Recent Scientific Progress on Developing Supported Ni Catalysts for Dry (CO\(_2\)) Reforming of Methane

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Abstract: Two major greenhouse gases (CO\(_2\) and CH\(_4\)) can be converted into useful synthetic gas (H\(_2\) and CO) during dry reforming of methane (DRM) reaction, and a lot of scientific efforts have been made to develop efficient catalysts for dry reforming of methane (DRM). Noble metal-based catalysts can effectively assist DRM reaction, however they are not economically viable. Alternatively, non-noble based catalysts have been studied so far, and supported Ni catalysts have been considered as a promising candidate for DRM catalyst. Main drawback of Ni catalysts is its catalytic instability under operating conditions of DRM (>700 °C). Recently, it has been demonstrated that the appropriate choice of metal-oxide supports can address this issue since the chemical and physical of metal-oxide supports can prevent coke formation and stabilize the small Ni nanoparticles under harsh conditions of DRM operation. This mini-review covers the recent scientific findings on the development of supported Ni catalysts for DRM reaction, including the synthetic methods of supported Ni nanoparticles with high sintering resistance.

Keywords: dry reforming of methane; Ni; metal-oxide supports; surface basicity; confinement effect

1. Introduction

Human have largely relied on fossil fuels as an energy source for the last centuries and a large amount of CO\(_2\) gas has been emitted into atmosphere by burning fossil fuels. This extensive amount CO\(_2\) accumulated for centuries is considered to be the main reason for the global climate change, such as artic-sea ice melting and increase of sea-level [1,2]. Therefore, for last decades, a lot of attention has been paid for measures to reduce the amount of CO\(_2\) gas from the atmosphere and extensive scientific researches have been done on CO\(_2\) capturing, sequestration, and conversion of CO\(_2\) into other valuable chemical resources [3–7].

CO\(_2\) can be considered as a possible carbon source in chemical industry and CO\(_2\) reforming of methane (CH\(_4\)), which is often referred as dry reforming of methane (DRM), has been attracted much attention [8–13]. In the DRM reaction, two major greenhouse gases (CH\(_4\) and CO\(_2\)) are converted into H\(_2\) and CO. The generated H\(_2\) and CO are important syngas that can be used as reagents of other synthetic chemical reaction. In addition, DRM reaction can provide the syngas (H\(_2\) + CO) with a desirable ratio (H\(_2\)/CO ratio < ~1) for the subsequent Fischer-Tropsh (FT) synthesis of liquid hydrocarbons and the synthesis of oxygenated chemical compounds [14,15].

DRM reaction can be assisted by heterogeneous metal catalysts and a variety of metal-based catalysts have been studied so far. The noble metals, such as Rh, Pt, Ir, Pd, and Ru, exhibit higher catalytic activity and stability for DRM reactions when compared to other transition metal-based catalysts (Co and Ni) [15,16]. It has been also proved that an addition of small amount of noble metals into transition metal-based catalysts resulted in enhanced catalytic performances [9,16–22]. However, to realize the industrial implementation of CRM reaction, the utilization of noble metals should be avoided due to their high cost and limited availability.
Among the non-noble metal-based catalysts, Ni-based catalysts are most practical choice in favor of their high catalytic activity, low cost and large abundance [10,23–25]. However, Ni-based catalysts have a critical drawback as DRM catalysts. Although initial catalytic activity of Ni-based catalyst is comparable to noble-based catalysts, its initial activity is easily deactivated during CRM reaction due to coke formation on active Ni surface and aggregation of catalytic Ni nanoparticles [23,24].

DRM is a highly endothermic reaction, and thus, it requires a lot of energy input as heat to move the reaction in forward direction. That is to say, inevitably DRM reaction should be performed at very high temperature (<700 °C), and at this high temperature catalytic Ni nanoparticles are easily aggregated together losing their initial activity and high resistance to coke formation.

There have been a lot of efforts devoted to improving the catalytic activity and stability of Ni-based DRM catalyst in the last decades. The formation of bimetallic states with noble-metals and other transition metal has been extensively studied [18–20,25], and it has also been demonstrated that catalytic performances of Ni catalysts are strongly related to the basicity of metal-oxide supports [26–34]. In addition, many scientific results indicate that coke formation on Ni catalyst is less favored when their size are in a nano meter scale [35–38]. