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A short review on Ni-based catalyst supporter for carbon monoxide (CO) methanation process

A.H. Hatta¹, A.A. Jalil^{1,2*}, N.S. Hassan¹, M.Y.S. Hamid^{1,2}, A.F.A. Rahman¹, and M.A.H. Aziz³

¹School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

²Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

³Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

E-mail: aishahaj@utm.my

Abstract. Since the discovery of methane synthesis by the interaction between carbon oxide and hydrogen by Sabatier and Senderens in 1902, the methanation reaction has been extensively established and is frequently utilized in chemical manufacturing, comprising the elimination of trace quantities of CO from feed gas containing a rich amount of hydrogen, refining of the reformat gas for fuel cells, and production of new energy sources, which is synthetic natural gas (SNG). It is feasible for SNG to be carried and distributed using the present pipeline infrastructure, which is favourable from a cost-effectiveness standpoint. Since CO methanation is highly exothermic, the development of exceedingly effective catalysts with promising activity in the CO methanation process is essential to address this problem. Because of their economical price and high catalytic performance, nickel-based catalysts have been extensively studied as CO methanation catalysts. Coke deposition and Ni sintering invariably occur on Ni-based catalysts, and these catalysts also have inadequate low-temperature activity and stabilities. So, the advancement of exceedingly effective nickel-based catalysts with outstanding low-temperature catalytic capabilities has emerged as the primary research attention as well as a significant technical encounter in this sector. This brief overview covers recent developments for a supporter for extremely efficient nickel-based catalysts for CO methanation.

1. Introduction

In this new modern era where everything developed exponentially, global energy sources experienced a tremendous burden on the high usage of energy. CO methanation is amongst the most significant reactions to developed synthetic natural gas (SNG), which is a new source of energy created mainly from hydrogen and carbon monoxide. These sources of CO and H₂, called syngas, were generated from industrial wastage or renewable feedstock. CO methanation has also been widely utilized in a variety of industrial processes, including the elimination of minimal quantities of CO from hydrogen-rich input gas, the reformat gas purification for NH₃ production and fuel-cells applications, and operations related to Fischer–Tropsch synthesis. Thermodynamically, CO is an extremely stable molecule, and its conversion requires a significant amount of energy. Because of this, effective catalysts and catalytic processes are necessary in order to make CO conversion economically profitable.



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There has been a substantial amount of effort put into the development of CO methanation catalysts, such as Ni [1-12], Co[13-15], Ru[16-18], Rh[19, 20], and Pd[21] based catalysts. Ni-based catalysts were shown to be superior to other types of catalysts due to their comparatively strong methanation capabilities and inexpensive cost. As a result, Ni-based catalysts are currently being used in the majority of the published research on CO methanation. However, due to sintering and coke deposition, Ni-based catalysts frequently suffer from poor performance at low-temperatures and deactivation at high-temperatures, resulting in poor performance. As a result, creating an effective Ni-based catalyst for the methanation process would be desirable to overcome the difficulties. Support plays a vital role in overcoming these difficulties. The amount of Ni metal loaded into the supported Ni catalysts, Ni metal particles sizes, metal-support synergistic relations, and the support composition all have a noteworthy impact on the capability and selectivity of the supported-Ni catalyst.

Consequently, there has been a significant increase in the number of investigations being done on carbon monoxide methanation over supported Ni catalysts over the last ten years. A vital step in the CO methanation process is the creation of active and stable Ni catalysts. To achieve this goal, the authors have written this review paper to present a critical overview of carbon monoxide methanation catalyst manufacturing and research that has occurred in recent years. We are examining the characteristics of supports, particularly their effectiveness in CO methanation, in light of existing studies on supported Ni catalysts for CO methanation. We hope to acquire a better knowledge of the CO methanation reaction over a supported Ni catalyst. When selecting and understanding the reference of each supported Ni catalyst, it is critical to make the right choice. The purpose of this analysis is to provide an overview of the furthestmost current progresses in the field of supported Ni catalysts, as well as to explore the benefits of using both single and bi-supported Ni catalyst systems for the CO methanation process.

