass as fuel [9] for the catalytic production of CH<sub>4</sub> [25]. Methanation is one of the essential phases in SNG production. The CO methanation is an exceedingly exothermic reaction, accompanied by various reactions [Eqs. (1)–(6)] [26,27] stated with Gibbs free energy ( $\Delta G = \Delta H - T\Delta S$  with T being temperature (K)), which may happen throughout the CO methanation.

When  $\Delta G = 0$ , a reaction is considered to be in equilibrium. For  $\Delta G < 0$ , the corresponding reaction is preferred, and the equilibrium is changed in favor of the products. If  $\Delta G > 0$ , the equilibrium is changed in favor of the reactants [27]. Methane generation from carbon oxide and hydrogen is preferred up to a maximum temperature of around 685 °C, according to the Gibbs free energy,  $\Delta G$ . It will be shifted to the left, favoring reactants if the temperature exceeds that value. According to Eq. (6), hydrogen, an undesirable product, and carbon (coke) creation from methane occur at temperatures greater than 540 °C, indicating that 540 °C is the maximum temperature for carbon oxide methanation, as coke formation limits the catalyst's effectiveness.

Furthermore, high temperatures can also promote active metals sintering [28]. Research into CO and CO<sub>2</sub> methanation methods was revived in the early 21st century due to the increasing environmental awareness and critical need to reduce anthropogenic greenhouse gas emissions.

## Necessity for bimetallic catalysts in CO methanation

CO methanation is usually done with the presence of a catalyst. Since it is an exothermic reaction, the catalyst cannot

sustain for a long time, coke formation and sintering will happen, and it is quickly deactivated [29]. So further improvement and development of the catalyst need to be done to overcome this problem. There is also an attempt to build a catalyst that can give high catalytic activity at low temperatures. Therefore, a long-standing objective of creating an effective CO methanation catalyst is essential and possesses significant challenges.

Metal-based catalysts have been of enormous importance in this regard for a large number of high-performance catalytic applications. However, it is very desirable to fine-tune the structure and properties of such catalysts to satisfy the specific energy and environmental requirements. Thus, the selection of metal loading is the success key to synthesize an effective CO methanation catalyst. Metals in groups 8–10 are active for the methanation process, and this discovery is led by findings of nickel catalyzing the reaction between carbon monoxide and hydrogen that results in the formation of methane and water vapor by Sabatier and Senderens [25]. In terms of active catalyst, as shown in Fig. 1, there are two categories: noble metals (such as Pt and Ru, as well as Rh), and base metals (Fe, Co, and Ni), and the most promising catalysts are Ru and Ni [30]. The methanation activity order starts with  $Ru > Rh > Ni > Co > Fe > Pd$  [31], which showed that noble metals are higher ranked for methanation activity. On the other hand, the order is  $Ru > Fe > Ni > Co > Rh > Pd$  with respect to the number of surface metal atoms [31].

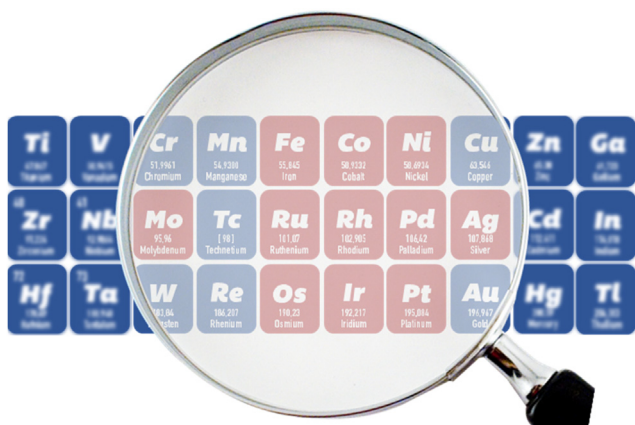
Using the pioneering work as a focus, the most active metal for CO methanation is Ru [11]. Nevertheless, Ni is the one that is commonly used in the industry considering the lower cost and higher activity [30]. The shortcoming of using Ni would be the possibility of getting coke deposits, suffering metal sintering, and even deactivating at high temperatures [15–19,29].

Numerous researchers examined the particular reaction rate and selectivity of the various metals and concluded that the reaction rates decreases in the order of Ru, Fe, Ni, Co, and Mo, while selectivity decreases in the order of Ni, Co, Fe, and Ru [11]. It is well established that Fe-based catalysts have high

reaction rates but a very low selectivity for methane. Ru is the furthestmost active metal for the methanation of CO, CO<sub>2</sub>, and their mixtures. Ru, on the other hand, is more expensive than Ni [9]. Ni-based catalysts have been largely used for methanation processes in comparison to Ru-based catalysts due to their inexpensive cost, high reaction rates, and good selectivity [30]. Nevertheless, the deactivation of metallic catalysts (coking and sintering) limits their future usage [14–18]. Tao, Meng [18] demonstrated that typical nickel-based catalysts are susceptible to significant deactivation due to sintering and carbon deposition. Hou, Gao [19] demonstrated that Ni catalysts deactivate as a result of expanding Ni nano-particles and carbon deposition on the surface of the catalyst during auto-thermal reforming of methane in a fluidized-bed reactor. Yan, Liu [16] demonstrated that nanoparticles of Ni (NPs) were growing, and the dispersion considerably reduced in the CO methanation reaction environment.

In a word, whereas other metal-based catalysts have lower active activity than Ni-based catalysts, the key issues for Ni-based catalysts are carbon deposition and sintering. These disadvantages, however, are not limited to Ni-based catalysts only. For example, as Carvalho, Ordonsky [32] demonstrated, it is possible for cobalt-based catalysts to become deactivated as a result of carbon deposition and the agglomeration of cobalt particles, resulting in a reduction in the concentration of cobalt active sites and the intrinsic activity of the catalyst. While Mo-based catalysts have excellent sulfur-resistance qualities, they still require work to improve their methanation activity [33]. Although Ru is the greatest active metal for methanation of CO, it also suffers from significant deactivation and loss of selectivity during reaction, particularly for Ru/TiO<sub>2</sub>, which makes commercial usage difficult [34]. The observed deactivation can be attributed mostly to the blockage of active sites caused by the accumulation of carbon-containing substances on the surface of the catalyst [34]. Therefore, it can be stated that monometallic catalysts as a whole have considerable disadvantages and disadvantages for CO methanation.

It was later discovered that bimetallic catalysts outperform their monometallic counterparts in terms of catalytic capabilities [35–37]. In the area of heterogeneous catalytic, the study of bimetallic catalysts was recently focused on predominantly since it offers a higher potential for activity and selectivity paired with increased stability. Numerous bimetallic catalysts have been industrialized for use in industrial processes such as ecological treatment, chemical synthesis, and petroleum purification. Bimetallic catalysts demonstrate that the properties of two different metals are combined and that they create new and distinct properties through synergistic effects between the two present metallic elements [38]. The bimetallic particle's structure can be randomly oriented, such as alloy or intermetallic composite, cluster-in-cluster, or core-shell structures. Core-shell nanocomposites, bimetallic nanocomposites, structured nanoparticles, nano-dendrites, and other structures are among the many types of nanocomposites that exist [39]. Four main types of mixing patterns, as shown in Fig. 2, can be identified. Nevertheless, their concluding structure depends on the composition, procedure, synthesis method, relative strengths, the surface energy of bulk materials, and many more [39].



**Fig. 1 – Active metals (red color) for methanation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)**



During the 1960s, the Exxon Research and Engineering Company began exploring the possibility of using a bimetallic catalyst [40]. Then, in the early 1980s, John H. Sinfelt invented the phrase “bimetallic cluster” to describe a distributed supported metallic catalyst composed of silica and alumina [41]. Ru–Cu, Ni–Cu, Pt–Ru, and Pt–Ir were among the significant bimetallic catalysts of that time. In recent decades, the bimetallic catalyst library has been enriched substantially. These bimetallic catalysts' potentials are assessed for many reaction processes such as hydrogenation [42–44], dehydrogenation [45–48], and isomerization [49–52] process, and all of the catalysts displayed synergistic effect between bimetallic particles thus showed high activity in their respective reaction. The reasons behind the high activity include electronic effect, structure modification, dispersion, surface altering, and many more.

Hence, it is nothing unusual that bimetallic catalyst is extensively researched in the methanation field. The stability and activity of bimetallic catalysts have been shown to be superior to monometallic catalysts [53,54]. Hammer and Norskov [55] demonstrated that the interaction amongst the two metal exteriors might alter the electrical and geometric constructions of the single-crystal metal surface upon deposition of another metal. This alteration leads to diverse physicochemical properties of double metal surfaces than the single-crystal metal surface.

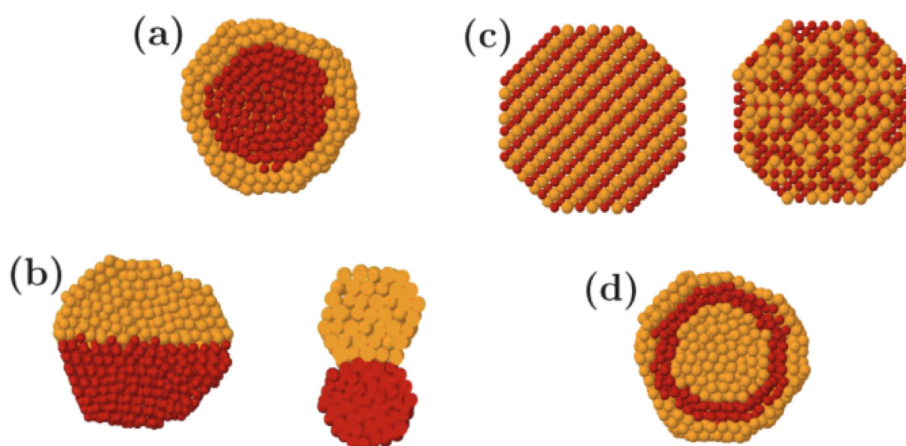
The incorporation of a trace quantity of an additional metal alters the catalytic effectiveness of monometallic catalysts, resulting in increased activity at lower temperatures and increased selectivity for CO methanation. For instance, Tada, Kikuchi [56] showed the addition of Ni into Ru/TiO<sub>2</sub> showed that the formate species' breakdown, which occurs as a result of CO<sub>2</sub> methanation (side reaction for CO methanation), is slowed, resulting in decreased CO<sub>2</sub> conversion rate, which then results in the high catalytic activity of CO methanation at low and high temperature. They also showed that Ru could reduce NiO's reduction via spill-over of H<sub>2</sub> from Ru metal, which necessitates close interactivity between Ni and Ru, indicating high metal-metal interaction. Yu, Jin [57] also showed that when compared to monometallic Ni and Co-based catalysts, the Ni–Co bimetallic catalysts demonstrated advanced

methanation reactivity and excellent stability. Zhang, Xin [58] stated that adding a little of MoO<sub>3</sub> (<2%) into a nickel-based catalyst can enhance the nickel atom's concentration at the catalyst surface while adding comparatively high MoO<sub>3</sub> levels can lessen the nickel atom concentration. Kustov, Frey [59] investigated the Fe–Ni bimetallic catalysts, and they displayed substantially superior activities and, in some situations, greater methane selectivity than the classic monometallic Ni and Fe catalysts. The addition of lanthanides onto Ni/SiO<sub>2</sub> increases the catalytic activity as a result of the existence of synergy between Ni and the 4f-block element, which affects their basicity, catalyst particle size is reduced, and the catalyst's stability on the gaseous stream is increased [60].

There was also an attempt to use a bimetallic catalyst to improve methanation's catalytic activity at a lower temperature. For instance, Ren, Qin [53] reported in their investigations of CO<sub>2</sub> methanation over Ni/ZrO<sub>2</sub> added with second metal (Fe, Co, Cu) and found out that with the addition of metal, catalytic activity increased markedly for temperature below 250 °C. In another literature, experimental results discovered that Fe's addition to the catalyst could excellently improve low-temperature CO methanation catalytic performance [61]. Hence, in this field of CO methanation, the bimetallic catalyst is proven to displayed high catalytic capabilities, CO conversion and CH<sub>4</sub> selectivity, excellent stability, reduced rate of CO<sub>2</sub> formation, and can be performed well at low temperature.

### Synthesis methods for bimetallic catalyst

The method of preparation generally affects the catalyst properties and hence affects the catalytic performance of bimetallic catalysts. Several methods have been reported for bimetallic catalyst synthesis, including impregnation, sol-gel, evaporation-induced self-assembly (EISA), hydrothermal and precipitation method including co-precipitation and deposition-precipitation. The preparation procedure would have a noteworthy outcome on the physicochemical characteristics of the catalyst, which would include the morphology, porosity, reducibility, and stability [62,63].



**Fig. 2** – Graphic illustration of probable mixing designs: (a) core-shell, (b) subcluster segregated, (c) mixed, (d) three shell. Adapted from Ferrando, Jellinek [39].

For bimetallic catalysts, it requires more than one metal precursor. Several reports used methods such as co-precipitation and co-impregnation, where they used two metal precursors in one preparation procedure [64–68]. In most cases, the co-impregnation technique results in a supported bimetallic or alloy type catalyst, in which the two metal atoms are distributed uniformly throughout the particle. The sequential impregnation procedure, on the other hand, is widely used to generate core-shell materials, in which a less active metal is prepared first, and then the active metal is deposited onto the less active metal. While some reported that they used more than two preparation methods to synthesis a bimetallic catalyst, for example, Xiao, Song [69] synthesized their Ni/Ni–Al<sub>2</sub>O<sub>3</sub> catalyst for CO methanation using the EISA technique to put the Ni inside the pore wall of the support and then used incipient impregnation method to load another Ni onto the surface of the support. Md Ali, Ku Hamid [70] then prepared Ni–Co/SiO<sub>2</sub> catalyst through successive reverse co-precipitation and wet impregnation methods.

### Impregnation

The impregnation method has been widely used for catalyst synthesis, whether it is a monometallic or bimetallic catalyst. It is due to the straightforward, uncomplicated procedure and inexpensive [71]. In this technique, a solution containing the active phase's precursor had a physical interaction with support or another active solid phase, which is subsequently dehydrated to eradicate the solvent that has been absorbed by the active phase's precursor [72]. In comparison to other techniques of preparing a coating of active materials on the catalyst's surface, this procedure is faster, less expensive, and more straightforward. Nevertheless, it is complex to manufacture a catalyst with a high concentration of precursors and to achieve uniform precursor dispersion on the support's surface. There are two impregnation types to synthesize bimetallic catalyst since it involves two metals: sequential impregnation and co-impregnation. Sequential impregnation means the metal was impregnated into the catalyst one by one, where co-impregnation means both metals were impregnated simultaneously. Guo and Lu [73] found that the impregnation techniques had no effect on the reduction behavior but that the Mg–Ni/SiO<sub>2</sub> catalysts created by the co-impregnation technique had advanced activity and stability than those organized by the successive impregnation technique. Catalysts prepared by the sequential impregnation technique displayed better NiO dispersion but were quicker to overload and became bulkier than catalysts developed by the co-impregnation method, which resulted in a significant increase in Ni sintering of the catalyst when conducted to a stability test.

