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Review

CO₂ methanation over heterogeneous catalysts: recent progress and future prospects

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M. A. A. Aziz,^a A. A. Jalil^{a,b}, S. Triwahyono^{c*} and A. Ahmad^{a,b}

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Catalytic approaches for CO₂ fixation can play an important role, because CO₂ can be artificially converted into reusable chemicals. Among the catalytic reactions of CO₂, hydrogenation of CO₂, the so-called methanation reaction, is a suitable technique for the fixation of CO₂. This technique can be used to convert exhausted CO₂ into methane (CH₄), which can be recycled for use as a fuel or a chemical as well as by contributing to the reduction of CO₂ emissions. Heterogeneous catalysts have been used to hydrogenate CO₂ to methane. Heterogeneous catalysts are preferable than homogenous catalysts in terms of stability, separation, handling, and reuse, which reflects in lower costs for large-scale productions. Significant progress has been made in this direction which is the exploitation of novel heterogeneous catalysts. In this review, we discussed recent developments in this area, with emphases on catalytic reactivity and its physicochemical properties and reaction mechanism. Apart from materials aspects and catalytic performance, we also discuss fundamental strategies for the rational design of materials for effective transformations of CO₂ to methane with the help of H₂ and power source.

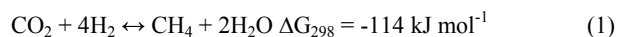
Introduction

Global warming-induced climate change is one of the significant civilization threats of the modern times.¹ Increases of greenhouse gases (GHGs) in the atmosphere produce a positive radiative forcing of the climate system and a consequent warming of surface temperatures and rising sea level caused by thermal expansion of the warmer seawater. In addition, it is also contribute to the melting in glaciers and ice sheets as well as to the environment such as agriculture, water resources, and human health.² Although other factors exist, the importance of the aforementioned relationship should not be undermined. Unfortunately, it is predicted that this trend of increasing atmospheric GHGs concentration will not be altered within next several decades, because fossil fuels will be still the dominant energy source.

CO₂ has covered about 82% of total GHGs. Therefore, CO₂ as a raw material has been a focus in CO₂ reduction research area. This is due to the advantages of CO₂ which is attractive as highly functional, widely available, inexpensive, renewable carbon source and an environmentally friendly chemical reagent.^{3,4} The different proposed technologies follow one of two major approaches: to capture and geologically sequester CO₂, or to convert CO₂ into useful low-carbon fuels. In today's world of high energy demands, CO₂ conversion and utilization seems to be a more attractive and promising solution. Presently, the use of CO₂ as chemical feedstock is limited to a few industrial processes; synthesis of urea and its derivatives, salicylic acid, carbonates and methanol.⁵⁻⁸ This increasing interest is focused on the concept of recovered CO₂ being used to synthesize fuels (through, for example, Fischer-Tropsch chemistry), and such an approach could substantially reduce carbon emissions.⁹ The products of CO₂ hydrogenation such as methanol, dimethyl ether (DME) are excellent fuels in internal combustion engines, and also are easy for storage and transportation. Although

the production of methanol and DME from CO₂ are among the promising processes, however, these processes need to be performed under high pressure of reaction (~5 Mpa).¹⁰ In addition, the literature showed that the CO₂ conversion to methanol is still very low (<20%) and difficult to achieve 100% conversion of CO₂.¹¹ The CO₂ hydrogenation to methane (CO₂ methanation) presents several advantages over other chemicals because it can be directly injected into already existing natural gas pipelines, and it can be used as a fuel or raw material for the production of chemicals. In addition, methane formation from CO₂ is more simple reaction which can generate methane under atmospheric pressure. Furthermore, the formation of CH₄ from CO₂ at (low) room temperature has become an important breakthrough in the knowledge of the role and in the use of CO₂, although the conversion was still very low.¹²

CO₂ methanation remains the most advantageous reaction with respect to thermodynamics, since the reaction is considerably faster than other reactions which form hydrocarbons or alcohols.¹³ This CO₂ methanation reaction is called Sabatier reaction and could be applied in industrial application, provided that hydrogen is generated from renewable sources.



The methanation of carbon dioxide is an important catalytic process of fundamental academic interest with potential commercial application.¹⁴⁻¹⁶ Because the interest in the large-scale manufacture of substitute natural gas from the products of coal gasification has greatly diminished in recent decades,¹⁷ carbon dioxide methanation, in the fuel cell and ammonia synthesis industry, can be used for the removal of trace CO from H₂-rich stream to prevent catalyst poisoning.¹⁸ In addition, the National Aeronautics Space Administration (NASA) is also interested in applications of the Sabatier reaction for use in future manned space colonization on

Mars.¹⁵ Bringing Terrene hydrogen to Mars will make it possible to convert the Martian carbon dioxide atmosphere into methane and water for fuel and astronaut life-support systems.¹⁹

In recent years, CO₂ methanation via heterogeneous catalysts has recently attracted a considerable amount of attention, as demonstrated by the burgeoning number of publications (Fig. 1). Metals, such as Ru, Rh, Ni, Co, and so forth on various supports have been reported to be effective methanation catalysts. The latest review on CO₂ methanation on various catalytic system was done by Wang et al.²⁰ However, the review primarily focus on general aspects of CO₂ methanation and was published on the last 3 years and no latest report has been published yet. Therefore, the present review attempts to provide current understanding of catalytic performance and insight of reaction mechanism over heterogeneous catalysts between January 2011 and January 2015, as well as the future prospect of CO₂ methanation.

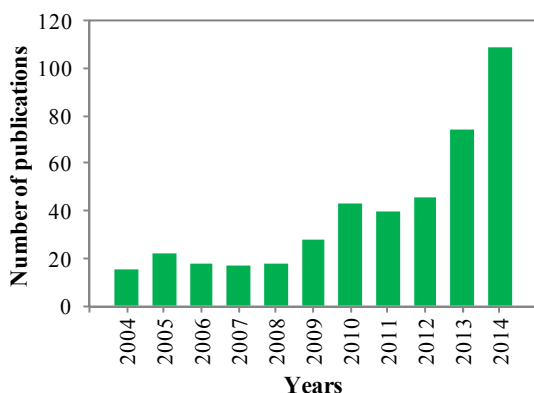


Fig. 1 Number of publication dealing with CO₂ methanation versus years (2004–2014) extracted from ISI Web of Science (Thomson Reuters) database retrieved using the keywords "CO₂ methanation".

Metal-based heterogeneous catalysts

Ni-based catalysts

Hydrogenation of CO₂ toward methane has been extensively studied using supported nickel catalysts.^{21–58} Ni-based catalysts have been widely investigated for industrial purposes due to its low cost and easily available. The methanation of carbon dioxide over Ni catalysts was studied in detail by a lot of researchers at laboratory scale because of the theoretical significance and possible practical application of this reaction. The performance of catalysts toward CO₂ methanation is depend on various parameters such as effect of support, effect of nickel loading, effect of second metal and effect of preparation method.

Effect of support. Because the support has a significant influence on the morphology of the active phase, adsorption, and catalytic properties,⁵⁹ preparation of highly dispersed supported metal catalysts has been the focus of significant research. Therefore, high surface area supports, usually oxides, are used extensively in industry for the preparation of metal catalysts including silica, alumina, silica-alumina, and zeolites. Tada et al. has studied the effect of various support (CeO₂, α -Al₂O₃, TiO₂ and MgO) on Ni catalyst on CO₂ methanation.²⁶ From their report, Ni/CeO₂ showed high CO₂ conversion especially at low temperatures compared to

Ni/ α -Al₂O₃, and the selectivity to CH₄ was very close to 100%. As shown in Fig. 2, Ni/CeO₂ shows the highest yield to methane followed by Ni/ α -Al₂O₃, Ni/TiO₂ and Ni/MgO. The surface coverage by CO₂-derived species on CeO₂ surface and the partial reduction of CeO₂ surface could result in the high CO₂ conversion over Ni/CeO₂.²⁶ The excellent of CeO₂ support was also studied on a different support materials for methanation of CO₂, including SiO₂, Al₂O₃, ZrO₂, and CeO₂, doped with a different percentage of active nickel and cobalt metals using a standard coprecipitation method.²⁸ It was found that the ZrO₂-CeO₂-supported catalyst can attain $\geq 95\%$ CO₂ conversion at 400 °C and has a CH₄ selectivity of 99%.²⁸

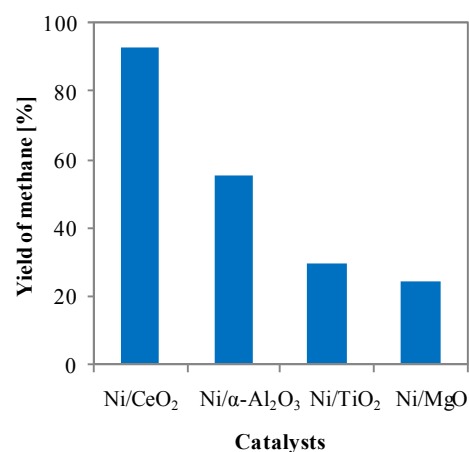


Fig. 2 Effect of support materials on yield of methane over Ni/CeO₂, Ni/ α -Al₂O₃, Ni/TiO₂, and Ni/MgO. Reaction conditions: reaction temperature = 350 °C, 20 vol% CO₂, 80 vol% H₂, GHSV = 10,000 h⁻¹. Results are calculated based on the conversion of CO₂ and selectivity to CH₄ adopted from Tada et al.²⁶