2. Supporter for Ni-Based Catalysts

Ni-based catalyst capability is significantly influenced by the support structure used in the catalyst. Supports having huge specific surface areas and a tremendous amount of pore volumes, which are necessary for catalysis, can adapt the active nickel particles in an extremely dispersed form, which is essential for catalysis. Enhancing the oxidation-reduction characteristic of electron transport amongst the active sites of the metal and the support will result in an upsurge in the metal electron density. These electrons have the potential to increase the interaction between nickel and carbon, therefore promoting the cracking of the C=O bond and the creation of CH₄ in the reaction. Furthermore, the physicochemical features of various supports will have an impact on the nickel crystal size and surface characteristics, together with the reducibility and catalytic capabilities of catalysts, among other things. Meanwhile, the structure of the support has a noteworthy impact on the Ni dispersion over the catalyst surface, as previously stated. Aside from that, the CO's chemisorption and activation on the high-alkalinity support could be accelerated, and the activated CO would react rapidly owing to the small kinetic barrier, which would result in the catalyst being furnished with coke deposition resistance capability. As a result, the support of the catalyst is highly related to the catalytic activity of that catalyst [22].

2.1 Single-Supported Ni Catalyst

Catalytic supports for nickel catalysts for CO methanation, such as TiO₂, Al₂O₃, ZrO₂, SiO₂, and other similar materials, are typically composed of a single kind of catalytic support with a variety of morphologies. For example, when used in conjunction with an active component, TiO₂, which is well-known as a semiconducting material with excellent thermal stability, could effortlessly create a robust metal-support relationship, and this supported by an investigation by Tada, Kikuchi, Wada, Osada, Akiyama, Satokawa and Kawashima [12] that stated Ni/TiO₂ demonstrated long-standing endurance for 7000 hours. The fractional replacement of Ni in the TiO₂ lattice, which results in the formation of oxide vacancies, has been ascribed to the increased performance and strong coke deposition resistance of the catalyst. The excellent resistance to carbon deposition is partly a result of the robust metal-to-support interaction [11].

CO methanation over Ni/Al₂O₃ catalyst was explored, and it was shown that the catalytic efficiency of metal nanoparticles is influenced by their size and structure, as well as the interactions between the metals and the supporting materials. In general, the CO methanation activity of Al₂O₃ supports is substantially greater than that of SiO₂ supports [8]. As a result, Ni supported on Al₂O₃ catalysts has been widely investigated. As a consequence of their investigation into the Ni/Al₂O₃ catalyst, Hu, Gao, Ping, Jia, Gunawan, Zhong, Xu, Gu and Su [6] discovered that it was possible to achieve 100% CO conversion over a broad range of reaction temperatures around 300 to 550 °C, and that the CH₄ selectivity amplified with growing temperature, peaking at 96.5% at a comparatively low reaction temperature of 350 °C. In the following study, Xiao, Song, Liu, Shi, Ge, Zhu, Liu and Liu [23] investigated the optimal catalyst of NiO/NiO-OMA, the extraordinary activity at temperatures as low as 300 °C was accomplished with the methane space-time yield exceeding 7.6 g_{cat}⁻¹ h⁻¹. As a result of the high temperature of 600 °C and 120,000 mL g⁻¹ h⁻¹ of gas hourly space velocity (GHSV), long-standing stability for 400 hours was proven with no evidence of deactivation. The outcomes were well elucidated by the combined advantages of free Ni for extraordinary dispersion and contained Ni in the Al₂O₃ matrix for anti-sintering properties, which were combined to provide the desired outcomes. To summarise, a tremendous Al₂O₃ support surface area, reasonable interactivity between Ni and the Al₂O₃ support, and a comparatively low calcination temperature all led to the establishment of tiny NiO particles and NiO species that is easily reduced, resulting in enhanced catalytic capability and robust carbon deposition resistance in the end outcome [4, 6].