### Precipitation

Precipitation is a straightforward, cost-effective, and commercially viable approach that is one of the most extensively used procedures for the manufacture of catalysts [74]. It is a chemical reaction in which aqueous metal salts and alkali solutions are combined to form an indissoluble metal hydroxide or carbonate [75]. This method can be made by changing circumstances, for

instance, temperature, pH value, evaporation, and salt concentration. These constraints caused progressive deviations in crystal development and accumulation as a result of the alterations. Using the co-precipitation method, one can achieve uniform configuration in two or more cations in a homogeneous solution through a precipitation reaction [75]. This method is essential for the production of composites containing two or more distinct kinds of metal elements. When it comes to managing particle size and size distribution, co-precipitation is an inexpensive and straightforward strategy that involves manipulating the relative rates of nucleation and growth throughout the synthesis process. The formation of a high number of tiny particles is dependent on the success of the nucleation process. It is broadly understood that the products are insoluble species that develop under conditions of high supersaturation [75]. Yao, Yang [63] compared three synthesis methods for Ni catalyst for pyrolysis-steam reforming: co-precipitation, impregnation, and so-gel. They discovered that the co-precipitation prepared catalyst had the least effective catalytic performance as a result of the uniform dispersion of Ni, resulting in the accumulation of amorphous coke deposits on the catalyst. While this catalyst may not give a good result for pyrolysis-steam reforming since the process temperature is over 500 °C which leading to high coke deposits on the catalyst, it gives an excellent result for the methanation process since the process temperature is usually below 500 °C [67,76,77]. Using the precipitation method, Liu, Cao [67] discovered that the mesoporous NiCo–Al<sub>2</sub>O<sub>3</sub> catalysts were developed, with nanoparticles of NiCo alloy fluctuating in size from 7.9 to 9.2 nm that were extremely disseminated in an alumina medium. The NiCo–Al<sub>2</sub>O<sub>3</sub> catalysts shown outstanding catalytic capabilities throughout the stability test at 500 and 600 °C for 300 h while also demonstrating exceptional anti-sintering and anti-carbon deposition abilities, which were ascribed to the production of Ni–Co alloys in the catalysts. Razzaq, Zhu [77] studied diverse supports, comprising SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and CeO<sub>2</sub>, that were doped with a varying amount of additional metals using a typical impregnation and co-precipitation approach. The ZrO<sub>2</sub>–CeO<sub>2</sub>-supported catalyst synthesized by co-precipitation can achieve 100% of CO conversion at roughly 300 °C, and it has a CH<sub>4</sub> selectivity of 99%.

In contrast, deposition precipitation is a generic term that refers to the process of displacing small particles of metallic elements such as metal oxides, metallic sulphides, or metallic hydroxides onto a prepared support material [78]. The metal deposition is generated by a process that occurs in the liquid phase of the solution. This chemical reaction results in the creation of a metal composite that has low solubility in the solvent used in the reaction [75]. The precipitation that occurs as a result of this is directed to happen fully on the exterior of the suspended support material. This is an effective method to manufacture highly organized bimetallic catalysts, and it is an alternative to the organometal precursor process, where organometallic complexes often disintegrate prematurely, leading to inactive phases in the catalyst support [79]. Two processes are involved, which is the precipitation process, followed by the deposition process. It is the precipitation process that produces solids from bulk solutions that are dependent on the presence of enough gravity force to bring the solid particles collected, whereas the deposition procedure is defined as the interactivity of precipitate particles with a

support surface [80]. The Ni/Al@Al<sub>2</sub>O<sub>3</sub> catalysts prepared using the deposition-precipitation method demonstrated significantly enhanced catalytic capabilities in methanation when compared to the Ni/Al@Al<sub>2</sub>O<sub>3</sub> catalysts prepared using the wet impregnation method, owing to an intensification in dispersion and a higher catalytic active surface area [81]. Le, Kim [81] reported that the catalytic capabilities for both CO and CO<sub>2</sub> methanation had been proven to be steady over Ni/Al@Al<sub>2</sub>O<sub>3</sub>, with high coking-resistance for 50 h in the presence of a catalyst. The activation energies of Ni/Al@Al<sub>2</sub>O<sub>3</sub> prepared by impregnation were determined to be 110 kJ/mol, whereas the activation energies of Ni/Al@Al<sub>2</sub>O<sub>3</sub> prepared by deposition precipitation were 96 kJ/mol, demonstrating that deposition precipitation can lower the activation energies of the catalyst significantly.

It is also reported that the catalyst prepared by deposition precipitation can be reduced at lower temperatures compared to those assembled by the impregnation technique [81]. As reported by Zhang, Ai [82], the catalytic activity of a La<sub>2</sub>O<sub>3</sub>-Ni/Al<sub>2</sub>O<sub>3</sub> catalyst developed by the deposition precipitation technique is suggestively higher than that of a catalyst developed by either the traditional impregnation technique or the co-impregnation method. A large part of this may be credited to the activation of La<sub>2</sub>O<sub>3</sub> on the exterior of the catalyst, as well as to the catalyst's anomalous dispersion on the catalyst's surface.

### Sol-gel

Sol-gel technology has existed as long ago as the mid-1800s [83]. Among the most widely utilized techniques, sol-gel is primarily employed in the production of thin-film and powder catalysts [84–86]. The sol-gel method is an advantageous and extraordinary system for the development of nano-sized particles because it has numerous advantages over other approaches, comprising high homogeneity, appropriate stoichiometric control, low cost, high purity, and the capability of producing ultrafine particles with a confined distribution of size in a rapid period of time at low temperatures [87]. In a recent study, Cheng, Wu [88] developed three different methods for producing Ni-Fe/TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts (precipitation, co-precipitation, and sol-gel), and they reported that the Fe and Ni were discovered to be extremely distributed on the sol-gel catalyst, resulting in an outstanding catalytic capabilities for CO methanation at low temperatures with CO conversion approximately 96.7% and methane selectivity approximately 94.7% at 262 °C [88]. Furthermore, less amorphous carbon was formed on the catalyst that was utilized, which was produced using the sol-gel technique. This may be attributed to the demonstrated core-in-cell assemblies with TiO<sub>2</sub> as the shell and Al<sub>2</sub>O<sub>3</sub> as the core in the catalyst composite produced by the sol-gel system, which resulted in the significant stability of the catalyst [88]. It is reported that the compound formed by the sol-gel technique has extra mesopores and delivers more “accessible” active sites. The catalyst also shows high uniformity of particle size (4 nm), whereas catalysts assembled by precipitation and co-precipitation have a broader range of particle size (3–6 nm). Yao, Yang [63] discovered that the catalyst porosity and the dispersion of

Ni were considerably enhanced using the sol-gel technique, resulting in the highest reactivity when compared to the catalyst made using the impregnation and co-precipitation method, resulting in the highest activity.

### Other

Apart from the method above, some other low-profile preparation methods are also reported for bimetallic Ni catalysts. The evaporation-induced self-assembly (EISA) process is a well-known alternative synthetic approach that enables tuning inorganic condensation by forming a meso-organized liquid-crystal template [89]. A mesophase is gradually produced when the solvent is removed. The build-up of inorganic material around the void of this liquid crystalline phase enables one to obtain well-defined mesostructured hybrids, segregating the nanoscale organic and mineral domains [89,90]. This method is very effective for synthesizing permeable nanocrystals and has the benefits of uniform pores, manageable morphologies, and insignificant reaction circumstances [91]. In general, “self-assembly” refers to the impulsive organization of materials caused by non-covalent interactivities. Hydrogen bonding, van der Waals forces, and electrostatic forces are examples of non-covalent interactions that occur without the involvement of external factors [92]. Zhao, Fang [93] reported that their Ni-Co/Al<sub>2</sub>O<sub>3</sub> catalyst developed by the EISA technique presented the outstanding catalytic activity of CO<sub>2</sub> methanation and higher stability compared to the catalyst developed by the impregnation technique and the catalyst showed an ordered mesoporous structure. It has been proven that Ni-OMA produced by the one-pot EISA process has superior anti-sintering and coke resistance features, which may be accredited to the more effective interaction of Ni nanoparticles with the Al<sub>2</sub>O<sub>3</sub> framework than Ni-OMA produced by other methods [69]. Furthermore, even after impregnating with as much as 15 wt % NiO, the ordered arrangement was still well-preserved. The BET surface area was between 230 and 290 m<sup>2</sup> g<sup>-1</sup>, the total pore volume fluctuated between 0.3 and 0.5 cm<sup>3</sup> g<sup>-1</sup>, and the mean pore diameter ranged between 4.0 and 6.0 nm [69]. There were regular and narrow distributions of small Ni particles, with average diameters ranging from 4.0 to 9.0 nm [69].

The other catalyst preparation methods are hydrothermal. The term “hydrothermal synthesis” refers to the fusion of compounds by chemical reactions in a vacuum-packed and heated solution at temperatures and pressures above the surrounding environment [94]. The hydrothermal treatment is well known to significantly impact the catalyst's properties, a larger specific area of the surface, and larger pores [95]. This method also results in improved confinement of metal particles to the mesoporous support, which can also trigger an anti-sintering property of the catalyst [96]. Zhang, Xin [58] evaluated the impregnation and hydrothermal methods for developing a catalyst and discovered that the hydrothermal method produces the best reaction capabilities with 100% of CO conversion and 99% of CH<sub>4</sub> yield at 400 °C, 20 bar, and 12 k mL/g/h. Meeyoo, Panchan [97] stated that Ni-Ce-ZrO catalysts were synthesized using a one-pot hydrothermal

synthesis method and discovered that Ni might be partly integrated into the Ce–ZrO lattice, consequential in an upsurge of oxygen surface species in the catalyst. Furthermore, even with significant Ni loadings, the external areas of the catalysts remain substantial.

All preparation procedures, as shown in Table 1, provide catalysts with higher catalytic activity than the original ones. The impregnation method has gained popularity for catalyst production due to its ease of use, clear procedure, low cost and some researchers believe it is preferable to alternative approaches. However, there is a report that indicates that a different methodology is superior to the impregnation method previously indicated in their respective catalyst. While the impregnation method concentrated on applying metal particles to the surface catalyst in order to upsurge the number of available active sites for methanation, the other preparation method concentrated on incorporating the metal element within the catalyst in order to increase the catalyst's stability by making reduction difficult. This is just one of the numerous instances demonstrating that various preparation methods target distinct qualities of catalysts and that any of them can result in good attributes depending on the approach's objective. In a nutshell, diverse metals, catalyst supports, metal-support catalyst combinations, and catalyst objectives necessitate the utilization of a variety of synthesis methodologies.

### Influence of physicochemical properties of bimetallic catalytic system on CO methanation

Bimetallic catalysts, frequently demonstrating electronic and chemical properties which differ from their parent metals, allow achieving enhanced conversion, advanced activity, and improved stability for CO methanation catalysts. The

discovery of these surprising physicochemical features of bimetallic catalysts has sparked a burst of comprehensive research into CO methanation, intending to create a connection concerning the reaction performance and the physicochemical properties of the catalyst. Fig. 3 summarizes the outcome of various variables on the catalytic characteristics. Additionally, the next section discusses the consequences of a few other selected elements. Catalyst morphology, pore size, surface area, porosity, metal dispersion, basicity, oxygen vacancies, the reducibility of the catalyst, and interactivity between metal-support and metal-metal are some of the physicochemical properties that have been studied in the literature for CO methanation and summarized in this chapter.

### Physical properties

#### Morphology

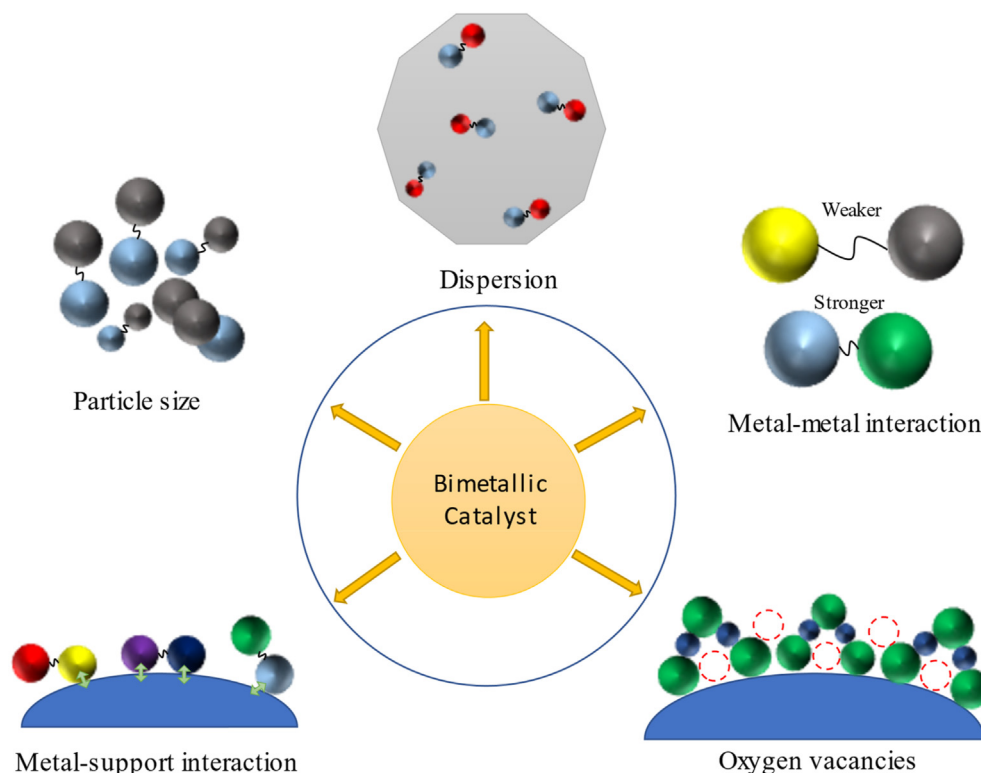
From the past literature, the performance of a catalyst has been found to be closely related to its morphology and structure. The morphology of the catalyst can be modified by varying synthesis factors such as support, metal loading, calcination temperature, and synthesis process [106]. Catalysts can have various morphologies (nanoparticle, microsphere, nanosheets, nanorods, nanowires, and nanotubes), affecting their surface area, reducibility, porosity, and catalytic activity efficiency [107]. Nevertheless, based on the literature, adding the second metal did not directly change the support's morphology, indicating that the second metal is well dispersed inside/over the support without changing its structure.