The hydrogenation of carbon dioxide producing methane and CO has been investigated over Ni/Al₂O₃ catalysts.⁵² Catalytic activity needs the presence of Ni metal particles which may form in situ if the Ni loading is higher than that needed to cover the alumina surface with a complete monolayer. If Ni content is lower, pre-reduction is needed. Catalysts containing very small Ni particles obtained by reducing moderate loading materials are very selective to methane without CO formation. The larger the Ni particles, due to higher Ni loadings, the higher the CO production. Cubic Ni metal particles are found in the spent catalysts mostly without carbon whiskers. The fast methanation occurs at the expense of CO intermediate on the corners of nanoparticles interacting with alumina, likely with a "via oxygenate" mechanism.⁵² Abello et al. has reported the methanation of carbon dioxide over a high-loaded Ni–Al mixed oxide catalyst (ca. molar ratio Ni/Al = 5).⁵¹ Despite the high nickel loading (ca. 70 wt.%), which is theoretically thought to be counterproductive for the nickel-based catalyst performance, the Ni–Al activated catalyst exhibited high CO₂ conversion, and rendered a CH₄ selectivity very close to 100%. This is originated by the formation of small metallic nickel crystallites (ca. 6 nm) dispersed over NiO–alumina upon partial reduction of the mixed oxide. The catalyst experiences complete reduction during reaction, which slightly increases the Ni crystallite size, but preserves the high activity in ca. 500 h lifetime tests even at high space velocity.⁵¹

Recently, the important of support was clearly observed when nickel nanoparticles (NPs, particle radius <8 nm) were compared to 125% Ni/Al₂O₃ tested on CO₂ methanation.⁵³ At 773 K, the best

catalytic activity was obtained on 125% Ni/Al₂O₃, while Ni NPs result poorly active in catalysing this reaction. The support effect is evident in the methanation of CO₂ on Ni/Al₂O₃, supposed to justify the high activity of this catalyst and the very low activity of Ni NP in this reaction.⁵³

Zeolite and TiO₂ are among of the support used Ni catalyst in CO₂ methanation. High catalytic activity of sorption catalysts based on Ni/zeolite was due to the properties of zeolites which are chemically active nanostructures and has space for enhancing the sorption properties of the catalysts.³⁷ Therefore, CO₂ hydrogenation into methane was carried out over catalysts containing nickel and cerium species supported on a HNaUSY zeolite.⁴⁸ An enhancement of the catalysts performances was noticed when doping the Ni-zeolites catalysts with 3–15% of Ce. The presence of CeO₂ after reduction might promote CO₂ activation into CO. Comparing these results with those reported in literature, it is possible to conclude that zeolites have great potential to be used as catalyst supports for the CO₂ methanation reaction.⁴⁸ Ni nanoparticles (NPs) on TiO₂ support was synthesized via a deposition–precipitation method followed by a calcination–reduction process. The Ni NPs are highly dispersed on the TiO₂ surface (particle size: 2.2 nm), with a low Ni–Ni coordination number.³⁵

Recently, ceria-zirconia mixed oxides has become one of the potential supports for CO₂ methanation reaction. It turned out to be greatly efficient in terms of activity and stability due to their high oxygen storage capacity and its properties to activate CO₂.^{23,33} In addition, the interactions between Ni and the ceria-zirconia support was found to be a key parameter for the methanation reaction.³³ Ocampo et al. was first reported the carbon dioxide methanation over a series of Ni-Ce_xZr_{1-x}O₂ catalysts prepared by a pseudo sol-gel method.²³ The catalysts gave impressive CO₂ conversion and extremely high selectivity to methane (superior to 98%). The incorporation Ni²⁺ into the ceria-zirconia structure was proved to enhance catalysts specific activity. The high activity was depended on the surface of available metallic nickel, the composition of the support (CeO₂/ZrO₂ = 60/40) and on its modification by Ni²⁺ doping.²³ This indicated that the nature of support plays a crucial role in the interaction between the nickel and the support, and thus determines catalytic performances toward activity and selectivity for the methanation of CO₂.

In contrast to Ocampo et al. which reported the composite catalysts support of CeO₂/ZrO₂ catalysts, Liu et al. has tested the performance of CeO₂/Al₂O₃ support catalyst with 15 wt.% of nickel content prepared via impregnating boehmite.³⁴ The catalyst was found to be highly active and stable for methanation of carbon dioxide with hydrogen at a H₂/CO₂ molar ratio of 4. The catalytic performance was strongly dependent on the CeO₂ content in Ni-CeO₂/Al₂O₃ catalysts and that the catalysts with 2 wt% CeO₂ had the highest catalytic activity among the tested ones at 350 °C. The addition of CeO₂ decreased the reduction temperature by altering the interaction between Ni and Al₂O₃, and improved the reducibility of the catalyst. Preliminary stability test of 120 h on stream over the Ni-2CeO₂/Al₂O₃ catalyst at 350 °C revealed that the catalyst was much better than the unpromoted one (without CeO₂).³⁴

The novel nickel-based catalysts with a nickel content of 12 wt.% were prepared with the zirconia-alumina composite as a supports.²¹ ZrO₂ was reported to improve the alumina support for CO₂ methanation. The new Ni catalyst with new support (ZrO₂-Al₂O₃) showed higher catalytic activity and better stability than Ni/γ-Al₂O₃. The highly dispersed zirconium oxide on the surface of γ-Al₂O₃ inhibited the formation of nickel aluminate-like phase, which was responsible for the better dispersion of Ni species and easier reduction of NiO species, leading to the enhanced catalytic performance of catalyst.²¹ The effect of ZrO₂ was also studied on

Ni/SiO₂ system for CO₂ methanation.²⁵ However, the effect of ZrO₂ on the Ni/SiO₂ is less relevant for the methanation of CO₂. From their report, the addition of ZrO₂ is significant only on the methanation of CO due to the active surface of ZrO₂ which is capable to adsorb CO.²⁵ The role of Ni was reported as a dissociation sites for hydrogen and less incapable to adsorb CO₂.²⁷ In the methanation of CO₂ over the mixing of Rh/γ-Al₂O₃ and Ni/activated carbon, methane is produced with 100% of selectivity due to a significant synergy between two mixing of different catalysts.²⁷

It is widely accepted that the surface defects of nanocatalysts serving as an active site play a decisive role in the adsorption and reactivity in catalytic reactions. The formation or introduction of abundant and specific defect site on the surface of supported nanocatalysts is a promising approach for tailoring the surface morphology and electronic structure to enhance heterogeneous catalytic activity.⁶⁰⁻⁶² Therefore, a flowerlike Al₂O₃ matrix was fabricated as a surface defect and promoted to Ni nanocatalyst for CO₂ methanation.³⁹ The Ni nanocatalyst shows high dispersion and high particle density embedded on a hierarchical Al₂O₃ matrix and exhibits excellent activity and stability for the reaction of CO₂ methanation. The existence of abundant surface vacancy clusters served as active sites, accounting for the significantly enhanced low temperature activity of the supported Ni nanoparticles. In addition, the anchoring effect from the support gives rise to a high reaction stability, without sintering and/or aggregation of active species during long-term use.³⁹

Another excellent support with surface defect has been recently reported by Aziz et al.⁴¹ They reported the potential of mesostructured silica nanoparticles (Ni/MSN) to be used as a support for Ni catalyst for CO₂ methanation. The sequence of catalytic activity under various catalyst supports is as follows: Ni/MSN > Ni/MCM-41 > Ni/HY > Ni/SiO₂ > Ni/γ-Al₂O₃. The Ni/MSN catalyst exhibited the highest activity even at low temperatures (573 K). The high activity of Ni/MSN is due to the presence of both intra- and inter-particle porosity which led to the high concentration of basic sites and/or oxygen vacancy sites. The methanation activity increased with increasing of the concentration of basic sites. The presence of defect sites or oxygen vacancies in MSN was responsible for the formation of surface carbon species, while Ni sites dissociated hydrogen to form atomic hydrogen. The surface carbon species then interacted with atomic hydrogen to form methane. The Ni/MSN catalyst was also performed with good stability and no deactivation up to 200 h.⁴¹

Recently, metal-organic frameworks (MOFs) materials has emerged as catalyst support because they have very high surface areas, up to more than 1000 m²/g. Zhen et al. has explored the potential of MOFs for heterogeneous CO₂ methanation.⁵⁵ In their work, Ni@MOF-5 was used as a support for catalyst of CO₂ methanation. Very high dispersion of Ni(41.8%) over MOF-5 (2961 m²/g) has been achieved in this catalyst. These highly uniform dispersed Ni in the framework in MOF-5 resulted in significant activity enhancement at low temperature. The catalyst showed almost no deactivation in long term stability tests up to 100 h.

Over the past several years, natural clays have attracted considerable attention due to their environmental compatibility, low cost, high selectivity, reusability and operational simplicity. Usually raw clays are not suitable for the catalyst support due to their small specific surface area. However, after proper modifications, e.g., by forming the pillared structure²⁷ or by the acid treatment,²⁸ the surface areas can be increased significantly. The reason why the removal of a fraction of aluminum in clay via the acid treatment can lead to a much larger specific surface area is due to the formation of macropores, which can be further used to confine Ni species or fix

them at specific sites to prevent them from sintering to a certain degree during the reaction.

In this light, Lu et al. has reported the usage of raw bentonite (RB) and acid-alkali treated bentonite (B) as support for Ni catalysts and tested for methanation of CO₂ to produce synthetic natural gas (SNG).⁵⁶ The results showed that the Ni catalysts supported on the B support were more active than that supported on the RB support because of the improved Ni particles dispersion on the former that had larger specific surface area due to the generation of mesopores within the catalyst. Therefore, a proper treatment to the RB support is beneficial to the dispersion of Ni species which is important to high activity of CO₂ methanation.

The clay was also modified with mesoporous zirconia supported Ni catalyst as reported by Lu et al.⁵⁷ It is found that the zirconia-modified clays have the typical bimodal pore size distribution. Most of the pores with the sizes smaller than 10 nm are resulted from the zirconia pillared clays and the mesopores with the sizes larger than 10 nm and the macropores with the sizes larger than 50 nm are resulted from the partly damaged clay layers. The bimodal pore structure is beneficial to the dispersion of Ni on the layers of the zirconia-modified clays and the zirconia nanoparticles are highly dispersed on the partly damaged clay layers.