For ZrO₂ support, the existence of active spots on the surface of ZrO₂ is assumed to be accountable for the extraordinary capability of the Ni/ZrO₂ catalyst toward the carbon monoxide methanation. This happens on ZrO₂ due to its capability to adsorb CO as well as the hydrogen spill-over phenomena that occur on the surface of the material [2]. This catalyst support demonstrated exceptional catalytic activity, achieving 100% CO conversion at low temperatures, which is lower than 250 °C, as well as long-standing stability [7]. Jia, Rui, Zhang, Hu and Liu [7] discovered that heating the Ni/ZrO₂ catalyst from 220 to 230 °C results in a rapid increase in CO conversion from 19% to 96%, with entire CO consumption achieved at temperatures over 240 °C. The yield of CH₄ increases at a similar rate to the rate of CO transformation. Ni/ZrO₂ produced by the impregnation technique was explored by Liu, Dong, Mo and Lin [24] for selective catalytic methanation of carbon monoxide in hydrogen-rich gases. The findings revealed that the Ni loadings had an extensive impact on the capability of the Ni/ZrO₂ catalyst. If the Ni loading was less than 1.6 wt percent, the NiO was extensively distributed over the exterior of the ZrO₂ support. Increases in Ni loading, particularly at three wt percent or above, resulted in the formation of free bulk NiO species, which were detrimental to efforts to improve the selectivity of the catalyst.

Lakshmanan, Kim and Park [25] organized Ni/SiO₂ catalysts with varying loadings, and it was discovered that the Ni@SiO₂ catalysts exhibited superior capability. The sintering of the Ni nanoparticles was avoided, but significant sintering was seen in the Ni nanoparticles that were not supported by a support. A study conducted by Yan, Liu, Zhao, Wang, Wang and Liu [26] studied the preparation technique of Ni/SiO₂ and discovered that the catalyst produced by plasma decomposition has extraordinary dispersion, improved contact amongst Ni and the SiO₂ support, and has fewer defect sites on the Ni particles. Increased resistance to Ni sintering has also been reported, owing to the fact that it effectively prevents the production of inactive carbon species, resulting in considerably better activity combined with increased stability. Then, Li, Li, Li, Tian and Yu [27] studied the CO methanation performance of Ni-NiO/SiO₂ using a one-pot technique, and they discovered that the catalyst exhibited a large specific surface area, which resulted in better CO methanation performance. After undergoing a 50-hour stability test, the catalyst maintained an extremely high level of stability retention. The catalytic stability test for CO methanation was carried out over Ni/SiO₂ at 180 °C [28]. The initial CO conversion rate is constant for a total of 24 hours. The XRD examination verified that the crystalline structure had not been altered. Due to the presence of crystallized carbon (graphite and whisker carbon) and NiO, there was no visible XRD signal. The used catalyst did not appear to have undergone any morphological changes.

According to the results of Table 1, all type of support exhibit superior catalytic activity in their respective catalysts. TiO₂ could create a robust metal-support relationship between itself and nickel. The slight addition of Ni in the TiO₂ lattice, which results in the formation of oxide vacancies, has been ascribed to the catalyst's increased performance and strong coke deposition resistance. Al₂O₃ also have great interactivity between itself and nickel, which led to the establishment of tiny NiO particles that is easily reduced, resulting in the enhanced catalytic capability of CO methanation. ZrO₂ as support have their own active sites, which is assumed to be accountable for its capability to adsorb CO on the surface of the support; hence, high activity of CO methanation is reported for ZrO₂ support. SiO₂ supports exhibited high surface area even after impregnating nickel onto them, which resulted in high dispersion of NiO particles; hence, the sintering of Ni nanoparticles was avoided. This is one of a multitude of examples indicating that different supports can target different characteristics of catalysts, and any of it can result in beneficial characteristics depending on the goal. Overall, the use of various catalyst supports is necessitated by the presence of a broad catalyst support population, metal-support catalyst combinations, and catalytic aims.

Table 1. The synopses of the Ni-based catalysts catalytic capabilities toward CO methanation.