Most literature reported that the bimetallic catalysts showed almost the same morphology as the monometallic catalyst. For example, Zhang and Liu [108] observed that an LN/M catalyst exhibits a foam-like structure with numerous bulky

**Table 1 – Literatures on bimetallic CO methanation catalyst.**

Catalyst	Synthesis Method	Condition T (°C), P (atm)	CO Conversion (%)	CH <sub>4</sub> Selectivity (%)	Refs.
Ni–Co/SiO <sub>2</sub>	Impregnation	380, 1	98.00	~90.00	[98]
Co–Mo/AC	Impregnation	400, 30	~90.00	–	[99]
15Co–5Fe/γ-Al <sub>2</sub> O <sub>3</sub>	Impregnation	300, 10	~99.00	~96.00	[100]
Mo–Ni/S15-CA	Impregnation	250, 1	98.70	91.90	[65]
LR0.08N0.92-S	Impregnation	300, 1	~98.00	~80.00	[30]
Ni–Co/CeZrO <sub>2</sub>	Co-Precipitation	360, 1	~90.00	~30.00	[76]
5Ni5Co–Al <sub>2</sub> O <sub>3</sub>	Co-Precipitation	250, 1	~99.00	~85.00	[67]
15Ni–5Co/ZrO <sub>2</sub>	Co-Precipitation	300, 70	100.00	99.00	[77]
La <sub>2</sub> O <sub>3</sub> –Ni/Al <sub>2</sub> O <sub>3</sub>	Deposition-Precipitation	400, 1	~99.00	~80.00	[82]
Ni/Al@Al <sub>2</sub> O <sub>3</sub>	Deposition-Precipitation	250, 1	~98.00	–	[81]
Ni–ZrO <sub>2</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	Deposition-Precipitation	400, 1	~99.00	~85.00	[101]
CeO <sub>2</sub> –Ni/γ-Al <sub>2</sub> O <sub>3</sub>	Deposition-Precipitation	350, 1	~99.00	~82.00	[102]
Ni <sub>2</sub> OMoC	Sol-Gel	240, 70	59.31	67.73	[93]
Ni–Fe/TiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub>	Sol-Gel	262, 1	96.70	94.70	[88]
2Ni/13Ni-OMA	EISA	400, 1	~98.00	~88.00	[69]
NiO–TiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub>	EISA	380, 1	~95.00	~99.00	[103]
Ni–Mo/Al <sub>2</sub> O <sub>3</sub>	EISA	375, 1	97.90	95.80	[104]
Ni–Zr–Al	EISA	400, 1	~90.00	~80.00	[105]





**Fig. 3 – Factors influencing the catalytic characteristics of bimetallic catalysts.**

exterior pores and that after doping with cobalt species, the bimetallic catalyst preserves a similar shape after doping with cobalt species. This finding implies that the Co species are well scattered within the channels rather than on the surface of the catalysts, as initially assumed. For Ru–Ni, Tada, Kikuchi [56] reported that Ru–Ni/TiO<sub>2</sub> crystals displayed nearly the same shape as those on Ni/TiO<sub>2</sub> surfaces, indicating the addition of another metal does not affect the catalyst structure.

The morphology of bimetallic catalysts is directly affected by the synthesis method. Nickel-iron oxide catalysts containing La, Ce, Sm, Dy, and Yb, which is 4f-block elements, were synthesized and studied by Ferreira and Branco [109]. It was discovered that altering the heating value during treatment enables the modification of the morphology of the product, with the goal of producing either nanoparticles or nanofibers. The low heating value usage promotes the stability of nanofibers, whereas the elevated heating value usage causes the structure of nanofibers to collapse and the creation of bimetallic oxide nanoparticles to be favored.

Pandey, Ray [110] observed that SEM images of the pure Ni sample revealed that the elements had a flat and smooth surface, but that with the Fe addition, the particles seemed to have an irregular form and sharp edges. As shown in Fig. 4, the coarseness and unevenness of the particles seemed to escalate with an increase in Fe content, and subsequent characterization tests confirmed that the surface area climbed linearly with an upsurge in Fe content.

The following conclusion can be drawn from the foregoing explanation: by adding a suitable amount of the second metal, the catalyst morphology will remain the same, suggesting that the second metal is completely dispersed and has no effect on

the catalyst structure. However, while the structure remains unchanged, the surface characteristics vary in response to the number of foreign compounds that are introduced. This variation is expected since the second metal has been distributed onto the catalyst surface and has the potential to affect the surface distinctiveness of the catalyst.

#### *Particle size and dispersion*

One of the most critical properties of the catalyst is the particles size of the catalyst and metal. Usually, tiny nanoparticles of less than 10 nm with a small distribution of particles are the most active [111]. Depending on the mechanism, active sites are thought to be either on the metal surface or at the metal-support interface [112]. Thus, altering the size of the metal particle alters the amount of accessible active sites. Assuming that CO conversion occurs on the metal surface; thus, increasing the particle size reduces the available metal surface area.

The size of the catalyst particle is acknowledged to be critical in preventing carbon deposition [113]. The fact that deposition of carbon occurs only while the metal agglomeration is greater than the critical size means that using catalyst sizes more minor than the critical size can successfully avoid coking [114]. Furthermore, the anti-coking and anti-sintering characteristics of the catalyst will be improved, as demonstrated by the lowering in the upsurge of metal particle size and the lessening in the quantity of carbon deposition in the catalyst. As a result, by optimizing the size of the catalyst particles and the active site's structure, it is possible to increase the catalytic performance and reactivity of the catalyst.

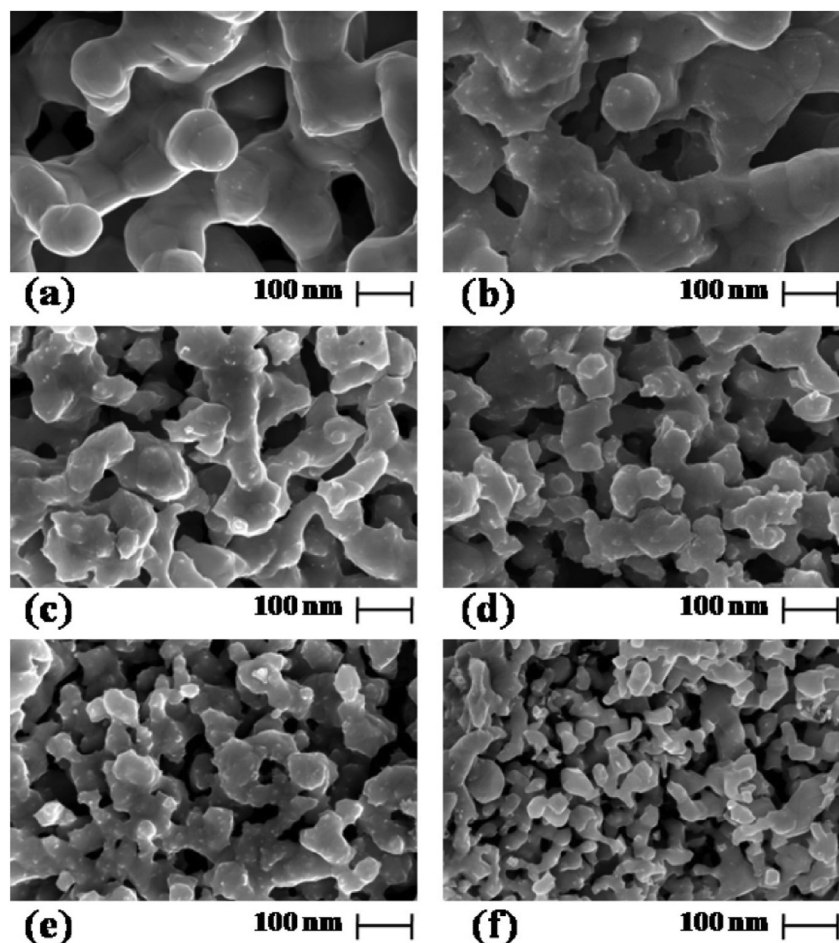


Fig. 4 – SEM images of: (a) Ni, (b) 90%Ni–10%Fe, (c) 75%Ni–25%Fe, (d) 50%Ni–50%Fe, (e) 25%Ni–75%Fe, (f) Fe. Adapted from Pandey, Ray [110].

As a result of the addition of second metals (La, Ce, Fe, and Co) to the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst with mesoporous nanocrystalline structure, Rahmani, Meshkani [115] confirmed that the bimetallic catalysts crystallite sizes were reduced from 18.9 to 5.1 nm. The addition of f-block elements, such as La, Ce, Pr, Eu, and Gd, on a nickel catalyst, as demonstrated by Ahmad, Younis [116], exhibited the maximum conversion of 98.2% at 300 °C when compared to the presence of an untainted nickel catalyst. When compared to the Ni monometallic catalyst, the superior metal dispersion on the catalyst surface, as well as the smaller particle size, were found to be accountable for the increased nickel activity of the catalyst. Kudo and Kato [117], working with lanthanide-doped Ni catalysts, demonstrate that the particle size of Ni decreases significantly, from 2 to 3 μm to 0.1–0.7 μm, resulting in an upsurge in the active area and catalytic capabilities of the catalyst. The SEM pictures demonstrated that when the Fe content increased, the particle size of the Ni–Fe samples dropped [110].

Another critical property that these catalytic systems must exhibit is good dispersion of the metallic hydrogenating phase [113]. This can be regulated primarily by selecting the preparation conditions and addition of promoters; second metal and certain compensating cations can also be beneficial [18,113]. High dispersion indicates the active sites are

distributing widely and evenly onto the catalyst surface [18]. The apparent activation energy is minimal at high dispersion. It is widely established that metal loading greatly impacts the dispersion of a supported catalyst, hence changing its catalytic activity. Generally, the inferior the metal loading, the greater the dispersion of the metal, and vice versa.

Literature advocates that the incorporation of second metal could enhanced the first metal's dispersion onto the catalyst. Ni-based catalyst is the furthermost extensively researched catalyst in this aspect since Ni's dispersion is crucial for enhancement in catalytic activity. The incorporation of Fe could enhance the Ni dispersion and its reducibility [13,53,61,118]. By incorporating the metal Ru onto the Ni catalyst, Crisafulli, Scire [119] discovered that the robust metal-metal interactivity increased the Ni dispersion, promoting the production of additional reactive intermediate carbonaceous species, thereby inhibiting the catalyst's deactivation and extending its lifetime.

In another study, Lu, Yang [120] used small amounts of lattice, cerium, cobalt, or iron in the Ni–ZrO<sub>2</sub> catalyst to encourage the NiO nanoparticles dispersion while increasing the amount of reduced active nickel species, thereby refining the thermal stability of the catalyst. Yu, Jin [57] compared their mono- and bimetallic Ni–Co catalysts and reported that the

higher dispersion of metal might enhance the adsorption and activation of CO, which then resulted in higher CO methanation performance, as shown in Table 2 and Fig. 5. In general, it can be concluded that by adding second metal, the metal-metal interaction increases, thus result in high dispersion, which then affects the reducibility, adsorption energy, thus lead to high catalytic activity.

To summarize, in accordance with the previous explanation, it can be stated that by adding an adequate amount of a second metal, the particle size reduces while the dispersion increases. The increase in the active area and catalytic capabilities of the catalyst as a result of this modification was significant. Variations in particle sizes and dispersion can be accredited to changes in the metal-support interactivity, respectively. The higher the interactivity amongst the metal and the support, the greater the dispersion. As previously stated, the second metal can increase the first metal-support interaction, which will be discussed in further detail later in this article.

#### Surface area and porosity

Methanation reactions are a complicated process that involves interactivities between the exterior of a solid catalyst and the reactants in a gaseous state. It is essential to understand the concept of an active site, namely a surface atom or group of surface atoms with distinct structure and properties, where the catalyzed transformation occurs to understand the mechanics of catalytic reaction mechanisms [121]. Generally, the number of active sites per surface area for materials of a specific type is very similar, and so the extent of a catalyst's exposed surface area defines the degree of its overall activity [121,122]. The larger surface area allows more reactants to reach the catalyst atoms/molecules. As the surface area increases, the proportion of surface atoms concerning the bulk increases markedly.

Generally, adding a considerable percentage of foreign substances, which in this case, a second metal, will decrease the catalyst's surface area [123]. Hence, it is crucial to determine the second metal's optimum percentage to prevent the support surface's physical blocking. Adding a second metal with an appropriate amount leading to negligible surface area changes. 1% of the second metal (La, Ce, Co, or Fe) added onto Ni/ZrO<sub>2</sub> catalyst did not suggestively affect the catalyst surface area and pore volume as reported by Ref. [120]. However, Rahmani, Meshkani [115] added 10% of the same metal to the Ni/γ-Al<sub>2</sub>O<sub>3</sub> catalyst, and the findings discovered that the bimetallic catalyst's specific surface area had been reduced. This outcome occurs perhaps because 10% of metal is too

much, and that amount can easily block the support pore. Another reason is probably on the support pore size. The smaller the pore size of the support, the easier it is for it to be blocked by foreign metal.

Doping of Co, Fe, and Ru onto a Ni-based catalyst produced minor changes in surface area, indicating that no physical blockage of the support has occurred [56,57,124]. According to a study conducted by Kustov, Frey [59], Ni-Fe/MgAl<sub>2</sub>O<sub>4</sub> catalysts were investigated, and it was discovered that adding 20 wt% metal did not significantly reduce the specific surface areas, indicating that there was no physical blocking of the exterior of the support with metal particles after impregnation. A significant drop in catalyst surface areas is observed when the metal loading is increased to 25 and 30 wt%, which is most likely due to the development of large oxide masses that restrict contact to the catalysts' interior surface. Zhang, Xin [58] discovered that the addition of only 0.5% MoO<sub>3</sub> to Ni-Mo/SiO<sub>2</sub> catalysts results in a reduction in total pore volumes and specific surface areas. When MoO<sub>3</sub> content (0.5–5%) is increased, specific surface area decreases significantly, indicating that Mo is not a suitable metal to be used as a catalyst in situations where a high surface area is required for a certain reaction.

When you add a significant percentage of foreign substances to a catalyst's surface area, like in this case, a second metal, the surface area of the catalyst will be reduced. In accordance with the previous explanation, it can be concluded that it is critical to find the optimal percentage of the second metal in order to prevent the support surface from becoming physically blocked. It is necessary to optimize the amount of second metal used in order to advance the efficiency of catalytic CO methanation.