Different types of support possessed different order of basicity. In general, the generation of basic sites on the surface oxide of the catalyst can be exposed by pretreatment at high temperature.⁶³ The nature of the basic sites generated by removing the molecules covering the surfaces depends on the severity of the pretreatment. Mori and co-workers investigated the effect of various supports of Ni catalysts and found the reactivity of the catalysts depended strongly on the kind of supports in the order of γ -Al₂O₃ \approx MgO \approx SiO₂ > α -Al₂O₃ > TiO₂ \approx SiO₂-Al₂O₃.⁶⁴ The reason for higher activity of Ni/MgO catalyst was attributed to the basic properties of the MgO support on which CO₂ could be strongly adsorbed and kept on the catalyst even at higher temperatures. Incorporation of suitable promoters is believed to improve the basicity, metal dispersion and reducibility of the catalyst. It is believed that the rare earth oxide will impart adequate basicity to the methanation catalysts, thus improving the activity. Among the rare earth oxides, CeO₂ and La₂O₃ are commonly used as promoters for hydrogenation.⁶⁵ Higher basicity of the catalyst promoted to lower reaction temperature. For instance, the amount of CO₂ adsorbed on Ni/CeO₂ demonstrated by CO₂-TPD was much larger than that on Ni/ α -Al₂O₃. From these results, CO₂ reduction to CO over Ni/CeO₂ can be enhanced at low temperatures compared to Ni/ α -Al₂O₃. Therefore, Ni/CeO₂ displayed excellent activity for CO₂ methanation resulting in prompt conversion of CO, and consequently in the high CH₄ selectivity.²⁶ Similar result was observed by Xavier et al. in which the CeO₂ doped on Ni/Al₂O₃ improved the reducibility thus lowered the reaction temperature.⁶⁶ Ni/Ceria-zirconia mixed oxide and Ni-silica was compared in the CO₂ methanation because of their properties to activate CO₂.³³ The better activity of Ni/Ceria-zirconia compared to Ni-silica can be explained by the importance of weak basic sites the adsorption of CO₂.

In summary, the nature of support play a crucial role in high activity of CO₂ methanation. Single metal oxide, mixed oxide, zeolite, mesoporous material and clay possessed different characteristic and showed good potential to be used as a support for Ni catalyst. For example, CeO₂ has shown an excellent support due to its high oxygen storage capacity and its properties to activate CO₂. The addition of CeO₂ onto another oxide material (i.e Al₂O₃) can decreased the reduction temperature by altering the interaction between Ni and Al₂O₃, and improved the reducibility of the catalyst. Other mixed oxide support such as ZrO₂ and Al₂O₃ also exhibited high activity toward CO₂ methanation. ZrO₂ was improved the

alumina support for CO₂ methanation by inhibited the formation of nickel aluminate-like phase, which was responsible for the better dispersion of Ni species and easier reduction of NiO species. While, high catalytic activity of Ni/zeolite was due to its active nanostructures as well as possessed a large space for enhancing the sorption properties of the catalysts. The formation or introduction of abundant and specific defect site on the surface of supported nanocatalysts is a promising approach to enhance CO₂ methanation. This will include a flowerlike Al₂O₃ matrix, mesostructured silica nanoparticles and metal-organic frameworks (MOFs) materials. The presence of defect sites or oxygen vacancies in MSN and high surface area of MOFs were responsible for high activity of catalytic reaction. Natural clays could also be a good support after proper modifications (i.e. by forming the pillared structure or by the acid treatment) to generate larger specific surface area with the formation of macro-mesopores. Some of the potential clays are raw bentonite, acid-alkali treated bentonite and zirconia-modified clays. High basicity of the catalyst is of important due to its role to promote to lower reaction temperature. Therefore, basicity of catalyst could a vital factor for high activity of CO₂ methanation.

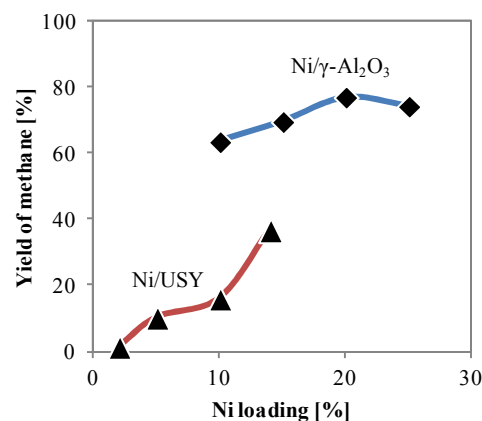


Fig. 3 Effect of Ni loading on yield of methane. For Ni/ γ -Al₂O₃ (◆), Reaction conditions: reaction temperature = 350 °C, GHSV = 9000 ml/g_{cat} h, H₂/CO₂ molar ratio = 3.5. For Ni/USY (▲), Reaction conditions: reaction temperature = 350 °C, GHSV = 43000 h⁻¹, H₂:CO₂:N₂ = 36:9:10. Results are calculated based on the conversion of CO₂ and selectivity to CH₄ adopted from Graca et al. and Rahmani et al.^{48,49}

Effect of nickel loading. The nickel loading on the support was found to be affected both the interaction of nickel with the support and the nickel dispersion on the support (Ni particle sizes), which further affected the catalytic behaviors during methanation. In general, the metal species tend to be highly dispersed across the carrier at low metal loadings, whereas the metal particles tend to aggregate at high metal loadings, forming large particles. Understanding this relationship can help researchers to understand dispersion-activity relationships and prepare active, selective, and stable Ni catalysts. The effect of nickel content on the structure and activity of co-precipitated Ni-Al layered double hydroxides (LDHs) as catalyst precursors for CO₂ methanation was studied by variation of the Ni²⁺/Al³⁺ molar ratio (Ni²⁺/Al³⁺ = 3.0, 1.5 and 0.5).²⁹ After reduction at 400 and 450 °C, a sample of Ni²⁺/Al³⁺ = 3.0 has demonstrated the highest conversion degree at all the reaction temperatures and space velocities.²⁹ The effect of Ni NPs loading on TiO₂ shows that 15 wt% of Ni exhibits excellent catalytic behavior

towards CO₂ methanation (conversion: 96%; selectivity: 99%) at a reaction temperature as low as 260 °C.³⁵ The good dispersion of Ni NPs with large unsaturation facilitates a high exposure of active sites, which accelerates the formation of surface-dissociated hydrogen and the subsequent hydrogenation removal of surface nickel carbonyl species, accounting for the resulting enhanced low-temperature catalytic performance.³⁵

The effect of Ni contents on mesoporous nanocrystalline γ -Al₂O₃ with high surface area was prepared and employed in carbon dioxide methanation reaction.⁴⁹ As shown in Fig. 3, the catalytic results showed that the CO₂ conversion increased with increasing Ni content from 10 to 20 wt.%. Increasing in nickel loading higher than 20 wt.% decreased the yield of methane, due to decreasing the nickel dispersion as a result of bigger crystallite size. The increasing in nickel content from 10 to 25 wt.% increased the reducibility of catalyst. The catalytic results revealed that the catalyst with 20 wt.% of Ni possessed high activity and stability in CO₂ methanation reaction.⁴⁹ Fig. 3 also shows the effect of Ni loading on USY support and the yield of methane increased with the Ni content on zeolite from 2 to 14%, due to the higher amount of Ni^o species after reduction.⁴⁸ In conclusion, the amount of Ni loading is depend on the type of support used. The amount of Ni loading on support will determined its crystallite size and dispersion on the surface of the support.

Effect of second metal on nickel catalyst. It is known that conventional nickel-based catalysts suffer from severe catalyst deactivation in the carbon dioxide methanation reaction, because nickel particles are sintered during the exothermic methanation reaction.²³ To overcome this problem, addition of second metal such as Fe, Zr, Co, La, Y, and Mg has been attempted to enhance the stability and catalytic activity of nickel-based catalysts in the carbon dioxide methanation reaction.^{24,30,32} The addition of second metal (M = Fe, Zr, Ni, Y, and Mg) has been introduced in mesoporous nickel (35 wt%)-M (5 wt%)-alumina xerogel (denoted as 35Ni5MAX) catalysts in the methane production from carbon dioxide and hydrogen. In the carbon dioxide methanation reaction, yield for CH₄ decreased in the order of 35Ni5FeAX > 35Ni5ZrAX > 35Ni5NiAX > 35Ni5YAX > 35Ni5MgAX. This indicated that the catalytic performance was greatly influenced by the identity of second metal in the carbon dioxide methanation reaction. The CO dissociation energy and metal-support interaction of the catalyst played key roles in determining the catalytic performance of 35Ni5MAX catalysts in the reaction, in which the 35Ni5FeAX catalyst retained the most optimal CO dissociation energy and the weakest metal-support interaction, exhibited the best catalytic performance in terms of conversion of CO₂ and yield for CH₄.³²

La₂O₃ was used by modification with Ni/SiC as reported by Zhi et al.²⁴ As shown in Fig. 4, It can be seen that CO₂ methanation over Ni-La/SiC has been ignited at 150 °C, while Ni/SiC only becomes active at about 200 °C. CO₂ conversions of both catalysts have an obvious increase with the temperature rising. However, methane yield of Ni-La/SiC is higher than Ni/SiC at the same temperature. The Ni-La/SiC catalyst also shows better stability than pure Ni/SiC. This is due to the La₂O₃ which can effectively restrain the growth of NiO nanoparticles, improve the dispersion of NiO and strengthen the interaction between NiO and SiC. In addition, La₂O₃ can change the electron environment surrounding Ni atoms and thus reactant CO₂ on the Ni atoms can be activated more easily.²⁴

The effect of Fe metal on NiAl₂O₃ has been studied by Kang et al. for CO₂ methanation.²² The bimetallic (Ni and Fe) composition in Al₂O₃ was Ni_xFe_{1-x} (x is 0.1, 0.3, 0.5, 0.7 and 0.9) and the result shows that Ni_{0.7}Fe_{0.3}/Al₂O₃ catalyst gave the maximum carbon conversion and CH₄ selectivity. Further, increase of Fe content led to

enhancing the water gas shift reaction and hydrocarbon.²² Mg-modified Ni/SiO₂ catalysts with different MgO contents were prepared by impregnation methods.⁵⁴ The modification of MgO acted as a key factor in enhancing the capacity of CO₂ adsorption and accelerating the activation of CO₂. Moreover, modified MgO could also increase Ni species dispersion and suppress the metallic Ni sintering and oxidation. The introduction of 1 wt.% MgO as a promoter to the 10 wt.% Ni/SiO₂ catalyst led to superior catalytic activity and stability (near 100%) at 623 K for 50 h because of the synergistic effect of Ni and Mg species. However, the addition of higher amount of MgO (2 or 4 wt.%) resulted in a slight decrease in catalytic activities due to the blockage of active sites. Therefore, the improved stability and activity of MgO doped Ni/SiO₂ catalysts for CO₂ methanation could be achieved by adding different amounts of MgO.⁵⁴ In addition, Guo et al. reported that the addition of 4 wt.% of Mg on 10 wt.% Ni/SiO₂ inhibited the catalytic property of the catalyst significantly due to the low reducibility of the nickel species.⁵⁸