Catalyst	Ni Content (wt%)	Reaction Condition	CO Conversion (%)	CH ₄ Selectivity (%)	Ref.
Ni/ZrO ₂	10.0	200 °C 1 atm	~99.0	-	[2]
Ni/ZrO ₂	10.0	240 °C 1 atm	~99.0	~99.0	[7]
Ni/TiO ₂	23.0	300 °C 10 atm	~99.0	~96.0	[11]
Ni/Al ₂ O ₃	20.0	350 °C 30 atm	~99.0	~80.0	[6]
Ni/Al ₂ O ₃	10.0	400 °C 30 atm	~98.0	~90.0	[4]
Ni-NiO/SiO ₂	87.8	350 °C 1 atm	97.1	81.9	[27]
Ni@SiO ₂	55.0	210 °C 1 atm	~99.0	-	[25]
Ni/ZrO ₂ /Al ₂ O ₃	20.0	350 °C 15 atm	~99.0	~99.0	[5]
Ni/ZrO ₂ -Al ₂ O ₃	20.0	400 °C 30 atm	~99.0	~82.0	[9]
Ni-Co/CeO ₂ -ZrO ₂	30.0	300 °C 20 atm	100.0	99.0	[10]
Ni/Al ₂ O ₃ -CeO ₂	10..0	350 °C 1 atm	91.6	92.0	[3]

2.2 Bi-Supported Ni Catalyst

The bi-supported, also known as composite supports for nickel-based catalysts for methanation of CO, are primarily composed of ZrO₂-Al₂O₃, CeO₂-ZrO₂, and CeO₂-Al₂O₃, among other materials. They have the ability to integrate the properties of various supports together in order to impose more catalytic activities on the catalyst than single support. Furthermore, the cooperation amongst the two supports would have an impact on the catalytic activities of CO methanation in a positive way.

Guo, Wu, Qin and Zhang [5] studied the performance of a Ni/Al₂O₃ catalyst that had been enhanced with ZrO₂, and they discovered that they could generate a methanation catalyst that has highly active and thermally stable that had exceptional resistance to carbon creation and nickel sintering. Findings from this study indicated that incorporating ZrO₂ inhibits the production of NiAl₂O₄, deteriorates the Ni-Al₂O₃ connection, and makes the catalyst extra readily reduced, resulting in a substantial increase in the reactivity of the catalyst. A Ni/Al₂O₃-ZrO₂ catalysts were organized through a sol-gel technique for methanation and almost 100% selectivity of CH₄ was attained at the temperature of 300 °C, and no catalyst inactivation was noticed after 100 hours of reaction. According to Liu, Gu, Gao, Li, Xu and Su [9], they studied the same catalyst and discovered that the catalyst exhibited excellent stability and resistance to coking, with just 0.4 weight percent of deposited carbon on the catalyst surface. Instead, following a 60-hour stability test, the amount of carbon deposited over the catalyst exclusive of ZrO₂ reached 1.5 weight percent of the total carbon. Improvements in catalytic performance were ascribed to the selective ZrO₂ particles deposition on the NiO surface, instead of Al₂O₃, during the synthesis method, which could be straightforwardly regulated by altering the electrostatic interactivity. When used in syngas methanation, this unusual structure has the potential to improve CO dissociation while also generating surface oxygen intermediates, therefore avoiding Ni particles carbon deposition.

For nickel supported on CeO₂-ZrO₂, an investigation was done by Atzori, Rombi, Meloni, Sini, Monaci and Cutrufello [1], and they stated that nearly complete conversion of CO was achieved on the catalyst. The enhanced reducibility of NiO and the improved capacity to adsorb and stimulate the CO may explain the positive impact of the Ce content. According to the results of the catalytic structure and morphological investigations, the increased catalytic performance of the ZrO₂-CeO₂ may be ascribed to improved metal and support synergistic interactivity, more significant reduction of active metal sites, and enhanced catalyst crystallinity structure. Furthermore, the ZrO₂-CeO₂ support encourages the development of oxygen vacancies underneath a decreased Ce⁴⁺/Ce³⁺ valence ratio, consequential in enhanced CO adsorption capability and, as a result, more significant catalytic activity in the presence of Ce⁴⁺ [10]. A standard impregnation and co-precipitation approach was used to investigate a variety of supports, comprising SiO₂, Al₂O₃, ZrO₂, and CeO₂, that were incapacitated with variable amounts of additional metals by Razzaq, Zhu, Jiang, Muhammad, Li and Zhang [10]. The findings revealed that the co-precipitated ZrO₂-CeO₂-supported catalyst can accomplish 100% of CO conversion at around 300 °C and has a CH₄ selectivity of 99%.