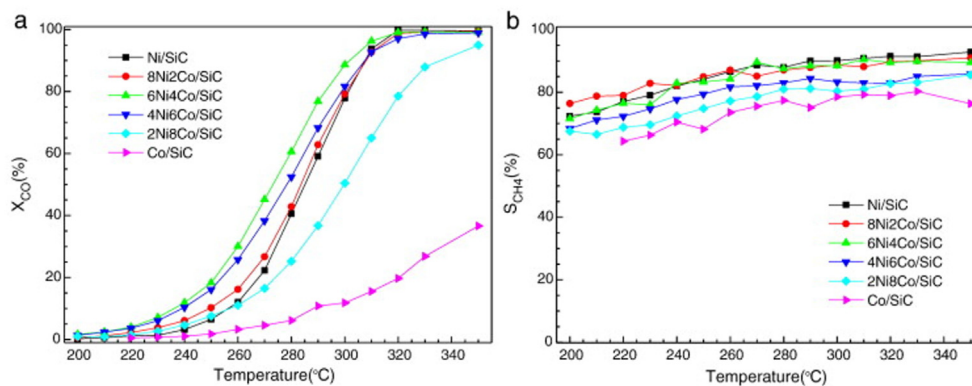
#### Chemical properties

##### Metal-support interaction

The interaction between metal catalysts and their supports is critical for increasing catalytic efficiency, yet it is still a difficult problem to solve and remains an open challenge. In general, it is well established that catalyst particles sizes and the metal-support contact are critical factors in preventing carbon deposition [113]. The electronic and geometric effects resulting from robust metal-support interactivities are accountable for the activity, selectivity, and stability of the catalyst, all of which are essential considerations in determining performance and efficiency [125]. Generally, strong electronic metal-support interaction is directly proportional to the catalyst's stability but inversely proportional to the catalyst's reducibility [126]. The catalyst's stability is enhanced with more vital metal-support interactivity, hence avoiding the sintering of the metal but decreasing the chances for the metal to be reduced. Therefore, metal-support interaction can be weakened or enhanced depends on the end properties target of the catalyst. Weakening the interaction favors higher reducibility of the catalyst, while strengthening the interaction favors robust catalyst stability. A high degree of strong metal-support interaction (SMSI) had a substantial suppressive consequence on methanation activity in general, whereas a low degree of SMSI enabled the improvement of the selectivity and also stability of CO methanation [127]. Therefore,

**Table 2 – Dispersion of metal of mono- and bimetallic catalyst of Ni-Co/SiC. Adapted from Yu, Jin [57].**

Catalyst	Metal Dispersion (%)
Ni/SiC	6.96
8Ni2Co/SiC	8.19
6Ni4Co/SiC	10.50
4Ni6Co/SiC	8.98
2Ni8Co/SiC	7.06
Co/SiC	3.84



**Fig. 5 – The catalytic activity of mono- and bimetallic catalysts with varying Ni:Co ratios in the methanation of CO process. (a) CO conversion and (b) CH<sub>4</sub> selectivity. Reaction condition: P = 20 bar, and ratio of H<sub>2</sub>/CO = 3. Adapted from Yu, Jin [57].**

finding the optimum condition for the catalyst is needed for optimum results.

Bimetallic catalysts recently demonstrated strong catalytic capabilities owing to enhanced interaction of metal support and electronic influence as the second metal promoters could boost the interactivity between the loaded metal and catalyst support [128]. The second metal was put onto Ni-based catalyst was widely investigated since Ni is known as the best metal for the methanation process, but further improvement is needed, especially in Ni-support interaction [129]. The robust interactivity between Ni particle and the support consequences in additional activated H atoms and endorses the creation of activated CH\* species, which are essential intermediates in the methanation of CO [130]. This increases the CO conversion into CH<sub>4</sub> and reduces the formation of deposition of carbon, which is detrimental to the catalytic reactions [130]. Furthermore, because of the strong Ni-support connection, the catalyst is exceptionally resilient to the sintering of Ni particles during the catalytic processes [130].

The addition of a second metal (Mo, La, or Fe) to a mesoporous silica Ni/SBA-15 catalyst was investigated by Tao, Zhou [65], and it was discovered that the metal improved the interactivity of nickel with the support, thereby inhibiting the accumulation of nickel species during heat treatment and further increasing the sintering resistance of the catalysts. The CO conversion and CH<sub>4</sub> selectivity of Mo–Ni/S5–CA catalyst were 98.7% and 91.9%, respectively, at a reaction temperature of 250 °C. As an added bonus, the catalytic activity of Mo–Ni/S15-CA was nearly unchanged after being calcined at 700 °C for 2 h, demonstrating a significant improvement in sintering resistance as a result of the synergistic outcome of the improvement of the metal-support interactivity and the confinement effect of support [65]. Kathiraser, Ashok [113] added Fe onto Ni/SBA-15 and reported that there is a consistent distribution of bimetallic Ni–Fe species with significant metal–support interactivities on the mesoporous SBA-15 support. Al<sub>2</sub>O<sub>3</sub> is used to alter the surface of SiC in order to improve the interactions concerning the metal and the support and to prevent the active constituent of nickel from sintering or to lose its shape throughout the reaction process [131]. Firm metal-support contact reduces the Ni particle's movement and flexibility, which further

enhances the anti-sintering capabilities of the compound. As the Ni atoms move through the support, they come into contact with other particles and combine to generate larger particles. The robust contact between Ni and its supporting materials can reduce the movement of Ni atoms on the supporting materials and hence prevent Ni from sintering. As a result, the robust metal-support contact contributes to the stabilization of Ni particles' excellent dispersion and the preservation of catalytic activity even after prolonged exposure to high temperatures [132]. Strong metal-support interactions could efficiently increase electron transport between metal and support, resulting in a stable catalytic capability for the metal and support [125]. While robust metal-support interactivity favor the anti-sintering ability for Ni-based catalyst, weakening the metal-support interaction is desired for low temperature methanation. Meng, Zhong [61] investigated methanation at low temperatures using a Ni–Fe/Al<sub>2</sub>O<sub>3</sub> catalyst, and their findings discovered that the adding of Fe improved the catalytic capabilities of the catalyst at low temperatures, but that the addition of Fe decreased the interactivity between nickel and support. A boost in iron content significantly increased CO conversion, with the maximum conversion achieved with a catalyst having 4% iron content, which had remarkable CO conversion and CH<sub>4</sub> yield, with 97.2% conversion and 84.9%, correspondingly [61].

In the case of molybdenum promoter, several reports conveyed that Mo can either weaken or boost the interactivity between the first metal and the support. Chen, Tian [133] stated that the Mo promoter's addition decreases the NiO and the support interaction but improved the dispersion of NiO. MoO<sub>3</sub> can be utilized to reduce the NiO species and the SiO<sub>2</sub> support interaction, hence enhancing the reducibility of the Ni–SiO<sub>2</sub> catalyst [58]. Then, Zhang, Xin [134] impregnated Mo onto Ni/MCM-41 and find out that the incorporation of MoO<sub>3</sub> enhanced the interactivity between the nickel and the MCM-41 support, making the catalyst hard to sinter. Two different phenomena happen with different support, which is SiO<sub>2</sub> and MCM-41. By adding MoO<sub>3</sub>, both supports displayed different results in their Ni-support interaction and also their reducibility. Hence, further investigation was needed onto Mo as second metal to further describe its role in metal-support interactivity.



In general, the strength of the electronic metal-support contact is directly associated to the stability of the catalyst, but it is inversely proportional to the reducibility of the catalyst. The stability of the catalyst is improved by increasing the critical metal-support interaction, so minimizing the sintering of the metal while decreasing the likelihood of the metal being reduced in the process. As a result, depending on the final qualities that the catalyst is intended to achieve, the metal-support interaction might be weakened or strengthened. In accordance with the explanations provided above, a second metal can both improve and weaken the interactivity between the metal and the support. Increased reducibility of the catalyst is favored by weakening the interaction, whereas increased catalytic stability is favored by strengthening the interactions.

#### *Metal-metal interaction*

In the earlier section on the dispersion discussion, we discussed that metal-metal interaction correlates directly with dispersion—the higher metal-metal interaction consequences in better dispersion of the active metal. Depending on the specific relations between metal species in bimetallic catalysts, the adsorption characteristics of CO and hydrogen can be vastly different. Increased activity and improved anti-sintering ability may be facilitated by the interaction between the two metals, according to some researchers. One possible explanation for the synergistic interaction between the two metals is that one of the metals provides physical promotion to the other metal. The other type of transfer involves electron transmission from one of the metal active sites to the other metal active site [135]. The Ru addition to Ni/SiO<sub>2</sub> catalysts for the CO<sub>2</sub> reforming of methane reaction was investigated by Crisafulli, Scire [119], and they found out that a strong Ni and Ru interaction increased the metallic Ni dispersion, which then favored the development of additional reactive transitional carbonaceous species, thereby overpowering the inactivation of the catalyst. Yu, Jin [57] conducted a comparison of their monometallic Ni and bimetallic Ni–Co catalysts and found that the interactivity between Ni and Co may enhance the CO adsorption and its activation, hence increasing the bimetallic methanation catalysts activity. Strong metal-metal interaction adds to the stagnant reduction rate of metal oxide as well as increased Co relocation to Ni, resulting in the development of homogeneous Ni–Co alloy when the reduction of metal oxide is completed [67,98].

When using bimetallic catalysts, the interactions between metal species frequently result in profoundly distinct CO and H<sub>2</sub> adsorption characteristics. It was discovered that the bimetallic Ni–Fe or Co–Fe catalysts reduction frequently occurs at substantially lower temperatures than the reduction of monometallic Fe catalysts [136]. By increasing the Fe amount (3–10 wt%), the methanation activity enhanced noticeably at lower temperatures, particularly for the 7 wt% Fe content catalyst, which also demonstrated outstanding stability and constancy. This enhancement can be attributed to the cooperative effect amongst two metals as well as the ability to reduce materials with ease [137].

#### *The basicity and oxygen vacancies*

A clear association between basicity and catalyst activity has been demonstrated in the literature, establishing a direct relationship between CO adsorption on basic sites and the CO methanation catalyst activity in the existence of basic sites. Basicity plays a central role in the CO methanation based on Teh, Triwahyono [138] study. It is reported that advanced catalytic capability of CO<sub>2</sub> methanation results from a large proportion of basic sites and the occurrence of defects sites or oxygen vacancies [139]. In another study, basic sites were documented as necessary for refining the reactivity of CO<sub>2</sub> methanation [140]. The generation of surface defects, especially oxygen vacancies, acts as a vital active site for the absorption of CO and H<sub>2</sub> molecules, and many other catalytic reactions are essential to influence the activity of catalyst [140].

One of the efficacious ways to boost catalytic activity is to tailor the surface morphology of the catalyst. He, Li [141] reported the formation of Ni nanoparticles on a hierarchical Al<sub>2</sub>O<sub>3</sub> matrix in the shape of a flower. During CO<sub>2</sub> methanation, surface defect-promoted Ni nanocatalyst proved to show excellent performance and stability, and this is due to the existence of the abundant surface vacancy. The surface vacancy serves as active sites, and the combination produced an anchoring effect that leads to sintering and accumulation resistance of active species during long-standing use. The presence of oxygen vacancy on the support is essential in multiple studies to improve methanation's catalytic activity. Zhu, Razzaq [142] studied CO methanation in coke oven gas using Co<sub>3</sub>O<sub>4</sub> catalysts at low temperature and found that Co<sub>3</sub>O<sub>4</sub> catalysts with smaller particles have higher methanation activity than the larger particles due to higher CO adsorption capacity. Creating an oxygen vacancy will lead to unpaired electrons residual and pulled in the catalyst in a very strong Lewis base. In theory, it is possible to increase the reactivity if there is an increase in the basicity [143].

Several works of literature reported that adding second metal enhanced catalyst basicity. Branco, Brito [60] studied the effects of adding lanthanides (La, Ce, Pr, Sm, Dy, and Yb) to the formulation of Ni-supported SiO<sub>2</sub> catalysts, and they found out that the catalyst increases in basicity, which then increases the methanation activity. The lanthanides were responsible for significantly improving the catalytic performance due to enhancing nickel reducibility and dispersion and increasing basic properties. Pr has been described as the most excellent promoter of all. Liang, Hu [144] studied the impact of adding alkaline earth metal to Ni/Al<sub>2</sub>O<sub>3</sub> for CO<sub>2</sub> methanation. They discovered that the Sr species-modified catalyst displayed more basicity, which generating a Lewis basic site capable of sturdily adsorbing and activating gaseous CO<sub>2</sub>. Lanthanides, such as Ce, provide a catalyst with intermediate strength basic sites (Lewis acid-base pairs), which can increase CO adsorption and stimulate the hydrogenation of the CO by the catalyst. Hamid, Jalil [145] arranged Ni–V<sub>2</sub>O<sub>5</sub>/KCC-1 for CO<sub>2</sub> methanation and revealed that the adding of V<sub>2</sub>O<sub>5</sub> boosted the catalyst's basicity. Qin, Wang [135] added 2% of Y into Co/TiO<sub>2</sub>, and it improves the basicity from 65 μmol g<sup>-1</sup> to 98 μmol g<sup>-1</sup>. Moreover, the total basicity of TiO<sub>2</sub> amplified from 32 to 65 μmol g<sup>-1</sup> after adding Co,

demonstrating that the Co also enlarged the surface basicity of the TiO<sub>2</sub>.

Increased basicity, as previously noted, is associated with oxygen vacancies, which further promote CO adsorption and activation. Numerous researches have demonstrated that active oxygen sites, known as oxygen vacancies, can operate as active spots for CO and hydrogen molecule adsorption and can also cooperate with active metals to enhance the catalyst's performance [140,146]. Oxygen vacancies serve as an activated phase and activator for the CO and H<sub>2</sub> activation, initiating the process that consequences in the formation of C\* or CO\* species. In the existence of H<sub>2</sub>, an upsurge in oxygen vacancy may promote these C\* or CO\* molecules to hydrogenates. Jia, Zhang [147] explained how the development or fulfill of oxygen vacancies with an electron would have a noteworthy impact on these active sites' electronic density. Through the release of adsorbed CO<sub>2</sub>, active CO<sub>2</sub> can furnish the adsorbed O<sub>2</sub><sup>-</sup> species by filling oxygen vacancies created by the adsorbed CO. The same was valid for activated CO in the case of CO methanation. In a nutshell, the development of strongly basic adsorbed O<sub>2</sub> as an outcome of the rise in oxygen vacancies is amongst the features that promote the greatly increased reactivity of the catalyst in methanation.

A recent study by Hussain, Jalil [148] examined the thermodynamics and mechanistic of methanation of CO using FSZSM-5 catalysts and discovered that the generation of an oxygen vacancy activated two unpaired electrons on the exterior of the catalyst. This enables catalysts to function as a robust Lewis base, allowing them to cooperate with the gas molecules of CO in an active manner. So, the capability of the basic exterior to donate electrons in the presence of CO molecules will intensify the capabilities and activity of the catalyst. As a result, it has been discovered that there is a very close association concerning basicity and the oxygen vacancies in catalysts; the greater the number of oxygen vacancies present on the catalyst, the sturdier the basicity of the catalyst, which might increase the catalytic capabilities of the catalyst. Ashok, Ang [149] investigated the methanation of nickel supported on CeZrO<sub>2</sub> in their research. They hypothesized that nickel ions (Ni<sup>2+</sup>) are integrated into the mixed oxide lattice, causing oxygen vacancies to form and so increasing the adsorption of oxygenating species.