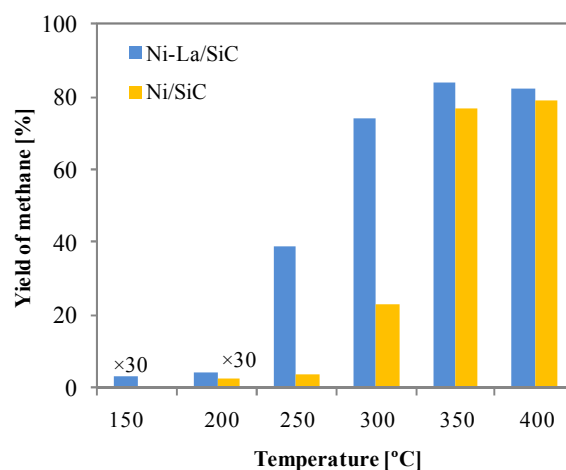


Fig. 4 Catalytic performance of Ni-La/SiC and Ni/SiC under various reaction temperature. Results are calculated based on the conversion of CO₂ and selectivity to CH₄ adopted from Zhi et al.²⁴

Furthermore, the presence of alkaline-earth metal oxides as a second metal such as SrO on Ni/SiO₂ has promoted the catalytic activity and enhanced the catalyst stability.⁵⁸ While, BaO addition on Ni/SiO₂ enhanced the reaction activity, but the catalyst deactivated significantly after 50 h of time-on-stream due to the sintering of metallic Ni. CaO addition on Ni/SiO₂ affected negligibly the performance of the catalyst.

Co was tested as a second metal in an active oxygen material Ce_xZr_{1-x}O₂-supported Ni-Co bimetallic nanosized catalyst.³⁰ The interaction between active metals (Ni and Co) and active oxygen sites in Ce_xZr_{1-x}O₂ support was found to be very important for catalytic performance. Appropriate Co metal addition can improve catalytic stability of catalysts significantly. The active oxygen site of Ce_xZr_{1-x}O₂ can considerably improve catalytic performance due to the presence of more oxygen vacancies.³⁰ The addition of proper amount of the VO_x on Ni/treated bentonite improved the catalytic activity of CO₂ methanation.⁵⁶ This could be attributed to the enhanced H₂ uptakes, increased Ni dispersion, reduced Ni nanoparticle size, and the electronic effect of VO_x that can promote dissociation of CO in the methanation reaction. In the lifetime test of CO₂ methanation under atmospheric pressure, the catalyst was high-

Table 1 Summary of various Ni catalysts for CO₂ methanation

Catalysts	Preparation method	Ni (nm)	T [°C]	X _{CO2} [%]	S _{CH4} [%]	Stability test, conversion [%]	Ref.
12 wt.% Ni/ZrO ₂ -Al ₂ O ₃	impregnation-precipitation	5.4 (6.3) ^a	360	69.8	100	Decreased by 1.6 % after 100 h	21
5 wt.% Ni-Ce _x Zr _{1-x} O ₂	pseudo sol-gel	20.8 (39) ^a	350	80	>98	Decreased by 18.8 % after 140 h	23
15 wt.% Ni-La/SiC	impregnation	8.3 (8) ^a	360	85	100	Stable after 70 h	24
10 wt.% Ni/CeO ₂	impregnation	17 ^b	350	93	100	n/a	26
10 wt.% Ni/β-zeolite	impregnation	25.8	360	97	n/a	n/a	31
10 wt.% Ni/β-zeolite-with plasma	impregnation	18.7 ^b	240	94	n/a	n/a	31
35 wt.% Ni/ 5 wt.% Fe/Alumina xerogel	single step sol-gel	7.39	220	63.4	99.5	n/a	32
5 wt.% Ni/ceria-zirconia	pseudo sol-gel	21	350	67.9	98.4	Decreased by 15 % after 90 h	33
5 wt.% Ni/ 2 wt.% ceria/Al ₂ O ₃	co-impregnating Boehmite with metal solutions		300	70	100	Stable after 120 h	34
15 wt.% Ni/TiO ₂	precipitation–deposition	2.1 ^c	260	96	99	Decreased by 2.9 % after 81 h	35
70 wt.% Ni/SBA-15	heat treatment	n/a	300-450	99.2	100	High thermal stability due to unchanged surface area after catalytic test.	36
Ni/SiO ₂	impregnation method and treated by glow discharge plasma (H ₂ atmosphere)	n/a	250	90	~100	Decreased by 15.54 % after 100 h	38
20 wt.% Ni/H-Al ₂ O ₃	in situ reduction of a hierarchical Ni ^{II} Al ^{III} -LDH precursor at reduction temperatures of 400 °C	5-8.1 ^c	300	99	>99	Decreased by 7 % after 252 h	39
5 wt.% Ni-Ce _x Zr _{1-x} O ₂	hydration-impregnation	n/a	420	75.66	>80	Decreased by 15 % after 60 h	44
14 wt.% Ni/USY	impregnation	n/a	400	65.5	94.2	Stable after 10 h	48
20 wt.% Ni/nanocrystalline γ-Al ₂ O ₃	impregnation	18.9	350	78	100	Stable after 600 min	49

^a used catalyst; determined by Sherrer formula.

^b after reduced at 600 °C; determined by Sherrer formula.

^c determined by TEM.

n/a: not available

ly stable as it had superior anti-coking and anti-sintering performance to the catalyst without the addition of VO_x.

As the discussion above attest, it can be concluded that the presence of second metal into the Ni catalyst showed a positive effect toward CO₂ methanation. The metal such as Fe, La₂O₃, MgO, Co and VO_x have been used as a second metal on Ni catalyst. They showed a variety of advantages compared to Ni catalyst. For instance, addition of La₂O₃ on Ni/SiC can effectively restrain the growth of NiO nanoparticles, improve the dispersion of NiO and strengthen the interaction between NiO and SiC. MgO and VO_x plays a key factor in enhancing the capacity of CO₂ adsorption and accelerating the activation of CO₂. While, Co metal addition can improve catalytic stability of catalysts significantly.

Effect of preparation method. The CO₂ methanation could be affected by the preparation method of the catalyst through the dispersion of active sites. Lu et al. has reported a well-dispersed NiO/SBA-15 with high loading prepared by a simple heat treatment (HT) and a conventional solvent impregnation (SI) method.³⁶ With low NiO loading, the NiO particles were preferentially dispersed on the outer surface of SBA-15 by HT method. However, with the SI method, the particles were preferentially occluded into the SBA-15 pores. With high NiO loading, there was no difference caused by preparation method in NiO particles location. The preparation

method affected the temperature achieved the maximum conversion. The producer gas conversion increased with increasing NiO loading, regardless of the preparation method. When the NiO loading exceeded 50 wt.%, the CH₄ selectivity was 100%. The NiO/SBA-15 by HT method had high thermal stability under methanation, while by SI method only the NiO/SBA-15 with high loading had high thermal stability.³⁶ Zhang et al. has reported the Ni/SiO₂ catalysts prepared by impregnation method and treated by glow discharge plasma.³⁸ The results showed that the plasma treatment can remarkably improve the dispersion of active components and enhance the reactivity of Ni/SiO₂ catalyst. The catalytic performance of Ni/SiO₂ in CO₂ methanation is also enhanced by the plasma treatment; the conversion of CO₂ and the space time yield of CH₄ over the plasma modified catalyst are higher than those over the Ni/SiO₂ catalyst obtained through conventional impregnation and calcination method.³⁸ Ni/ceria–zirconia solid solution (Ni/Ce_xZr_{1-x}O₂) with Ce and Ni enriched on the surface of the catalysts was prepared via a simple, low-cost method as reported by Cai et al.⁴⁴ The aqueous phase reactions simplify the preparation process, save the cost and lead the Ce to enriching on the surface of products. The impregnation method makes the Ni enriching on the surface of products which enhances the efficiency of active component. These catalysts exhibit significantly high catalytic performance.⁴⁴ The preparation method influenced the rate of reduction of Ni and nucleation of metallic Ni. The degree of interaction between Ni and

support also depend on the preparation route of catalyst. Therefore, on the basis of these reports above, the method preparation of catalyst can be a vital factor to improve the CO₂ methanation. Based on overall discussion on Ni catalyst, the current Ni catalysts used for CO₂ methanation is summarized in Table 1.