A mixture of CeO₂ with Al₂O₃ encourages nickel species reduction, as reported by Ding, Tu, Zhang, Wang, Tsubaki, Wang and Ma [3]. The findings of the characterization revealed that adding CeO₂ to Ni/Al₂O₃ increased the intensity of the NiO-CeO₂ interactivity through the diminishing of the interactivity concerning Al₂O₃ and Ni particles, therefore simplifying the dissociation of NiO from NiAl₂O₄. The increase in CeO₂ concentration can also help to prevent the development of carbon deposition.

All the results for the bi-supported Ni catalyst are summarized in Table 1. All combinations of support exhibit superior catalytic activity in their respective catalysts. The cooperation between the two supports significantly impacted the catalytic activities of CO methanation. Al₂O₃-ZrO₂ is exceedingly active and thermally stable that has exceptional resistance to carbon deposition and nickel sintering. The integration of ZrO₂ deteriorates the Ni-Al₂O₃ interactivity, making the catalyst effortlessly reduced. CeO₂-ZrO₂ supports, on the other hand, enhanced NiO reducibility, as well as the improved capacity to adsorb and activate CO, which may explain the positive impact of the Ce content. The development of oxygen vacancies also increased, resulting in enhanced CO adsorption capability and, as a result, more significant catalytic activity. A mixture of CeO₂ with Al₂O₃ encourages nickel species reduction. Adding CeO₂ to Ni/Al₂O₃ increased the intensity of the NiO-CeO₂ interactivity by diminishing the interactivity concerning Al₂O₃ and Ni particles, therefore simplifying the dissociation of NiO from NiAl₂O₄. As a result, this is just one of several examples indicating that different supports can target different characteristics of catalysts, and all of it can result in positive characteristics depending on the approach's goal. For the most part, various catalyst supports, support-support catalyst combinations, metal-support

combinations, and catalytic purposes need the use of a range of catalyst support combinations in order to achieve the desired results.

3. Conclusion

Nowadays, energy sources are depleted, and the need for alternative sources of energy is crucial to maintain world energy utilization. As a result, studying CO methanation technology is extremely important in terms of practical application to resolve the energy scarcity problem. Ni-based catalysts were shown to be superior to other catalysts due to their comparatively strong methanation activity and inexpensive cost. In general, the use of diverse supports has been the most active study area in the field of Ni-based catalysts.

To alter the textural characteristic of the catalyst, supports must be used in conjunction with the catalyst. This will affect the catalytic performance of the CO methanation process. Many different approaches were used to study supports, including intensifying the surface area and changing the morphology of the catalyst. Other approaches included controlling metal-support interactivity and altering the pore diameter, all of which might improve the dispersion of metallic Ni active sites.

One promising support that can be used for further research is CeO₂, whether as primary support or as a promoter. CeO₂ has exceptional characteristics, such as different oxidation states between Ce³⁺ and Ce⁴⁺, and fluorite-like assembly may be projected as a capable substitute to typical support such as TiO₂ or Al₂O₃. In addition, the existence of oxygen vacancies on the CeO₂ support will generate the extra driving force for the CO conversion, which will become a place for CO to adsorb on the surface of the catalyst.

For future research, many other aspects can be focused on, such as adding second metal, a promoter, or even using three different supports for a catalyst. The preparation method can also be investigated in the future since each synthesis method, such as impregnation or precipitation, has its own unique advantage. It will affect the characteristic physicochemical outcome of the catalyst. The Ni active sites' low-temperature catalytic capability and anti-sintering characteristics should focus on future Ni-based catalyst development. The advancement of a novel type of supports should be the top exploration. Moreover, investigating the mechanism of CO methanation on the Ni-based catalyst is advantageous to discover the paths to enhance the reactivity of catalysts.

Keywords: Single Supported Nickel catalyst; Bi-Supported Nickel catalyst; Methane; Carbon monoxide; CO methanation.

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