Several reports confirmed that adding the second metal improves the amount of oxygen vacancies. Liang, Hu [144] investigate adding Sr onto Ni/Al<sub>2</sub>O<sub>3</sub> and found out that the oxygen vacancies generated by the catalyst modified with Sr species prohibit electrons from being coupled, resulting in the formation of a Lewis basic state in the reaction. Afterward, it was discovered that by including V<sub>2</sub>O<sub>3</sub> as a second metal to a Ni-based catalyst, the oxidation-reduction cycle of V<sub>2</sub>O<sub>3</sub> could boost the oxygen vacancies, which improved the CO<sub>2</sub> by-product dissociation and created surface oxygen, thereby restricting carbon accumulation on the Ni particles [150]. Furthermore, Tian, Liu [151] observed that the addition of 3% VO<sub>x</sub> consequences in a significant upsurge in the amount of lattice oxygen atoms in the Ni/MCF catalyst. Y, as a catalytic promoter, has been extensively used with TiO<sub>2</sub> support [152,153] for the reason that the atomic radius of Y<sup>3+</sup> (90 p.m.) and Ti<sup>4+</sup> (60.5 p.m.) are somewhat dissimilar, Y<sup>3+</sup> possibly might be doped into the crystal lattice of TiO<sub>2</sub>, and extra

oxygen vacancies on the TiO<sub>2</sub> external are produced [135], which will boosted the catalytic capabilities of CO methanation. The existence of oxygen vacancies may cause gaseous CO to be strongly adsorbed and activated, hence increasing the catalytic activity for the methanation of CO.

### Reducibility

It is widely established that the reducibility of metal oxides is critical for any catalyst to function as an active site. Kustov, Frey [59] reported that the methanation activity enhanced with increasing metal concentrations, and these results could be accredited to higher reducibility. As discussed before, robust metal-support interaction is directly proportional to the catalyst's stability but inversely proportional to the catalyst's reducibility. Weakening the interaction favors higher reducibility of the catalyst, while strengthening the interaction favors robust catalyst stability. Hence, it can be concluded that high reducibility favors lower reaction temperature while low reducibility with excellent stability favors high-temperature reaction. As demand for the low-temperature catalyst is increasing since it can significantly cut costs, reducibility at low-temperature catalysts is needed.

Literature suggests that the incorporation of second metal could improve the first metal's reducibility. Ni-based catalyst is the most extensively researched catalyst in this aspect since Ni's reducibility is crucial for enhancement in catalytic activity. Rahmani, Meshkani [115] confirmed that the incorporation of second metals (Ce, La, Fe, and Co) to Ni/γ-Al<sub>2</sub>O<sub>3</sub> increased the reducibility of a nickel catalyst. Additionally, the adding of 10 wt% La to the 20 wt% Ni/γ-Al<sub>2</sub>O<sub>3</sub> amplified the CO<sub>2</sub> conversion from 42% to 80.3% [115]. Lu, Yang [120] investigated the same metal and found that adding trace amounts of the same metal to a Ni catalyst supported on ZrO<sub>2</sub> improved the NiO particles dispersion, improved the amount of reduced active Ni in the catalyst, and amplified the thermal steadiness for CO and CO<sub>2</sub> methanation. The surface enrichment of Co and the great dispersion of metals on the catalyst 7Ni3Co/LaAl may help to promote the reducibility of nickel species and the creation of surface's active sites on the catalyst, both of which are beneficial [154].

Ren, Qin [53] described that the Fe addition enhanced the dispersion and reduction degree of Ni while Meng, Zhong [61] results displayed that the introduction of Fe decreased the reduction temperature. As illustrated in Fig. 6 that the peaks of reduction of 16Ni<sub>x</sub>Fe/Al<sub>2</sub>O<sub>3</sub> were shifted to lower temperatures after the iron addition. The overall area of reduction peak improved progressively with the upsurge in iron quantity, demonstrating that the iron addition enabled and simplified the catalysts reduction. Catalyst 16Ni<sub>4</sub>Fe/Al<sub>2</sub>O<sub>3</sub> with the 4% Fe content displayed the greatest catalytic capabilities, which the CO conversion and the CH<sub>4</sub> yield reached 97.2% and 84.9%, correspondingly. The iron addition, it is hypothesized in this study, interrupted the interactivity between nickel and the support, altered the chemical characteristics of iron and nickel species on the catalyst surface, and so increased the quantity of reduction species produced. Results showed that incorporating the metal (Fe, La, Cu, Co, and Zr) into the catalyst led to improved reducibility and reduced NiO species at lower temperatures [137].

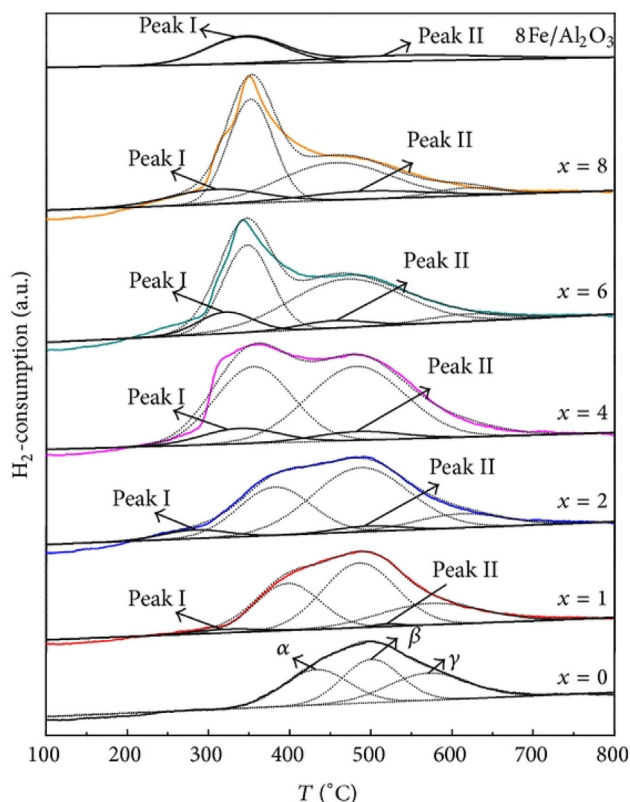


Fig. 6 – H<sub>2</sub>-TPR profiles of catalysts 16NiFe/Al<sub>2</sub>O<sub>3</sub>. Adapted from Meng, Zhong [61].

### Mechanism of CO methanation over bimetallic catalysts

Among the most widely used catalytic processes are hydrogenations, which can be found in a variety of applications extending from simple steps in organic chemical synthesis to batch procedures in medical drugs manufacture, stabilization of edible oils, and petroleum progression. Considering that hydrogenation processes are often exothermic in nature, it is preferable to carry out these processes at relatively low temperatures. Despite this, the mechanism of hydrogenation, particularly CO methanation, is still up for debate among scientists today.

CO methanation is thoroughly associated with Fischer-Tropsch Synthesis (FTS), which converts a mixture of CO and H<sub>2</sub> into heavier hydrocarbons in the form of liquid. The CO methanation mechanism can therefore be demonstrated under the FTS mechanism. When it comes to the first and rate-determining step of these two reactions, which is the cleavage of the C–O bond, the basic mechanism of both reactions is the same. The following phase takes place in two separate ways: C–H bond creation occurs during the methanation process, and C–C bond formation occurs during the FTS reaction, which is used to lengthen the carbon chain.

In the late 1970s, two dissimilar types of methanation methods were proposed, as shown in Fig. 7. One mechanism suggests that CO dissociation is directly followed by hydrogenation to produce the CH<sub>x</sub> species, which involves the direct

dissociation of the adsorbed CO<sub>ads</sub> and the formation of C<sub>ads</sub> as the intermediate.

The other mechanism suggests that the CO dissociation proceeds through the hydrogen-assisted intermediates (shown in Fig. 8), which involves the combination of H<sub>ads</sub> with CO<sub>ads</sub> to form the COH<sub>ads</sub>, CHO<sub>ads</sub>, or CHOH<sub>ads</sub> intermediates. In general, the rate-limiting step is the initial hydrogenation step, with the O1 and C4 atoms (terminal atoms) being preferred kinetically in a Markovnikov fashion. In spite of the higher adsorption of the C=C bond, the decrease of the C=O link is associated with lower energy barriers in the vast majority of situations.

As claimed by studies, the barrier to dissociation of CO and the stability of the major intermediates on the metal surface are the primary aspects affecting the methanation catalyst's activity [155]. The surface's active sites could be built by combining two metals in order to obtain the optimum CO dissociative adsorption energy on the surface of the metal [59].

The bimetallic catalyst reaction pathway is the same as the mono-metallic catalyst pathway. However, it changes the value of energy and rate in the mechanism. Examples incorporate the work of Qiu, Tao [156], who investigated the methanation of CO mechanism over Co–Cu and Cu surfaces and discovered that the best reaction route for methane formation from CO on Co–Cu surfaces is identical to that on the surface of Cu. On the other hand, the rate-limiting phase and its related energy barrier are distinct. When employed in combination with the Co dopant, it is possible to alter the rate-limiting step and lower the activation barrier. It is noteworthy to mention that the barrier for the H<sub>2</sub>COH breakdown was reduced from 100.96 kJ/mol to 61.26 kJ/mol, a significant reduction. As a result, as compared to the Cu surface, the Co–Cu exterior can increase the efficiency and selectivity toward methane. Xu, Lian [157] conducted a kinetic investigation on the impact of Co–Ni bimetallic synergy in enhancing the low-temperature catalytic activity of OMA-2Co8Ni, and their Arrhenius plots are shown in Fig. 9.

The slope of the reaction rate of OMA-2Co8Ni catalyst is significantly less than that over the OMA-10Ni as well as OMA-10Co, indicating that OMA-2Co8Ni with activation energy of 64.7 kJ/mol has significantly lower apparent activation energy than the monometallic catalysts OMA-10Ni with activation energy of 75.2 kJ/mol and OMA-10Co with activation energy of 79.0 kJ/mol. These consequences showed that the synergetic effect of Ni and Co can effectively reduce the apparent activation energy of methanation processes.

Wang, Su [158] investigated the CO methanation mechanism on both monometallic Ni and bimetallic Ni–Fe supported on Al<sub>2</sub>O<sub>3</sub> catalysts and discovered that CO directly dissociation is not preferred on either of the two catalysts under investigation. They also pointed out that the uppermost barrier for converting CO to CH<sub>4</sub> for the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst is 2.54 eV, but the highest barrier for the Ni<sub>3</sub>Fe/Al<sub>2</sub>O<sub>3</sub> catalyst is 2.14 eV, which is lower, resulting in increased efficiency and selectivity of CH<sub>4</sub> for CO methanation. The Ni–Co catalyst follows a conventional reaction path: first, the C–O link of CHO is broken, and next, hydrogenation of C–H occurred to create CH<sub>4</sub>. Nevertheless, in the case of monometallic Ni/SiO<sub>2</sub>, initially, the CHO interacts with \*H to create CHOH, after which the C–O bond breaks and methane is generated [159].

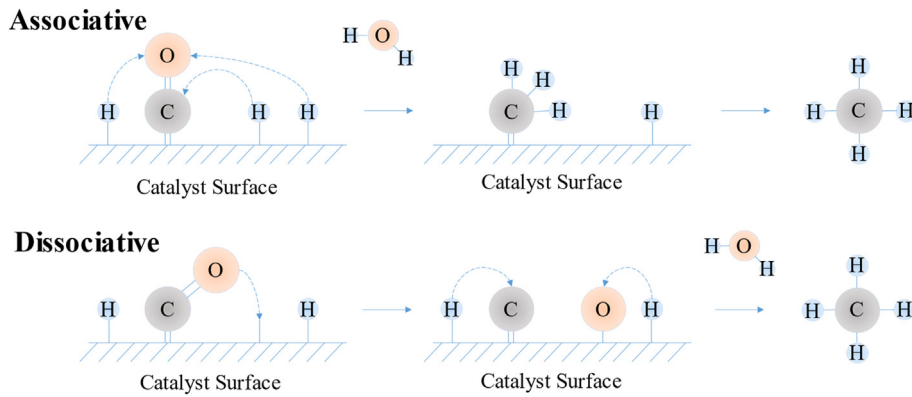


Fig. 7 – Mechanism of CO methanation. Modified from Miao, Ma [20].

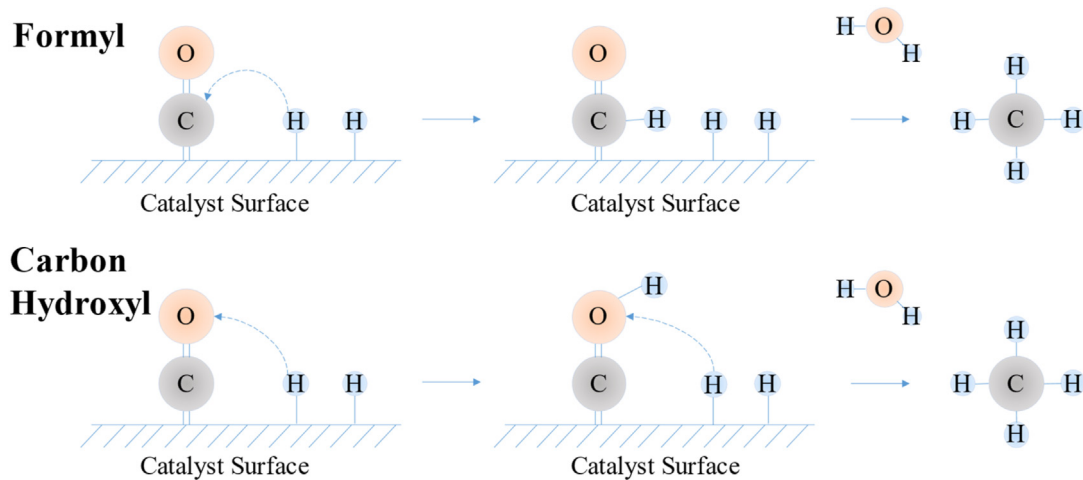


Fig. 8 – Two routes of associative mechanism. Modified from Miao, Ma [20].

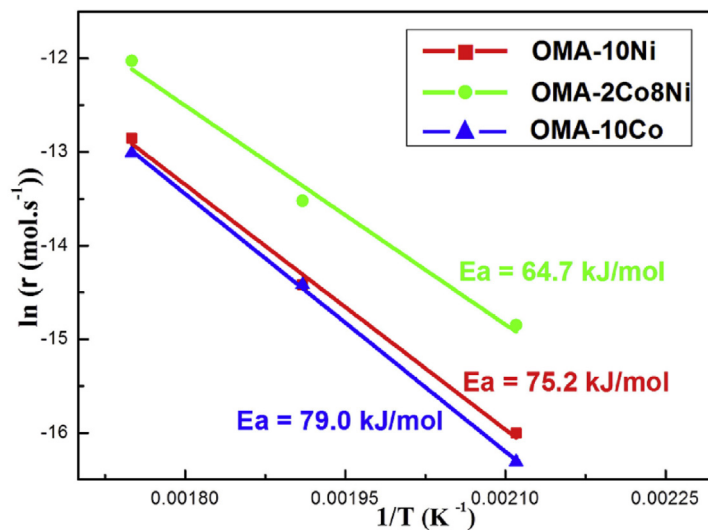


Fig. 9 – Arrhenius plots for the CO<sub>2</sub> reaction rate over OMA-CoNi catalyst. Adapted from Xu, Lian [157].