Noble metal-based catalysts

The hydrogenation of CO₂ to methane has been investigated over Ru catalysts supported on different support.^{40, 67-69, 70-75} Ruthenium is believed to be even more active in CO_x methanation than nickel, but is also considerably more expensive.⁷⁶ In contrast to Ni, which may be deactivated at low temperatures due the particles sintering, interaction of the metal particles with carbon monoxide, formation of mobile nickel subcarbonyls and formation of carbon deposits.^{77,78} Instead, ruthenium catalysts have been reported to be the most stable when operating over a wide range of temperatures.⁷⁵ Sharma et al. studied the methanation of CO₂ on ceria doped with Ni, Co, Pd, or Ru. Ce_{0.96}Ru_{0.04}O₂ and Ce_{0.95}Ru_{0.05}O₂ perform best, converting 55% of CO₂ with a 99% selectivity for methane, at a temperature of 450 °C.⁶⁸ They found that the methanation reaction takes place on the reduced Ce_{0.95}Ru_{0.05}O₂, and the role of the Ru dopant is to make the reduction possible at lower temperature than on pure ceria.⁶⁸ The catalytic conversion of CO₂ to CH₄ on cobalt oxide and Ru-doped cobalt oxide nanorods was studied by Zhu et al.⁷¹ Active phases of the two catalysts are metallic cobalt and bimetallic Co-Ru, respectively. As presented in Fig. 5, yield of CH₄ on the Ru-doped cobalt oxide are obviously enhanced by formation of bimetallic Co-Ru ultrathin film in its surface region in contrast to that of cobalt and Ru/SiO₂ catalyst in the temperature range of 200-340 °C. These comparisons indicate that the surface of the active phase of Ru-doped catalyst is bimetallic Co-Ru instead of pure Co or pure Ru.⁷¹ Recently, Upham et al. found that the activity of Ru_{0.05}Ce_{0.95}O_x is sensitive to the degree of surface reduction. They found that a surface that is too reduced (i.e. it has too many oxygen vacancies) or too oxidized, its performance is poor.⁷⁵

The effect of Ru loading on zeolite was studied on CO/CO₂ methanation.⁷³ Increasing the Ru loading causes an increase of the mean particle size from 0.9 nm (2.2 wt.% Ru) to 1.9 nm (5.6 wt.% Ru). At the same time, also the activity for CO methanation increases, while the selectivity for CO methanation, which is constant at 100% for reformat gases with 0.6% CO, decreases at low CO contents. The latter findings are interpreted in terms of a change in the physical effects governing the selectivity for CO methanation with increasing Ru particle size, from an inherently low activity for CO₂ dissociation and subsequent CO_{ad} methanation on very small Ru nanoparticles to a site blocking mechanism on larger Ru nanoparticles. In the latter mechanism, CO₂ methanation is

hindered by a reaction inhibiting adlayer of CO at higher CO_{ad} coverages, i.e., at not too low CO concentrations, but facile in the absence of a CO adlayer, at lower CO concentrations in the reaction gas mixture.⁷³ Table 2 illustrates the summary of various Ru catalysts for CO₂ methanation. The Ru loading and/or the size of metal cluster is of important factor for high activity of CO₂ methanation. The introduction of Ru metal promoted to the reduction of cerium oxide at lower temperature.

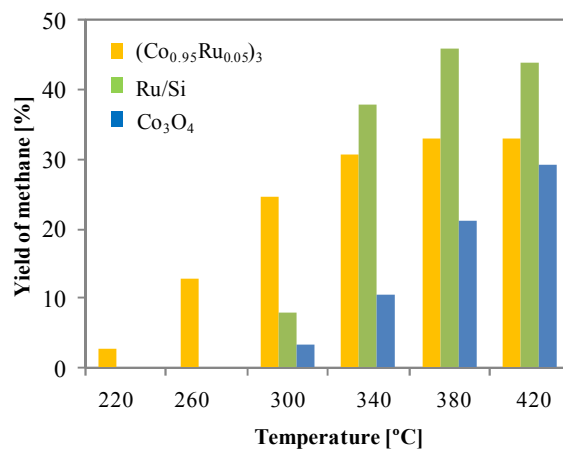


Fig. 5 Catalytic performances of Co₃O₄, (Co_{0.95}Ru_{0.05})₃O₄ and Ru/SiO₂. The measurements of catalytic conversion and selectivity were performed in a fixed-bed microreactor at 50 mL min⁻¹ of the flow rate, 1 bar of the reactant pressure, and the reactant mixing ratio CO₂:H₂ = 1:4. Weight of catalyst is 100 mg. Ru is 5 wt % of SiO₂. Results are calculated based on the conversion of CO₂ and selectivity to CH₄ adopted from Zhu et al.⁷¹

Hydrogenation of CO₂ toward methane has been extensively study using supported rhodium catalysts.^{12,27,79-83} The methanation of CO₂ at low temperature (between 50 and 150 °C) and pressure (2 bar) was performed on Rh/γ-Al₂O₃ catalyst in a pulse reactor and performed 100% selectivity to methane.¹² The oxidation state of the Rh plays an important role in the distribution of the adsorbed species on the catalysts: the gem-dicarbonyls species are the more reactive than the Rh-CO linear species. The preferential formation of these species will be at the origin of the difference in the reactivity of CO₂ and CO. Oxygen, in low amount, has a positive effect in the methanation while CO inhibits the methanation of CO₂.¹²

Table 2 Summary of various Ru catalysts for CO₂ methanation

Catalysts	Preparation method	T [°C]	X _{CO2} [%]	S _{CH4} [%]	Highlight	Ref.
Ce _{0.95} Ru _{0.05} O ₂	combustion	450	55	99	the methanation reaction takes place on the reduced Ce _{0.95} Ru _{0.05} O ₂ , and the role of the dopant (Ru) is to make the reduction possible at lower temperature than on pure ceria.	68
35Ni5Fe0.6RuAX	single-step sol-gel	220	68.2	98.9	optimal ruthenium content was required for the maximum production of methane from carbon dioxide and hydrogen.	40
(Co _{0.95} Ru _{0.05}) ₃ O ₄ nanorod	modified wet chemistry	380	33	97	active phases of the two catalysts are metallic cobalt and bimetallic Co-Ru, respectively.	71

Karelovic and Ruiz studied the effect of metal particle size on the performances of CO₂ methanation over Rh/ γ -Al₂O₃ catalysts.⁷⁹ Catalysts with varying Rh content gave rise to different Rh particle sizes (between 3.6 and 15.4 nm). In the condition studied, selectivity to methane was 100% over the entire range of temperature and Rh loading studied. The intrinsic activity of Rh/ γ -Al₂O₃ catalysts in CO₂ hydrogenation to methane was found to do not depend on particle size at temperatures between 185 and 200 °C, whereas at lower temperatures larger particles favored higher activity.

The mechanical mixtures of Rh/ γ -Al₂O₃ and Ni loaded Activated Carbon (AC) catalysts, show a significant catalytic synergy in the methanation of CO₂.²⁷ This effect is more important when the content of Ni is 1 wt.%. The production of methane over the mixed catalyst is higher compared with the methane formation observed with the individual catalysts. The synergy is explained by cooperation between the two catalysts during methanation. Particularly, 1 wt.% Rh/ γ -Al₂O₃ is highly efficient in CO₂ adsorption. On the other hand, 1 wt.% Ni/AC catalyst is able to absorb a high quantity of hydrogen and very little carbon dioxide. These properties joint together by a simple mixing catalyst induce an increase of carbon dioxide conversion and methane formation. In all cases only methane is formed. The augmentation of the catalytic performances would be attributed to a migration of activated hydrogen species from 1 wt.% Ni/AC catalysts toward 1 wt.% Rh/ γ -Al₂O₃. This hydrogen can then react with CO₂ species to form methane but also to preserve rhodium particles in an adequate reduced state essential for CO₂ hydrogenation.

CO₂ methanation at low temperature and atmospheric pressure was also studied over Rh/TiO₂ catalysts.⁸⁰ Catalysts with different Rh contents (0.5–5 wt.%) were prepared in order to obtain different mean cluster sizes. The rate of methane production per surface Rh atoms increases as metal particle size increases up to ca. 7 nm. Beyond this size, the rate does not change appreciably. Higher activation energies (up to 28.7 kcal/mol) are obtained for catalysts with small cluster size (ca. 2 nm), whereas for larger particles (>7 nm), the activation energy is lower and does not change with size (ca. 17 kcal/mol). They proposed that smaller Rh particles tend to bind CO(ads) intermediate stronger than larger ones. The activation energy for the dissociation of adsorbed CO species does not vary with Rh particle size, which suggests that smaller particles are not intrinsically less active, but they present less active sites than larger ones. The study of the kinetic parameters permits to propose that CO(ads) dissociation is aided by the presence of H species and that a likely surface intermediate is Rh carbonyl hydrides.⁸⁰

Recently, Beaumont et al. has reported the role of Pt nanoparticles (Pt NPs) in Co-Pt/SiO₂ on the methanation of CO₂.⁸³ The presence of Pt NPs deposited near Co NPs (within the same mesoporous oxide support) can enhance the CO₂ methanation rate by up to a factor of 6 per Co surface atom. The Pt NPs was also able to enhance reduction of the Co at temperatures relevant to CO₂ methanation. The hydrogen atoms dissociated on Pt may be transferred to the Co NPs via long-distance hydrogen atom spillover, aiding their reduction.

Pd/Al₂O₃ and Pd/MWCNT were investigated as bifunctional catalysts for CO₂ methanation and their role of the atomically dispersed metal centers in the overall catalytic performances were discussed by Kwak et al.⁷² The results of this study clearly show that atomically dispersed supported metals can be catalytically active even in the demanding reaction of CO₂ reduction. Their activity and selectivity patterns, however, differ by a large extent from those of 3D metal particles. The CO₂ hydrogenation reaction on Pd/Al₂O₃ and Pd/MWCNT catalysts have unambiguously proven the need of two different functionalities in an active catalyst. In the 1% Pd/MWCNT catalyst, Pd (present in atomic dispersion) can activate

H₂, but the functionality to activate CO₂ is absent. Therefore, this material is inactive in the reduction of CO₂ with H₂. In the other two systems that also contain Pd in atomic dispersion but in the presence of oxide components (0.5% Pd/Al₂O₃ and 1%Pd+2.3% La₂O₃/MWCNT) the reduction of CO₂ proceeds at high rates. This is due, most probably, to the concerted reaction between the oxide-activated CO₂ and the metal-activated hydrogen. But the reduction of CO₂ in these two systems produces primarily (or almost exclusively) CH₄, and not CO. This is the consequence of the absence of Pd metal clusters where the initially formed CO could be activated. The CO that forms from the oxide-activated CO₂ desorbs from these catalysts and is detected in the effluent. However, when Pd clusters are present in the system (10% Pd/Al₂O₃) the initially formed CO can readily be hydrogenated to CH₄ on the metal particles (both adsorbed CO and atomic hydrogen present on the metal clusters). The mechanistic is clearly presented in Fig. 6. Therefore, the methane selectivity over the catalyst that contains large metal clusters is high. The results obtained clearly show that the oxide support material, even when it is considered inert like Al₂O₃, can function as a critical, active component of complex catalyst systems.