Tian, Liu [151] then shown that VO<sub>x</sub> (vanadium oxide) can upsurge the electron density of Ni, ensuing in higher C–O bond dissociation and enhanced catalytic capability of the catalysts. The V<sup>3+</sup>, V<sup>4+</sup>, and V<sup>5+</sup> coexist on the Ni–V/MCF

catalyst, allowing for a rise in the Ni electron density via redox of V<sup>5+</sup>/V<sup>4+</sup>/V<sup>3+</sup>. The oxidation-reduction cycle of V<sub>2</sub>O<sub>3</sub> has also been shown to produce oxygen vacancies, which enhances CO<sub>2</sub> dissociation and generates surface oxygen, hence



avoiding carbon deposition on the Ni atoms during CO methanation [145,150]. Guo, Gao [160] investigated the in situ DRIFTS measurements and DFT calculations for the NiMgAl catalyst and discovered that the MgO and additional Ni(111) activated sites in the NiMgAl catalyst might encourage CO<sub>2</sub> activation and the formation of active intermediates, which contributed significantly to the improvement of the low-temperature activity. Enhancing CO<sub>2</sub> activation is also critical because it prevents the accumulation of CO<sub>2</sub> byproducts, which promotes CH<sub>4</sub> selectivity.

Based on the results of CO methanation mechanism studies for bimetallic catalysts, we suggest that the key to reducing activation energy and therefore increasing CO methanation performance is to add additional metals to upsurge the quantity of active metals. A considerable range of bimetallic catalysts developed exhibited vigorous CO methanation activity, thereby confirming the premise.

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## Conclusion and future prospects

In conclusion, we highlighted current advances in the area of bimetallic carbon monoxide catalysts for SNG production, as well as their synthesis procedure and physicochemical characteristics. Due to the significant exothermic features of methanation, it is critical to discover methanation catalysts with extraordinary activity at low temperatures and exceptional stability at high temperatures. The results of the bimetallic catalyst synthesis investigation suggested that different varieties of catalysts required unique synthesis approaches to optimize their methanation characteristics and capabilities.

An additional metal has little effect on the morphology of the catalyst, indicating that it is distributed evenly inside its channels. An appropriate amount of extra metal increased the surface area, porosity, dispersion, and particle size of the catalyst. According to our findings, it is critical to determine an adequate amount of second metal loading to minimize metallic particle aggregation and accumulation on the catalyst's exterior, which would degrade the catalyst's physical capabilities. Additionally, the bimetallic catalyst has the ability to strengthen or diminish the metal-support interaction. As previously stated, strong metal-support interaction is directly proportional to the catalyst's stability but inversely proportional to the catalyst's reducibility. Thus, it may be determined that high reducibility favors lower reaction temperatures, whereas low reducibility combined with strong stability favours higher reaction temperatures. Thus, selecting the appropriate second metal and its quantity is critical for managing the catalyst's metal-support interaction and maximizing methanation effectiveness at the stipulated temperature. Basicity and oxygen defects are associated with enhanced CO adsorption and activation, and it should be highlighted that by adding a second metal with high basicity, a greater concentration of Lewis's basic state can be generated, resulting in increased reaction effectiveness.

Bimetallic catalysts remain a mystery despite a variety of methodologies and promises, and further research is needed to discover whether or if their properties can be further improved. The scalability of renewable energy production

necessitates catalysts with high capacity, selectivity, and durability. In the case of CO methanation catalysts, the anticipated trade-off between cost and performance can be resolved by developing bimetallic catalysts with optimal second metal synergy.

As far as we are aware, research into bimetallic catalysts for CO methanation is currently limited and inadequate. There are so many different effects that can be induced by bimetallic system creation that each system must be thoroughly examined, and fundamental studies are required to better understand the promoter's effects and its interaction with the main metal. The synergy exhibited between bimetallic catalysts' components is still poorly understood. A better understanding will only be possible with additional in situ spectroscopic studies and advanced characterization of the bimetallic catalysts. Better catalysts can be developed using this information, current catalyst drawbacks can be overcome, and deactivation during catalytic processes which the most pressing issue can be understood.

Apart from bimetallic catalysts, additional metals such as trimetallic catalysts should be investigated. Alkali, alkaline-earth and the majority of rare earth elements have not yet been discovered as CO methanation promoters. Additionally, it is critical to have a detailed understanding of the underlying reaction process in order to foresee the optimal metal for a particular metal-based catalyst, as different metals have varying synergistic effects with one another. Recent improvements in this catalyst may shed light on how the efficacy of bimetallic and monometallic catalysts differs, enabling the development of catalysts with the best possible future performance.

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## Declaration of competing 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.

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## REFERENCES

- [1] Kidnay AJ, Parrish WR, McCartney DG. *Fundamentals of natural gas processing*. CRC press; 2019.
- [2] Bekhet HA, Matar A, Yasmin T. CO<sub>2</sub> emissions, energy consumption, economic growth, and financial development in GCC countries: dynamic simultaneous equation models. *Renew Sustain Energy Rev* 2017;70:117–32.
- [3] Safari A, Das N, Langhelle O, Roy J, Assadi M. Natural gas: a transition fuel for sustainable energy system transformation? *Energy Science & Engineering* 2019;7:1075–94.

- [4] Kopyscinski J, Schildhauer TJ, Biollaz SMA. Production of synthetic natural gas (SNG) from coal and dry biomass - a technology review from 1950 to 2009. *Fuel* 2010;89:1763–83.
- [5] Stephens E, Ross IL, Mussnug JH, Wagner LD, Borowitzka MA, Posten C, et al. Future prospects of microalgal biofuel production systems. *Trends Plant Sci* 2010;15:554–64.
- [6] Gong DD, Li SS, Guo SX, Tang HG, Wang H, Liu Y. Lanthanum and cerium co-modified Ni/SiO<sub>2</sub> catalyst for CO methanation from syngas. *Appl Surf Sci* 2018;434:351–64.
- [7] Peng WX, Wang LS, Mirzaee M, Ahmadi H, Esfahani MJ, Fremaux S. Hydrogen and syngas production by catalytic biomass gasification. *Energy Convers Manag* 2017;135:270–3.
- [8] Leonzio G. Process analysis of biological Sabatier reaction for bio-methane production. *Chem Eng J* 2016;290:490–8.
- [9] Ronsch S, Schneider J, Matthischke S, Schluter M, Gotz M, Lefebvre J, et al. Review on methanation - from fundamentals to current projects. *Fuel* 2016;166:276–96.
- [10] Nguyen TTM, Wissing L, Skjoth-Rasmussen MS. High temperature methanation: catalyst considerations. *Catal Today* 2013;215:233–8.
- [11] Gao JJ, Liu Q, Gu FN, Liu B, Zhong ZY, Su FB. Recent advances in methanation catalysts for the production of synthetic natural gas. *RSC Adv* 2015;5:22759–76.
- [12] Giorgianni G, Mebrahtu C, Schuster ME, Large AI, Held G, Ferrer P, et al. Elucidating the mechanism of the CO<sub>2</sub> methanation reaction over Ni-Fe hydrotalcite-derived catalysts via surface-sensitive in situ XPS and NEXAFS. *Phys Chem Chem Phys* 2020;22:18788–97.
- [13] Cheng CB, Shen DK, Xiao R, Wu CF. Methanation of syngas (H<sub>2</sub>/CO) over the different Ni-based catalysts. *Fuel* 2017;189:419–27.
- [14] Munoz-Murillo A, Martinez LM, Dominguez MI, Ordiozola JA, Centeno MA. Selective CO methanation with structured RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. *Appl Catal B Environ* 2018;236:420–7.
- [15] Lin XH, Lin LL, Huang K, Chen X, Dai WX, Fu XZ. CO methanation promoted by UV irradiation over Ni/TiO<sub>2</sub>. *Appl Catal B Environ* 2015;168:416–22.
- [16] Yan XL, Liu Y, Zhao BR, Wang Z, Wang Y, Liu CJ. Methanation over Ni/SiO<sub>2</sub>: effect of the catalyst preparation methodologies. *Int J Hydrogen Energy* 2013;38:2283–91.
- [17] Barrientos J, Lualdi M, Boutonnet M, Jaras S. Deactivation of supported nickel catalysts during CO methanation. *Appl Catal a-Gen.* 2014;486:143–9.
- [18] Tao M, Meng X, Lv YH, Bian ZC, Xin Z. Effect of impregnation solvent on Ni dispersion and catalytic properties of Ni/SBA-15 for CO methanation reaction. *Fuel* 2016;165:289–97.
- [19] Hou ZY, Gao J, Guo JZ, Liang D, Lou H, Zheng XM. Deactivation of Ni catalysts during methane autothermal reforming with CO<sub>2</sub> and O<sub>2</sub> in a fluidized-bed reactor. *J Catal* 2007;250:331–41.
- [20] Miao B, Ma SSK, Wang X, Su HB, Chan SH. Catalysis mechanisms of CO<sub>2</sub> and CO methanation. *Catal Sci Technol* 2016;6:4048–58.
- [21] Wolf MP. Minimierung des Druckverlusts durch Optimierung der CO-Entfernungsstufe für ein stationäres PEM-Brennstoffzellenheizgerät. KIT Scientific Publishing; 2011.
- [22] Kalamaras CM, Efstathiou AM. Hydrogen production technologies: current state and future developments. *Conference Papers in Energy* 2013;2013:690627.
- [23] Cao Y, Gao Z, Jin J, Zhou H, Cohron M, Zhao H, et al. Synthesis gas production with an adjustable H<sub>2</sub>/CO ratio through the coal gasification process: effects of coal ranks and methane addition. *Energy Fuels* 2008;22:1720–30.
- [24] Wang H, Pei Y, Qiao M, Zong B. Advances in methanation catalysis. *Catalysis*, 29. The Royal Society of Chemistry; 2017. p. 1–28.
- [25] Sabatier P, Senderens JB. New methane synthesis. *C R Acad Sci Paris*; 1902. p. 134.
- [26] Omoregbe O, Danh HT, Nguyen-Huy C, Setiabudi HD, Abidin SZ, Truong QD, et al. Syngas production from methane dry reforming over Ni/SBA-15 catalyst: effect of operating parameters. *Int J Hydrogen Energy* 2017;42:11283–94.
- [27] Schaaf T, Grünig J, Schuster MR, Rothenfluh T, Orth A. Methanation of CO<sub>2</sub> - storage of renewable energy in a gas distribution system. *Energy, Sustainability and Society* 2014;4:2.
- [28] Liu SS, Jin YY, Han YH, Zhao JX, Ren J. Highly stable and coking resistant Ce promoted Ni/SiC catalyst towards high temperature CO methanation. *Fuel Process Technol* 2018;177:266–74.
- [29] Wang C, Zhai P, Zhang ZC, Zhou Y, Zhang JK, Zhang H, et al. Nickel catalyst stabilization via graphene encapsulation for enhanced methanation reaction. *J Catal* 2016;334:42–51.
- [30] Li SS, Gong DD, Tang HG, Ma Z, Liu ZT, Liu Y. Preparation of bimetallic Ni@Ru nanoparticles supported on SiO<sub>2</sub> and their catalytic performance for CO methanation. *Chem Eng J* 2018;334:2167–78.
- [31] Fischer F. Liquid fuels from water gas. *Ind Eng Chem* 1925;17:574–6.
- [32] Carvalho A, Ordonsky VV, Luo Y, Marinova M, Muniz AR, Marcilio NR, et al. Elucidation of deactivation phenomena in cobalt catalyst for Fischer-Tropsch synthesis using SSITKA. *J Catal* 2016;344:669–79.
- [33] Wang BW, Yao YQ, Jiang MH, Li ZH, Ma XB, Qin SD, et al. Effect of cobalt and its adding sequence on the catalytic performance of MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> toward sulfur-resistant methanation. *J Energy Chem* 2014;23:35–42.
- [34] Abdel-Mageed AM, Widmann D, Olesen SE, Chorkendorff I, Behm RJ. Selective CO methanation on highly active Ru/TiO<sub>2</sub> catalysts: identifying the physical origin of the observed activation/deactivation and loss in selectivity. *ACS Catal* 2018;8:5399–414.
- [35] Cheah KW, Taylor MJ, Osatiashtiani A, Beaumont SK, Nowakowski DJ, Yusup S, et al. Monometallic and bimetallic catalysts based on Pd, Cu and Ni for hydrogen transfer deoxygenation of a prototypical fatty acid to diesel range hydrocarbons. *Catal Today* 2020;355:882–92.
- [36] Wang AQ, Liu XY, Mou CY, Zhang T. Understanding the synergistic effects of gold bimetallic catalysts. *J Catal* 2013;308:258–71.
- [37] Yu WT, Porosoff MD, Chen JGG. Review of Pt-based bimetallic catalysis: from model surfaces to supported catalysts. *Chem Rev* 2012;112:5780–817.
- [38] Wang DS, Li YD. Bimetallic nanocrystals: liquid-phase synthesis and catalytic applications. *Adv Mater* 2011;23:1044–60.
- [39] Ferrando R, Jellinek J, Johnston RL. Nanoalloys: from theory to applications of alloy clusters and nanoparticles. *Chem Rev* 2008;108:845–910.
- [40] Sinfelt JH. Bimetallic catalysts. *Sci Am* 1985;253:90–&.
- [41] Schwank J. Bimetallic catalysts: discoveries, concepts, and applications XI+ 164. John H. Sinfelt, John Wiley & Sons; 1983. p. 1985.
- [42] Snider JL, Streibel V, Hubert MA, Choksi TS, Valle E, Upham DC, et al. Revealing the synergy between oxide and alloy phases on the performance of bimetallic in-Pd catalysts for CO<sub>2</sub> hydrogenation to methanol. *ACS Catal* 2019;9:3399–412.
- [43] Qin L, Zeng ZT, Zeng GM, Lai C, Duan AB, Xiao R, et al. Cooperative catalytic performance of bimetallic Ni-Au

- nanocatalyst for highly efficient hydrogenation of nitroaromatics and corresponding mechanism insight. *Appl Catal B Environ* 2019;259.
- [44] Mitsudome T, Miyagawa K, Maeno Z, Mizugaki T, Jitsukawa K, Yamasaki J, et al. Mild hydrogenation of amides to amines over a platinum-vanadium bimetallic catalyst. *Angew Chem Int Ed* 2017;56:9381–5.
- [45] Liao TW, Yadav A, Ferrari P, Niu YB, Wei XK, Vernieres J, et al. Composition-tuned Pt-skinned PtNi- bimetallic clusters as: highly efficient methanol dehydrogenation catalysts. *Chem Mater* 2019;31:10040–8.
- [46] Sun QM, Wang N, Fan QY, Zeng L, Mayoral A, Miao S, et al. Subnanometer bimetallic platinum-zinc clusters in zeolites for propane dehydrogenation. *Angew Chem Int Ed* 2020;59:19450–9.
- [47] Ma ZX, Wu ZW, Miller JT. Effect of Cu content on the bimetallic Pt-Cu catalysts for propane dehydrogenation. *Catal Struct React* 2017;3:43–53.
- [48] Kumar A, Yang XC, Xu Q. Ultrafine bimetallic Pt-Ni nanoparticles immobilized on 3-dimensional N-doped graphene networks: a highly efficient catalyst for dehydrogenation of hydrous hydrazine. *J Mater Chem* 2019;7:112–5.
- [49] Gaide T, Bianga J, Schlipkoter K, Behr A, Vorholt AJ. Linear selective isomerization/hydroformylation of unsaturated fatty acid methyl esters: a bimetallic approach. *ACS Catal* 2017;7:4163–71.
- [50] Jarvis JS, Harray JH, He P, Wang AG, Liu LJ, Song H. Highly selective aromatization and isomerization of n-alkanes from bimetallic Pt-Zn nanoparticles supported on a uniform aluminosilicate. *Chem Commun* 2019;55:3355–8.
- [51] Wang CZ, Tian YN, Wu RF, Li HT, Yao BZ, Zhao YX, et al. Bimetallic synergy effects of phyllosilicate-derived NiCu@SiO<sub>2</sub> catalysts for 1,4-butanediol direct hydrogenation to 1,4-butanediol. *ChemCatChem* 2019;11:4777–87.
- [52] Xiao YH, Shang JW, Zhai ML, Qiao CZ. Hydrodeoxygenation of fatty acid methyl esters and simultaneous products isomerization over bimetallic Ni-Co/SAPO-11 catalysts. *Int J Energy Res* 2021;45:9648–56.
- [53] Ren J, Qin X, Yang JZ, Qin ZF, Guo HL, Lin JY, et al. Methanation of carbon dioxide over Ni-M/ZrO<sub>2</sub> (M = Fe, Co, Cu) catalysts: effect of addition of a second metal. *Fuel Process Technol* 2015;137:204–11.
- [54] Pandey D, Deo G. Effect of support on the catalytic activity of supported Ni-Fe catalysts for the CO<sub>2</sub> methanation reaction. *J Ind Eng Chem* 2016;33:99–107.
- [55] Hammer B, Norskov JK. Theoretical surface science and catalysis - calculations and concepts. *Adv Catal* 2000;45:71–129.
- [56] Tada S, Kikuchi R, Takagaki A, Sugawara T, Oyarria ST, Urasaki K, et al. Study of Ru-Ni/TiO<sub>2</sub> catalysts for selective CO methanation. *Appl Catal B Environ* 2013;140:258–64.
- [57] Yu Y, Jin GQ, Wang YY, Guo XY. Synthesis of natural gas from CO methanation over SiC supported Ni-Co bimetallic catalysts. *Catal Commun* 2013;31:5–10.
- [58] Zhang JY, Xin Z, Meng X, Lv YH, Tao M. Effect of MoO<sub>3</sub> on structures and properties of Ni-SiO<sub>2</sub> methanation catalysts prepared by the hydrothermal synthesis method. *Ind Eng Chem Res* 2013;52:14533–44.
- [59] Kustov AL, Frey AM, Larsen KE, Johannessen T, Norskov JK, Christensen CH. CO methanation over supported bimetallic Ni-Fe catalysts: from computational studies towards catalyst optimization. *Appl Catal a-Gen.* 2007;320:98–104.
- [60] Branco JB, Brito PE, Ferreira AC. Methanation of CO<sub>2</sub> over nickel-lanthanide bimetallic oxides supported on silica. *Chem Eng J* 2020:380.
- [61] Meng FH, Zhong PZ, Li Z, Cui XX, Zheng HY. Surface structure and catalytic performance of Ni-Fe catalyst for low-temperature CO hydrogenation. *J Chem Neuroanat* 2014;2014.
- [62] Goula MA, Charisiou ND, Papageridis KN, Delimitis A, Pachatouridou E, Iliopoulou EF. Nickel on alumina catalysts for the production of hydrogen rich mixtures via the biogas dry reforming reaction: influence of the synthesis method. *Int J Hydrogen Energy* 2015;40:9183–200.
- [63] Yao DD, Yang HP, Chen HP, Williams PT. Co-precipitation, impregnation and so-gel preparation of Ni catalysts for pyrolysis-catalytic steam reforming of waste plastics. *Appl Catal B Environ* 2018;239:565–77.
- [64] Tang HG, Li SS, Gong DD, Guan Y, Liu Y. Bimetallic Ni-Fe catalysts derived from layered double hydroxides for CO methanation from syngas. *Front Chem Sci Eng* 2017;11:613–23.
- [65] Tao M, Zhou CL, Shi YQ, Meng X, Gu J, Gao WL, et al. Enhanced sintering resistance of bimetal/SBA-15 catalysts with promising activity under a low temperature for CO methanation. *RSC Adv* 2020;10:20852–61.
- [66] Tada S, Minori D, Otsuka F, Kikuchi R, Osada K, Akiyama K, et al. Effect of Ru and Ni ratio on selective CO methanation over Ru-Ni/TiO<sub>2</sub>. *Fuel* 2014;129:219–24.
- [67] Liu JG, Cao A, Si J, Zhang LH, Hao QL, Liu Y. Nanoparticles of Ni-Co alloy derived from layered double hydroxides and their catalytic performance for CO methanation. *Nano* 2016;11.
- [68] Kang SH, Ryu JH, Kim JH, Seo SJ, Yoo YD, Prasad PSS, et al. Co-methanation of CO and CO(2) on the Ni(X)-Fe(1-X)/Al(2)O(3) catalysts; effect of Fe contents. *Kor J Chem Eng* 2011;28:2282–6.
- [69] Xiao YS, Song YH, Liu C, Shi XY, Ge HQ, Zhu ML, et al. Balancing free and confined metallic Ni for an active and stable catalyst-A case study of CO methanation over Ni/Ni-Al<sub>2</sub>O<sub>3</sub>. *J Energy Chem* 2020;50:73–84.
- [70] Md Ali SA, Ku Hamid KH, Ismail KN. Effect of Ni/Co ratio on bimetallic oxide supported silica catalyst in CO<sub>2</sub> methanation. *Appl Mech Mater* 2015;802:431–6.
- [71] Sun JF, Ge CY, Yao XJ, Zou WX, Hong X, Tang CJ, et al. Influence of different impregnation modes on the properties of CuO-CeO<sub>2</sub>/gamma-Al<sub>2</sub>O<sub>3</sub> catalysts for NO reduction by CO. *Appl Surf Sci* 2017;426:279–86.
- [72] Deraz NM. The comparative jurisprudence of catalysts preparation methods: I. Precipitation and impregnation methods. *J Ind Eng Chem* 2018;2:19–21.
- [73] Guo M, Lu GX. The effect of impregnation strategy on structural characters and CO<sub>2</sub> methanation properties over MgO modified Ni/SiO<sub>2</sub> catalysts. *Catal Commun* 2014;54:55–60.
- [74] Shan WP, Liu FD, He H, Shi XY, Zhang CB. The remarkable improvement of a Ce-Ti based catalyst for NO<sub>x</sub> abatement, prepared by a homogeneous precipitation method. *ChemCatChem* 2011;3:1286–9.
- [75] Munnik P, de Jongh PE, de Jong KP. Recent developments in the synthesis of supported catalysts. *Chem Rev* 2015;115:6687–718.
- [76] Bhavani AG, Youn H. Effect of cerium loading on stability of Ni-bimetallic/ZrO<sub>2</sub> mixed oxide catalysts for CO methanation to produce natural gas. *Korean Chem Eng Res* 2018;56:269–74.
- [77] Razzaq R, Zhu HW, Jiang L, Muhammad U, Li CS, Zhang SJ. Catalytic methanation of CO and CO<sub>2</sub> in coke oven gas over Ni-Co/ZrO<sub>2</sub>-CeO<sub>2</sub>. *Ind Eng Chem Res* 2013;52:2247–56.
- [78] Qian K, Fang J, Huang WX, He B, Jiang ZQ, Ma YS, et al. Understanding the deposition-precipitation process for the



- preparation of supported Au catalysts. *J Mol Catal Chem* 2010;320:97–105.
- [79] Plomp AJ, van Asten DMP, van der Eerden AMJ, Maki-Arvela P, Murzin DY, de Jong KP, et al. Catalysts based on platinum-tin and platinum-gallium in close contact for the selective hydrogenation of cinnamaldehyde. *J Catal* 2009;263:146–54.
- [80] Deraz NM. The comparative jurisprudence of catalysts preparation methods: II. Deposition-precipitation and adsorption methods. 2018.
- [81] Le TA, Kim J, Kang JK, Park ED. CO and CO<sub>2</sub> methanation over Ni/Al@Al<sub>2</sub>O<sub>3</sub> core-shell catalyst. *Catal Today* 2020;356:622–30.
- [82] Zhang TF, Ai HM, Liu Q. La<sub>2</sub>O<sub>3</sub>-Promoted Ni/Al<sub>2</sub>O<sub>3</sub> catalyst for CO methanation: enhanced catalytic activity and stability. *Energy Technol-Ger.* 2019;7.
- [83] Brinker CJ, Scherer GW. *Sol-gel science: the physics and chemistry of sol-gel processing.* Academic press; 2013.
- [84] Bhagwat AD, Sawant SS, Ankamwar BG, Mahajan CM. Synthesis of nanostructured tin oxide (SnO<sub>2</sub>) powders and thin films by sol-gel method. *J Nano Electron Phys* 2015;7.
- [85] Bogatu C, Perniu D, Sau C, Iorga O, Cosnita M, Duta A. Ultrasound assisted sol-gel TiO<sub>2</sub> powders and thin films for photocatalytic removal of toxic pollutants. *Ceram Int* 2017;43:7963–9.
- [86] Mohammadi A, Ghorbani M. A facile particulate sol-gel route to synthesize nanostructured CoTiO<sub>3</sub> thin films and powders and their characteristics. *J Mater Sci Mater Electron* 2015;26:5251–61.
- [87] Xu J, Yang HB, Fu WY, Du K, Sui YM, Chen JJ, et al. Preparation and magnetic properties of magnetite nanoparticles by sol-gel method. *J Magn Magn Mater* 2007;309:307–11.
- [88] Cheng CB, Wu CF, Shen DK. Preparation of different nickel-iron/titania-alumina catalysts for hydrogen/carbon monoxide methanation under atmospheric pressure. *Energy Technol-Ger* 2017;5:1218–27.
- [89] Xu X, Megarajan SK, Zhang Y, Jiang HQ. Ordered mesoporous alumina and their composites based on evaporation induced self-assembly for adsorption and catalysis. *Chem Mater* 2020;32:3–26.
- [90] Fang XZ, Peng C, Peng HG, Liu WM, Xu XL, Wang X, et al. Methane dry reforming over coke-resistant mesoporous Ni-Al<sub>2</sub>O<sub>3</sub> catalysts prepared by evaporation-induced self-assembly method. *ChemCatChem* 2015;7:3753–62.
- [91] Li XY, Peng K, Dou YW, Chen JS, Zhang Y, An G. Facile synthesis of wormhole-like mesoporous tin oxide via evaporation-induced self-assembly and the enhanced gas-sensing properties. *Nanoscale Res Lett* 2018;13.
- [92] Brinker CJ, Lu YF, Sellinger A, Fan HY. Evaporation-induced self-assembly: nanostructures made easy. *Adv Mater* 1999;11:579.
- [93] Zhao LH, Fang KG, Jiang D, Li DB, Sun YH. Sol-gel derived Ni-Mo bimetallic carbide catalysts and their performance for CO hydrogenation. *Catal Today* 2010;158:490–5.
- [94] Shi WD, Song SY, Zhang HJ. Hydrothermal synthetic strategies of inorganic semiconducting nanostructures. *Chem Soc Rev* 2013;42:5714–43.
- [95] Ghods B, Rezaei M, Meshkani F. CO<sub>2</sub> methanation on nickel catalysts supported on mesoporous high-surface-area MgSiO<sub>3</sub>. *Chem Eng Technol* 2017;40:1861–6.
- [96] Liu Q, Tian YY. One-pot synthesis of NiO/SBA-15 monolith catalyst with a three-dimensional framework for CO<sub>2</sub> methanation. *Int J Hydrogen Energy* 2017;42:12295–300.
- [97] Meeyoo V, Panchan N, Phongruksathat N, Traitangwong A, Guo XP, Li CS, et al. Low temperature methanation of CO<sub>2</sub> on high Ni content Ni-Ce-ZrO delta catalysts prepared via one-pot hydrothermal synthesis. *Catalysts* 2020;10.
- [98] Zhao BR, Liu P, Li S, Shi HF, Jia XZ, Wang QQ, et al. Bimetallic Ni-Co nanoparticles on SiO<sub>2</sub> as robust catalyst for CO methanation: effect of homogeneity of Ni-Co alloy. *Appl Catal B Environ* 2020:278.
- [99] Kim JM, Kim SH, Park SY, Kim SS, Lee SJ. Effects of preparation conditions on the CO methanation performance of Co-Mo carbide catalysts. *Chem Eng Sci* 2019;209.
- [100] Jo SB, Chae HJ, Kim TY, Lee CH, Oh JU, Kang SH, et al. Selective CO hydrogenation over bimetallic Co-Fe catalysts for the production of light paraffin hydrocarbons (C-2-C-4): effect of H-2/CO ratio and reaction temperature. *Catal Commun* 2018;117:74–8.
- [101] Liu Q, Gu FN, Gao JJ, Li HF, Xu GW, Su FB. Coking-resistant Ni-ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst for CO methanation. *J Energy Chem* 2014;23:761–70.
- [102] Liu Q, Gao JJ, Zhang MJ, Li HF, Gu FN, Xu GW, et al. Highly active and stable Ni/gamma-Al<sub>2</sub>O<sub>3</sub> catalysts selectively deposited with CeO<sub>2</sub> for CO methanation dagger. *RSC Adv* 2014;4:16094–103.
- [103] Liu Q, Tian YY, Ai HM. Methanation of carbon monoxide on ordered mesoporous NiO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite oxides. *RSC Adv* 2016;6:20971–8.
- [104] Zhang Y, Yang HY, Liu Q, Bian B. MoO<sub>x</sub>-doped ordered mesoporous Ni/Al<sub>2</sub>O<sub>3</sub> catalyst for CO methanation. *Energy Technol-Ger.* 2020;8.
- [105] Liu Q, Gu FN, Wang XY, Jin GJ, Li HF, Gao F, et al. Facile synthesis of ordered mesoporous Ni-Zr-Al catalysts with high hydrothermal stability for CO methanation. *RSC Adv* 2015;5:84186–94.
- [106] Munirathinam R, Minh DP, Nzihou A. Effect of the support and its surface modifications in cobalt-based fischer-tropsch synthesis. *Ind Eng Chem Res* 2018;57:16137–61.
- [107] Xie XW, Shen WJ. Morphology control of cobalt oxide nanocrystals for promoting their catalytic performance. *Nanoscale* 2009;1:50–60.
- [108] Zhang TF, Liu Q. Mesoporous cellular foam silica supported bimetallic LaNi<sub>1-x</sub>CoxO<sub>3</sub> catalyst for CO<sub>2</sub> methanation. *Int J Hydrogen Energy* 2020;45:4417–26.
- [109] Ferreira AC, Branco JB. Methanation of CO<sub>2</sub> over nanostructured nickel-4f block element bimetallic oxides. *Int J Hydrogen Energy* 2019;44:6505–13.
- [110] Pandey D, Ray K, Bhardwaj R, Bojja S, Chary KVR, Deo G. Promotion of unsupported nickel catalyst using iron for CO<sub>2</sub> methanation. *Int J Hydrogen Energy* 2018;43:4987–5000.
- [111] Maki-Arvela P, Murzin DY. Effect of catalyst synthesis parameters on the metal particle size. *Appl Catal a-Gen.* 2013;451:251–81.
- [112] Mebrahtu C, Krebs F, Abate S, Perathoner S, Centi G, Palkovits R. Chapter 5 - CO<sub>2</sub> methanation: principles and challenges. In: Albonetti S, Perathoner S, Quadrelli EA, editors. *Studies in surface science and catalysis.* Elsevier; 2019. p. 85–103.
- [113] Kathiraser Y, Ashok J, Kawi S. Synthesis and evaluation of highly dispersed SBA-15 supported Ni-Fe bimetallic catalysts for steam reforming of biomass derived tar reaction. *Catal Sci Technol* 2016;6:4327–36.
- [114] Zaera F. Shape-controlled nanostructures in heterogeneous catalysis. *ChemSuschem* 2013;6:1797–820.
- [115] Rahmani S, Meshkani F, Rezaei M. Preparation of Ni-M (M: La, Co, Ce, and Fe) catalysts supported on mesoporous nanocrystalline gamma-Al<sub>2</sub>O<sub>3</sub> for CO<sub>2</sub> methanation. *Environ Prog Sustain* 2019;38:118–26.
- [116] Ahmad W, Younis MN, Shawabkeh R, Ahmed S. Synthesis of lanthanide series (La, Ce, Pr, Eu & Gd) promoted Ni/gamma-Al<sub>2</sub>O<sub>3</sub> catalysts for methanation of CO<sub>2</sub> at low