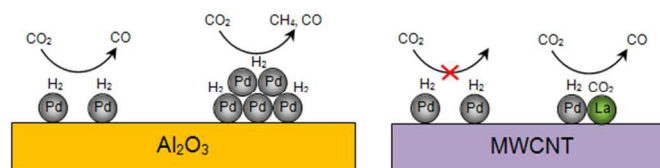


Fig. 6 Mechanistic of various catalysts on CO₂ methanation. The results showed the important of different functionalities in an active catalyst (i.e: Al₂O₃ as a metal oxide support and Pd in a metal cluster).⁷²

Shape-controlled Pd nanocubes and nanopolyhedra particles embedded in mesoporous silica shells were studied on CO₂ hydrogenation.⁸⁴ The catalysts were compared to Pd/SiO₂ prepared by wetness impregnation and found that the Pd/SiO₂ exhibits a strong deactivation. While, the activity of both embedded solids is remarkably stable. This difference is due to a significant Pd particles sintering in the SiO₂ while no increase of particle size is observed for the core@shell solids.⁸⁴

Supported gold, rhodium and bimetallic rhodium-core-gold-shell catalysts were studied on CO₂ methanation.⁸¹ The supports used were titanate nanotube and nanowire. The gold particles were highly dispersed besides the metallic form on all supports. The main product of CO₂ hydrogenation was CH₄ on all catalysts. IR spectra revealed the existence of CO and formate species on the surface. In addition, a new band was observed around 1,770 cm⁻¹ which was assigned as tilted CO which is bonded to Rh and interacts with a nearby the oxygen vacancy of the support.⁸¹

Others metal-based catalysts

Instead of Ni and noble metal-based catalysts, others metal such as Co,⁸⁵⁻⁸⁹ and Mg⁹⁰ were also tested to determine the potential of those metal catalysts on CO₂ methanation. Srisawad et al. reported the Co/Al₂O₃ catalysts prepared by the solid-state reaction between gibbsite and various cobalt salts such as cobalt acetate (CoAc), cobalt acetylacetonate, cobalt chloride, and cobalt nitrate (CoNT) for the hydrogenation of carbon dioxide.⁸⁵ Compared to the catalyst prepared by conventional impregnation of aqueous solution of cobalt

Table 3 Summary of various Co catalysts for CO₂ methanation

Catalysts	Preparation method	T [°C]	X _{CO₂} [%]	S _{CH₄} [%]	Ref.
Co/Al ₂ O ₃	Mechanical mixture of cobalt nitrate and gibbsite	270	76	82.2	85
Co/KIT-6	impregnation	260	46	100	86
Co/meso-SiO ₂	impregnation	360	30	100	86
Co/SSP	impregnation	220	27	89.5	89
Co/MCM	impregnation	220	28	91.4	89
Co/TiSSP	impregnation	220	16	92.1	89
Co/TiMCM	impregnation	220	34	94.9	89
Co ₄ N/γ-Al ₂ O ₃	NH ₃ -temperature programmed reaction	350	99	98	87
Co/γ-Al ₂ O ₃	impregnation	350	79	n/a	87

n/a: not available

nitrate on alumina (CoNTImp), the solid-state catalysts (CoNT and CoAc) exhibited much higher activity in the CO₂ hydrogenation with comparable CH₄ and CO selectivity. Unlike the impregnation catalysts, in which most of the Co₃O₄ particles/clusters were located deep inside the pores of alumina, the solid-state reaction resulted in the dispersion of cobalt oxides mostly on the external surface of alumina. As a consequence, CO₂ adsorption and dissociation to adsorbed CO and O (the initial steps in CO₂ hydrogenation) were not limited by the slow diffusion of CO₂ so high CO₂ hydrogenation activity was obtained. The average crystallite size of Co₃O₄ and the metal-support interaction depended on the cobalt precursor used during the solid-state synthesis. Nevertheless, the solid state reaction of gibbsite and cobalt chloride at 650 °C resulted in very poor CO₂ hydrogenation activity due to the formation of inactive cobalt aluminate.⁸⁵

Mesoporous Co/KIT-6 and Co/meso-SiO₂ catalysts with well-dispersed Co species were reported by Zhou et al. for CO₂ methanation.⁸⁶ The Co/KIT-6 catalyst has a large specific surface area (368.9 m² g⁻¹) and a highly ordered bicontinuous mesoporous structure. The Co/KIT-6 exhibits excellent CO₂ catalytic hydrogenation activity and methane product selectivity, which are both higher than those of the Co/meso-SiO₂ catalyst at high reaction temperatures. The high dispersion of the Co species and the large specific surface area of the prepared Co based catalysts contribute to the high catalytic activities. In addition, the highly ordered, bicontinuous, mesoporous structure of the Co/KIT-6 catalyst improves the selectivity for the methane product.⁸⁶

A model of cobalt catalysts for CO₂ hydrogenation prepared using colloidal chemistry was studied by Iablokov et al.⁸⁸ The turnover frequency at 6 bar and at 200–300 °C increased with cobalt nanoparticle size from 3 to 10 nm. They demonstrated that near monodisperse nanoparticles in the size range of 3–10 nm could be generated without using trioctylphosphine oxide.⁸⁸ Different supports, such as SSP, MCM-41, TiSSP and TiMCM were used to prepare Co catalysts for CO₂ hydrogenation for methanation.⁸⁹ It is found that after calcination of catalysts, Ti is present in the form of anatase. The introduction of Ti plays important roles in the properties of Co catalysts by: (i) facilitating the reduction of Co oxides species which are strongly interacted with support, (ii) preventing the formation of silicate compounds, and (iii) inhibiting the RWGS reaction. Based on CO₂ hydrogenation, the CoTiMCM catalyst exhibits the highest activity and stability.⁸⁹

An alumina supported cobalt oxide based catalysts doped with platinum prepared by wet impregnation method for CO₂ methanation was reported by Bakar et al.⁴⁵ The catalyst shown an excellent activity with 70.1% of CO₂ conversion into methane and 47% of

CH₄ formation at maximum temperature studied of 400°C. This catalyst possessed the active site Co₃O₄ in face-centered cubic and PtO₂ in the orthorhombic phase with Al₂O₃ existed in the cubic phase.⁴⁵

Recently, alumina-supported Co₄N catalysts prepared by NH₃-temperature programmed reaction (NH₃-TPR) were used to perform CO₂ methanation in a fixed bed reactor.⁸⁷ The activity results revealed that Co₄N was a superior active phase for CO₂ conversion than Co⁰. The formation of a Co₄N phase led to a strong metal-support interaction modulating the metal particle size and dispersion. The addition of N to form cobalt nitride greatly improved the overall adsorption capacity of the catalyst. Moreover, a 250 h stability test demonstrated that γ-Al₂O₃-supported Co₄N catalyst had excellent resistance to coking and metal sintering. This superior long-term performance could be related to increased surface basicity and stronger Co₄N-γ-Al₂O₃ interaction.

On the search for novel methanation catalysts, hydrogen storage alloys might be an alternative to classical catalysts for CO₂ methanation. Compared to MgH₂ and other Mg based alloys, e.g. Mg–Al or Mg₂Cu, Mg₂Ni exhibits a fast activation under reducing conditions for the surface layers. Therefore, Kato et al. has studied the potential of Mg–Ni hydride (Mg₂NiH₄) alloy for CO₂ methanation.⁵⁰ The Mg₂NiH₄ was investigated with respect to the catalytic property of the hydride surface for CO₂ methanation. The formation of surface oxide layers hinders the decomposition of the hydride. The surface oxidation is accompanied by segregation of Mg oxides and Ni at the disproportionated surface on Mg₂NiH_{4-x}. However, the active Ni sites at the surface are associated with the ready dissociation of hydrogen molecules and subsequent hydrogenation of the intermetallics Mg₂Ni. The simultaneously precipitated Ni-clusters are attributed to the catalytic activity of the hydrides surface, i.e. for dissociative adsorption of CO₂ molecules and their subsequent hydrogenation. As the Ni particles are formed during decomposition, the modified surface becomes further active in the CO₂ methanation.

The summary of Co catalyst is illustrated in Table 3. The previous studies showed that Co catalysts have specific catalyst preparation before being used on CO₂ methanation. Among the promising technique of the catalyst preparation is solid-state reaction, colloidal chemistry and NH₃-temperature programmed reaction. These technique showed superior catalytic activity compared to conventional impregnation method. The dispersion of cobalt oxide on the external surface plays an important factor for high activity of reaction and this can be achieved via a specific technique such as solid-state reaction. While, alloy-based catalyst such as Mg–Ni hydride can be potentially being used for CO₂

methanation due to its behaviours to exhibit a fast activation of CO₂ under reducing conditions.