- temperature under atmospheric pressure. *Catal Commun* 2017;100:121–6.
- [117] Kudo A, Kato H. Effect of lanthanide-doping into NaTaO<sub>3</sub> photocatalysts for efficient water splitting. *Chem Phys Lett* 2000;331:373–7.
- [118] Wang L, Li DL, Koike M, Koso S, Nakagawa Y, Xu Y, et al. Catalytic performance and characterization of Ni-Fe catalysts for the steam reforming of tar from biomass pyrolysis to synthesis gas. *Appl Catal a-Gen.* 2011;392:248–55.
- [119] Crisafulli C, Scire S, Minico S, Solarino L. Ni-Ru bimetallic catalysts for the CO<sub>2</sub> reforming of methane. *Appl Catal a-Gen.* 2002;225:1–9.
- [120] Lu HL, Yang XZ, Gao GJ, Wang J, Han CH, Liang XY, et al. Metal (Fe, Co, Ce or La) doped nickel catalyst supported on ZrO<sub>2</sub> modified mesoporous clays for CO and CO<sub>2</sub> methanation. *Fuel* 2016;183:335–44.
- [121] Darouhegi R, Meshkani F, Rezaei M. Characterization and evaluation of mesoporous high surface area promoted Ni-Al<sub>2</sub>O<sub>3</sub> catalysts in CO<sub>2</sub> methanation. *J Energy Inst* 2020;93:482–95.
- [122] Zhou JY, Ma HF, Liu CX, Zhang HT, Ying WY. High temperature methanation over Ni catalysts supported on high surface area Zn<sub>x</sub>Mg<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub>: influence on Zn loading. *Int J Hydrogen Energy* 2019;44:13253–61.
- [123] Chen YZ, Wang CM, Wu ZY, Xiong YJ, Xu Q, Yu SH, et al. From bimetallic metal-organic framework to porous carbon: high surface area and multicomponent active dopants for excellent electrocatalysis. *Adv Mater* 2015;27:5010–6.
- [124] Tian DY, Liu ZH, Li DD, Shi HL, Pan WX, Cheng Y. Bimetallic Ni-Fe total-methanation catalyst for the production of substitute natural gas under high pressure. *Fuel* 2013;104:224–9.
- [125] Bian L, Zhao TT, Zhang LJ, Li ZH. Enhanced metal-support interaction on NiSi-P catalyst for improved CO(x) methanation performance. *Appl Surf Sci* 2018;455:53–60.
- [126] Abdel-Mageed AM, Widmann D, Olesen SE, Chorkendorff I, Biskupek J, Behm RJ. Selective CO methanation on Ru/TiO<sub>2</sub> catalysts: role and influence of metal-support interactions. *ACS Catal* 2015;5:6753–63.
- [127] Wang WX, Li XK, Zhang Y, Zhang R, Ge H, Bi JC, et al. Strong metal-support interactions between Ni and ZnO particles and their effect on the methanation performance of Ni/ZnO. *Catal Sci Technol* 2017;7:4413–21.
- [128] Yang JY, Fan YP, Li ZL, Peng ZK, Yang JH, Liu BZ, et al. Bimetallic Pd-M (M = Pt, Ni, Cu, Co) nanoparticles catalysts with strong electrostatic metal-support interaction for hydrogenation of toluene and benzene. *Mol Catal* 2020:492.
- [129] Xu LL, Cui Y, Chen MD, Wen XY, Lv CF, Wu XY, et al. Screening transition metals (Mn, Fe, Co, and Cu) promoted Ni-based CO<sub>2</sub> methanation bimetal catalysts with advanced low-temperature activities. *Ind Eng Chem Res* 2021;60:8056–72.
- [130] Yan XL, Yuan C, Bao JH, Li S, Qi DZ, Wang QQ, et al. A Ni-based catalyst with enhanced Ni-support interaction for highly efficient CO methanation. *Catal Sci Technol* 2018;8:3474–83.
- [131] Jin GJ, Gu FN, Liu Q, Wang XY, Jia LH, Xu GW, et al. Highly stable Ni/SiC catalyst modified by Al<sub>2</sub>O<sub>3</sub> for CO methanation reaction. *RSC Adv* 2016;6:9631–9.
- [132] Zhao BR, Chen ZP, Yan XL, Ma XX, Hao QQ. CO methanation over Ni/SiO<sub>2</sub> catalyst prepared by ammonia impregnation and plasma decomposition. *Top Catal* 2017;60:879–89.
- [133] Chen YQ, Tian ZW, Liu Q, Bian B. A MoO<sub>x</sub>-doped Ni/3D-SBA-15 catalyst for CO methanation: the effect of a solvent and a MoO<sub>x</sub> promoter on the catalytic properties. *Sustain Energy Fuels* 2020;4:3042–50.
- [134] Zhang JY, Xin Z, Meng X, Lv YH, Tao M. Effect of MoO<sub>3</sub> on the heat resistant performances of nickel based MCM-41 methanation catalysts. *Fuel* 2014;116:25–33.
- [135] Qin ZZ, Wang XD, Dong LH, Su TM, Li B, Zhou YW, et al. CO<sub>2</sub> methanation on Co/TiO<sub>2</sub> catalyst: effects of Y on the support. *Chem Eng Sci* 2019;210.
- [136] Boellaard E, van der Kraan AM, Geus JW. Preparation, reduction and CO chemisorption properties of cyanide-derived Ni<sub>x</sub>Fe/Al<sub>2</sub>O<sub>3</sub> catalysts. *Appl Catal a-Gen.* 2002;224:1–20.
- [137] Moghacidam SV, Rezaei M, Meshkani F, Darouhegi R. Carbon dioxide methanation over Ni-M/Al<sub>2</sub>O<sub>3</sub> (M: Fe, CO, Zr, La and Cu) catalysts synthesized using the one-pot sol-gel synthesis method. *Int J Hydrogen Energy* 2018;43:16522–33.
- [138] Teh LP, Triwahyono S, Jalil AA, Firmansyah ML, Mamat CR, Majid ZA. Fibrous silica mesoporous ZSM-5 for carbon monoxide methanation. *Appl Catal a-Gen.* 2016;523:200–8.
- [139] Aziz MAA, Jalil AA, Triwahyono S, Sidika SM. Methanation of carbon dioxide on metal-promoted mesostructured silica nanoparticles. *Appl Catal a-Gen.* 2014;486:115–22.
- [140] Pan QS, Peng JX, Sun TJ, Wang S, Wang SD. Insight into the reaction route of CO<sub>2</sub> methanation: promotion effect of medium basic sites. *Catal Commun* 2014;45:74–8.
- [141] He S, Li CM, Chen H, Su DS, Zhang BS, Cao XZ, et al. A surface defect-promoted Ni nanocatalyst with simultaneously enhanced activity and stability. *Chem Mater* 2013;25:1040–6.
- [142] Zhu HW, Razzaq R, Jiang L, Li CS. Low-temperature methanation of CO in coke oven gas using single nanosized Co<sub>3</sub>O<sub>4</sub> catalysts. *Catal Commun* 2012;23:43–7.
- [143] Upham DC, Derk AR, Sharma S, Metiu H, McFarland EW. CO<sub>2</sub> methanation by Ru-doped ceria: the role of the oxidation state of the surface. *Catal Sci Technol* 2015;5:1783–91.
- [144] Liang CF, Hu X, Wei T, Jia P, Zhang ZM, Dong DH, et al. Methanation of CO<sub>2</sub> over Ni/Al<sub>2</sub>O<sub>3</sub> modified with alkaline earth metals: impacts of oxygen vacancies on catalytic activity. *Int J Hydrogen Energy* 2019;44:8197–213.
- [145] Hamid MYS, Jalil AA, Rahman AFA, Abdullah TAT. Enhanced reactive CO<sub>2</sub> species formation via V<sub>2</sub>O<sub>5</sub>-promoted Ni/KCC-1 for low temperature activation of CO<sub>2</sub> methanation. *React Chem Eng* 2019;4:1126–35.
- [146] Hamid MYS, Firmansyah ML, Triwahyono S, Jalil AA, Mukti RR, Febriyanti E, et al. Oxygen vacancy-rich mesoporous silica KCC-1 for CO<sub>2</sub> methanation. *Appl Catal a-Gen.* 2017;532:86–94.
- [147] Jia XY, Zhang XS, Rui N, Hu X, Liu CJ. Structural effect of Ni/ZrO<sub>2</sub> catalyst on CO<sub>2</sub> methanation with enhanced activity. *Appl Catal B Environ* 2019;244:159–69.
- [148] Hussain I, Jalil AA, Mamat CR, Siang TJ, Rahman AFA, Azami MS, et al. New insights on the effect of the H<sub>2</sub>/CO ratio for enhancement of CO methanation over metal-free fibrous silica ZSM-5: thermodynamic and mechanistic studies. *Energy Conversion and Management*; 2019. p. 199.
- [149] Ashok J, Ang ML, Kawi S. Enhanced activity of CO<sub>2</sub> methanation over Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts: influence of preparation methods. *Catal Today* 2017;281:304–11.
- [150] Liu Q, Gu FN, Lu XP, Liu YJ, Li HF, Zhong ZY, et al. Enhanced catalytic performances of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst via addition of V<sub>2</sub>O<sub>3</sub> for CO methanation. *Appl Catal a-Gen.* 2014;488:37–47.
- [151] Tian ZW, Liu Q, Bian B. Enhanced catalytic performance of CO methanation over VO<sub>x</sub> assisted Ni/MCF catalyst. *Sustain Energy Fuels* 2020;4:2396–403.
- [152] Takano H, Kirihata Y, Izumiya K, Kumagai N, Habazaki H, Hashimoto K. Highly active Ni/Y-doped

- ZrO<sub>2</sub> catalysts for CO<sub>2</sub> methanation. *Appl Surf Sci* 2016;388:653–63.
- [153] Zhang WJ, Wang KL, Zhu SL, Li Y, Wang FH, He HB. Yttrium-doped TiO<sub>2</sub> films prepared by means of DC reactive magnetron sputtering. *Chem Eng J* 2009;155:83–7.
- [154] Xu JK, Zhou W, Li ZJ, Wang JH, Ma JX. Biogas reforming for hydrogen production over nickel and cobalt bimetallic catalysts. *Int J Hydrogen Energy* 2009;34:6646–54.
- [155] Norskov JK, Bligaard T, Logadottir A, Bahn S, Hansen LB, Bollinger M, et al. Universality in heterogeneous catalysis. *J Catal* 2002;209:275–8.
- [156] Qiu M, Tao HL, Li Y, Zhang YF. Insight into the mechanism of CO<sub>2</sub> and CO methanation over Cu(100) and Co-modified Cu(100) surfaces: a DFT study. *Appl Surf Sci* 2019;495.
- [157] Xu L, Lian X, Chen M, Cui Y, Wang F, Li W, et al. CO<sub>2</sub> methanation over CoNi bimetal-doped ordered mesoporous Al<sub>2</sub>O<sub>3</sub> catalysts with enhanced low-temperature activities. *Int J Hydrogen Energy* 2018;43:17172–84.
- [158] Wang YX, Su Y, Zhu MY, Kang LH. Mechanism of CO methanation on the Ni-4/γ-Al<sub>2</sub>O<sub>3</sub> and Ni<sub>3</sub>Fe/γ-Al<sub>2</sub>O<sub>3</sub> catalysts: a density functional theory study. *Int J Hydrogen Energy* 2015;40:8864–76.
- [159] Liu P, Zhao BR, Li S, Shi HF, Ma M, Lu JJ, et al. Influence of the microstructure of Ni-Co bimetallic catalyst on CO methanation. *Ind Eng Chem Res* 2020;59:1845–54.
- [160] Guo XP, Gao DL, He HY, Traitangwong A, Gong MM, Meeyoo V, et al. Promotion of CO<sub>2</sub> methanation at low temperature over hydrotalcite-derived catalysts-effect of the tunable metal species and basicity. *Int J Hydrogen Energy* 2021;46:518–30.