Reaction mechanism

Although the methanation of CO₂ is a comparatively simple reaction, its mechanism appeared to be difficult to establish. Presently, there are still arguments on the nature of the intermediate compound involved in the process and on the methane formation scheme. The reaction mechanisms have been classified into two main categories. The first one involves the conversion of CO₂ to CO prior to methanation and the subsequent reaction follows the same mechanism as CO methanation.^{12, 79} The other reaction mechanism involves the formate species as the main intermediate during the reaction.³³ Note that, even for CO methanation, there is still no consensus on the kinetics and mechanism. It has been proposed that the rate-limiting step is either the formation of the intermediate CH_xO and its interaction with hydrogen or the formation of surface carbon on CO dissociation and its hydrogenation.⁹⁰

Numerous studies have been conducted on the adsorption and activation of CO₂ on metal surfaces such as Cu,⁹¹ Pt,⁹² Pd,⁹³ and Fe⁹¹ where the Fe(110) surface has been identified to be most suitable for CO₂ activation.⁹⁴ This has been attributed to a remarkable charge transfer (0.83 e⁻) from the surface to the CO₂ molecule and to the elongation of one of the C–O bonds (to ca. 1.30 Å) including bending of the CO₂ molecule.⁹⁴ The most widely used metals for CO₂ methanation, however, are Ni, Ru and Rh. Using density functional theory (DFT) calculations, it has been verified that the reaction on Ni also involves the formation of the bent CO₂ intermediate.⁹⁵

The findings on the fundamental insight into the CO₂ adsorption mechanism on CeO₂ has been explored by Hahn et al.⁹⁶ They employed the functional theory to study the adsorption of carbon dioxide on CeO₂(111). At low coverage (1/9 monolayer), CO₂ is found to preferably adsorb in a monodentate configuration forming a carbonate species with a surface O atom. In this configuration, the CO₂ molecule is bent with an O–C–O angle of 129° and a remarkable elongation (to 1.27 Å) of the C–O bond length compared to the gas phase molecule, indicating a high degree of CO₂ activation. A similar activation is observed when the CO₂ molecule adsorbs as bidentate carbonate; however, this configuration is less stable. Linear configurations are found to adsorb very weakly at low coverage by physisorption. Increasing the coverage leads to a decrease of the stability of mono- and bidentate configurations which can be attributed to repulsive interactions between adjacent adsorbates and the limited capacity of the CeO₂(111) surface to donate electrons to the adsorbates. In contrast, the binding energy of linearly adsorbed CO₂ is shown to be coverage independent. At coverages >1/4 monolayer, the stability of mixed configurations where monodentate, bidentate, and linear species are present simultaneously on the surface. The most stable configurations are found when 1/3 monolayer CO₂ is bound as monodentate species, and additional molecules are physisorbed forming partial layers of linear species. Analysis of the projected density of states has shown that the orbitals of linear species in the first partial layer lie at lower energies than the ones of the second partial layer suggesting stabilization of the former through interactions with preadsorbed monodentate species.⁹⁶

DFT calculations have also been performed to understand the complete hydrogenation mechanisms for CO₂ on Ni(110) surface.⁴⁶ The calculations show that the CO₂ hydrogenation passes via various stable intermediates, namely, carbon monoxide, methoxy, formate and yield the product methane. It is suggested that the methane formation via hydroxyl carbonyl intermediate requires a lower

energy barrier than via carbon monoxide and formate intermediates on the Ni(110) surface.

The mechanism of CO₂ methanation on a Ni/Ce_{0.5}Zr_{0.5}O₂ catalyst has been investigated using in situ FTIR spectroscopy.⁴⁷ It was proposed that CO₂ prefers to adsorb on surface oxygen sites adjacent to Ce(III) compared with those adjacent to Ce(IV)/Zr or surface hydroxyl sites. Five adsorption species were revealed for CO₂ adsorption on Ni/Ce_{0.5}Zr_{0.5}O₂. The adsorption sites and resulting species are as follows: (1) the surface oxygen sites adjacent to Ce(IV) or Zr resulting in monodentate carbonates; (2) the surface oxygen sites adjacent to Ce(III) which are connected with an oxygen vacancy resulting in monodentate carbonates; (3) the surface oxygen vacancy adjacent to Ce(III) resulting in bidentate carbonates; (4) the surface oxygen vacancy adjacent to Ce(IV) resulting in bidentate carbonates; (5) the surface hydroxyl sites of Ce(IV) or Zr resulting in hydrogen carbonates. It was found that monodentate carbonates on Ce(III) are easier to be hydrogenated than those on Ce(IV). Formate species were found to be the main intermediate species during the reaction and Ce(III) sites were proposed to be active sites for their hydrogenation. A reaction mechanism that could account for all of these observations is presented in Fig. 7.

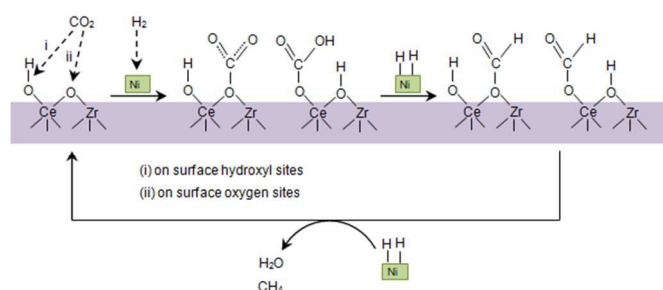


Fig. 7 Proposed reaction pathways for CO₂ methanation on a Ni/Ce_{0.5}Zr_{0.5}O₂ catalyst. Adopted from Pan et al.⁴⁷

Hydrogen carbonates and carbonates are sourced from CO₂ adsorption on surface hydroxyls and the surface oxygen sites in the cerium–zirconium solid solution, respectively. Since the bidentate carbonates are not stable enough to be hydrogenated to formate species, the formate species are derived from the hydrogenation of hydrogen carbonates and monodentate carbonates. Although the hydrogen that adsorbs on the surface oxygen of Ce_{0.5}Zr_{0.5}O₂ could convert carbonate to formate, nickel particles still play an important role in the dissociative adsorption of hydrogen. The subsequent hydrogenation reactions of formate using metal adsorbed hydrogen atoms lead to the formation of –CH₂OH. The –CH₂OH species are then hydrogenated to –CH₃ and CH₄.⁴⁷

Aldana et al. has studied the methanation of CO₂ over Ni-CZ_{sol-gel} and Ni-silica.³³ The results show that the Ni-CZ_{sol-gel} catalysts have much better activity compared to Ni-silica. The mechanism of CO₂ methanation over Ni-CZ_{sol-gel} explain the involvement of weak basic sites of the support for the adsorption of CO₂ and implies a stable metal-support interface. The mechanism for CO₂ methanation on the studied Ni-CZ_{sol-gel} catalyst is proposed. The main reaction pathway does not involve CO as an intermediate. Carbon dioxide adsorbs on sites of mild basicity to form covalent carbonates, hydrogen carbonates and then bidentate carbonates. These species are further reduced and hydrogenated by H atoms formed by dissociation of hydrogen at the surface of Ni⁰ particles to form formates and then probably formaldehyde-type and methoxy species (not observed) and to finally release methane. A parallel pathway may exist where CO is formed by a redox cycle on reduced ceria.

This pathway may decrease activity by CO-H₂ competitive adsorption on metal particles and enhance deactivation by Ni sintering through the formation of di- or tri-carbonyls and by the formation of stable polycarbonates which block the CO₂ adsorption sites.

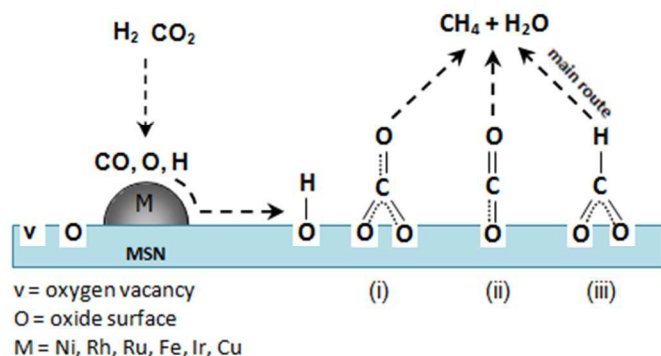


Fig. 8 Plausible mechanism of CO₂ methanation on M/MSN; (i) bridged carbonyl, (ii) linear carbonyl and (iii) bidentate formate. Adopted from Aziz et al.⁴²

Nickel promoted mesostructured silica nanoparticles (Ni/MSN) were highly active for CO₂ methanation due to the presence of intra and interparticle pores which led to increase the number of oxygen vacancy in the catalyst.⁴¹⁻⁴³ The presence of oxygen vacancies in Ni/MSN is necessary to explain the formation of surface carbon species, C(a). It is possible that a C(a) species could interact directly with an oxygen vacancy in MSN. The role of Ni sites in MSN may be to dissociate hydrogen to form atomic hydrogen, in which atomic hydrogen facilitates the formation of methane. However, the later finding on Ni/MSN reported that the Ni was also responsible to dissociate CO₂ to CO and CO.⁴² As presented in Fig. 8, firstly, CO₂ and H₂ was adsorbed onto metal sites, followed by dissociation to form CO, O and H atoms, and migration onto the MSN surface. The CO then interacted with oxide surfaces of the MSN to form bridged carbonyl and linear carbonyl. Bidentate formate was also formed through the interaction with atomic hydrogen. Meanwhile, the O atom spilt over onto the surface of the MSN and was stabilized in the oxygen vacancy site near the metal site. The adsorbed oxygen then reacted with atomic hydrogen to form hydroxyl on the MSN surface in which a further reaction with another atomic hydrogen formed a water molecule. Finally, the adsorbed carbon species was further hydrogenated to methane and another water molecule. In the

study, all three species (linear carbonyl, bridged carbonyl and bidentate formate) could be an intermediate for CO₂ methanation as reported by previous studies.^{33,47,82,97-99} However, the bidentate formate species could be the main intermediate for CO₂ methanation as agreement by the previous studies.^{33,47,97}

Two plausible reaction paths were found for the transformation of CO₂ to CH₄ on TiO₂-supported Ru nanoparticles by density functional theory (DFT) using the generalized gradient approximation with periodic boundary conditions.⁷⁴ CO₂ adsorbs with a bent structure on the modeled Ru cluster supported on the TiO₂ (1 0 1) surface. Two plausible sites for CO₂ adsorption were found through the optimized structure: the top and the side of the Ru cluster. The CO₂ molecule is readily adsorbed at both adsorption sites of the Ru cluster at moderate temperature, and the adsorbed CO₂ to the Ru cluster is more stable than to the Ru surface. This result is caused by the difference of the Ru structure between the Ru surface and the Ru nanoparticles. The adsorbed CO₂ on each site transforms into CO through different reaction paths, but the potential energy barriers for each reaction path are almost the same. Both adsorption sites, therefore, function as active sites of the transformation of CO₂ to CO at moderate temperature. The elementary reactions of the hydrogenation of adsorbed CO and of the production of CH₄ are possible to become the rate-determining steps over the methanation reaction, because these two reactions have a higher potential energy barrier than that of other elementary reactions in the overall reaction path. These potential energy barriers for the hydrogenation of CO and the production of CH₄ on TiO₂-supported Ru nanoparticles were lower than those on bulk Ru surface, which explains the high activity of the Ru nanoparticle-loaded TiO₂ catalyst. The lowering of these potential energy barriers can be caused by weak charge transfer between Ru atoms and adsorbed species on the TiO₂-supported Ru nanoparticles. The electron charge transfer from CO to the adsorbing Ru atoms on Ru/TiO₂ was less than that on the Ru surface, indicating that the interaction between the adsorbed species and Ru atoms on Ru/TiO₂ was weaker. Therefore, the adsorption of CO and CH₃ on Ru/TiO₂ is less energetically favorable than on the Ru slab, and thus the potential energy barriers of the hydrogenation reaction of CO and the production of CH₄ are smaller.⁷⁴

Panagiotopoulou et al. has reported the mechanism of methanation of CO₂ over 5%Ru/TiO₂ through in situ FTIR spectroscopy (DRIFTS) and transient mass spectrometry techniques.⁷⁰ It is shown that interaction of the prerduced catalyst with the reaction mixtures results in the development of various Ru-bonded carbonyl species on reduced and partially oxidized sites as well as on sites located at the metal-support interface. The nature and population of these species depend strongly on feed composition and reaction temperature. The reaction dominates at lower reaction temp-

Table 4 Comparison of reaction mechanism between Ni and Ru-based catalyst

Catalysts	H ₂ adsorption sites	CO ₂ adsorption sites	Intermediate species	Comments	Ref.
Ni-based	reduced Ni	<ul style="list-style-type: none"> reduced Ni oxygen vacancy 	<ul style="list-style-type: none"> monodentate carbonates at support surface bidentate carbonates at support surface bidentate formates at support surface (main intermediate) 	The formation of di- or tri-carbonyls and stable polycarbonates block the CO ₂ adsorption sites and these will lead to deactivation of Ni catalyst.	33, 42, 47
Ru-based	reduced Ru	<ul style="list-style-type: none"> reduced Ru partially oxidized Ru oxygen vacancy 	<ul style="list-style-type: none"> carbonyl species at the metal-support interface carbonyl species at the metal surface 	The nature and population of intermediate species depend strongly on feed composition and reaction temperature.	70,74

eratures which involves hydrogenation of surface carbon produced by dissociative adsorption of CO, whereas the latter involves hydrogenation of CO species adsorbed at the metal-support interface.

At low temperatures, typically <250 °C, dissociation of CO results in accumulation of adsorbed oxygen species which cannot be removed from the catalyst surface, rendering it inactive. Catalytic activity is restored at higher temperatures, where partially oxidized sites are reduced efficiently by adsorbed hydrogen atoms. The associative reaction pathway is the only one which is operable under conditions of CO₂ methanation and proceeds via intermediate formation of carbonyl species at the metal-support interface, produced by the RWGS reaction.

The comparison of reaction mechanism between Ni and Ru-based catalyst is presented in Table 4. It can be concluded that many researchers agreed that the formate species on Ni catalyst could be a main intermediate or precursor to the formation of methane. However, the Ni catalyst may deactivate due to the formation of di- or tri-carbonyls and stable polycarbonates which block the CO₂ adsorption sites. In contrast, carbonyl species is of important for Ru catalyst. This species may form on metal and/or metal-support interface. The nature and population of intermediate species for Ru catalyst is depend strongly on feed composition and reaction temperature (moderate temperature).

Summaries and future prospects

Global warming has pushed the necessity to reduce the emissions of gases responsible for the Greenhouse effect, mainly CO₂, caused by the use of fossil fuels. The increasing amounts of CO₂ in the atmosphere are causing climate changes on a global scale. Therefore, a reduction in CO₂ emission into the atmosphere is an urgent necessity. However, the levels of CO₂ are increasing with increasing in the world's population and improvement in living standards. Although various physical and chemical techniques have been proposed for the fixation of exhausted CO₂, such as fixation in carbonates, geological or ocean storage, or afforestation, their immediate practical application has drawbacks in terms of economic factors, safety, efficiency, and reliability. The use of CO₂ as a renewable and environmentally friendly source of carbon is a highly attractive approach.

Research direction. Various strategic considerations, technical approaches, and specific research directions have been presented in the methanation of CO₂. The prevalent view of the active site is the synergy between the primary catalyst and support or promoter. Because the catalyst for CO₂ methanation is sensitive to the structure of the catalyst, the preparation method, preparation conditions, and the component significantly influence its performance. In summary, the future research directions on the catalysts for CO₂ methanation would be proposed as follows:

1. To further explore new materials and optimize the catalyst synthesis conditions in order to achieve high active and stable Ni catalysts with low reaction temperature of CO₂ methanation.
2. To explore high surface area mesoporous material with tunable pore size to improve catalyst structures for the purpose of achieving higher volumetric surface areas. For example, explore innovative synthesis method to produce high surface area of mesoporous cerium oxide and/or hybrid catalysts of cerium with mesoporous material.
3. To explore a new way to generate or tailor the basic sites of the catalyst. For example, by incorporation of specific amount of metal chloride or alkali metal on the catalyst support.

4. To improve catalyst stability, for example, by exploring alternative metal other than nickel and/or enhancing the basicity of the catalyst by adding the alkaline earth metal (i.e. La₂O₃) as a promoter.

5. To fundamentally understand the mechanisms of CO₂ methanation and explore its relationship with catalyst active site structures using both theoretical calculations (molecular/electronic level modeling) and experimental approaches to tailor new catalyst structures.

Presently, it can be suggested that Ni is the most suitable metal in term of activity and economical point of view. Therefore, Ni catalyst has a potential to be widely used in the industrial process. High surface area of the support is crucial for methanation reaction which promotes for high dispersion of the metal or active phase on the surface of the catalyst support. High surface area such as MSN and MOFs are among of the best candidates which exhibited high performance in conversion and selectivity to methane. In addition, mesopores structure material with high porous volume and size also contributes to the high catalytic activity. An optimum catalyst should have a high specific surface area and ultrafine or nanostructured particles of the metal active sites. It is important to systematically characterize the nature of the active sites and interactions among active components, support, and promoter to be able to tailor the structure of the catalyst. For practical CO₂ utilization, however, better understanding of reaction mechanisms at atomic/molecular level is necessary for rational design of high performance catalyst.

Commercialization of CO₂ methanation. In view of commercialization of CO₂ methanation, this process is viable if the CO₂ and H₂ were generated from waste and renewable energy, respectively (Fig. 9). For instance, CO₂ can be generated from local biomass or power plants and H₂ can be produced via water electrolysis using inexpensive renewable power sources.

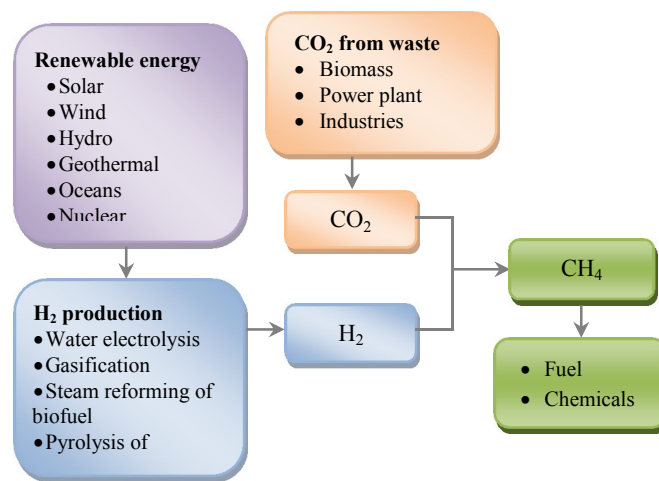


Fig. 9 Overview of CO₂ methanation.

Renewable energy sources including wind, solar, hydro and geothermal as well nuclear energy that are bound to play an increasing role in the world's energy mix, produce primarily electricity. However, the current promising renewable power sources would be hydroelectric power. Presently, the hydroelectric power is by far the world's largest renewable source of electricity, with about 850 GW of installed capacity and an annual production of over 3 PWh.¹⁰⁰ In terms of electricity produced, it is second only to fossil

fuel and generates about 10 times more power than geothermal, solar and wind power combined.¹⁰¹ Hydroelectricity generation is based on turbines that convert the energy of falling water into mechanical power with an efficiency of about 90%.

In term of the generation of hydrogen from renewable energy, the splitting of water would be the simplest way to produce synthetic hydrogen. The sole practical method to split water into hydrogen today is electrolysis, but others such as photochemical and thermal splitting as well as high temperature chemical cycles (vide infra) are also under investigation. Electrolysis of water has been practiced for more than 100 years and is efficient with overall system conversions higher than 75 to 80% with further improvements possible.

In general, water is concluded to be the only suitable source of hydrogen for reducing CO₂ emissions from various sources via its hydrogenation to methane. While having these advantages of availability, flexibility and high purity, to achieve widespread applications, hydrogen production using water electrolysis still needs improvements in energy efficiency, safety, durability, operability and portability and, above all, reduction in costs of installation and operation. These open up many new opportunities for research and development leading to technological advancements in water electrolysis.

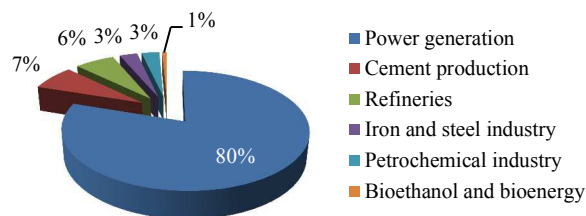


Fig. 10 Total annual CO₂ emissions in various industry sectors. Adopted from Metz et al.¹⁰²

Furthermore, the economy will be significantly improved when novel cost- and energy-efficient methods for providing large amounts of pure CO₂ are developed. Many industrial processes (Fig. 10), most notably power generation, cement manufacture, refineries and iron and steel making also intrinsically produce CO₂ and can be fitted with CO₂ capture technologies. Currently, carbon capture and storage (CCS) offers one of the very few remaining methods to reduce CO₂ emissions. The captured CO₂ is then pressurized to 100 bar (or more), prior to being transported to a storage site which later being used in methanation unit. After all, as a green carbon source and renewable feedstock, the methanation of CO₂ definitely has a promising future.

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Notes and References

^aInstitute of Hydrogen Economy, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

^bDepartment of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

^cDepartment of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.
Email: sugeng@utm.my

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Table of content

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This review describes an overview on much of the recent work in catalytic methanation of CO₂ and its future prospects.

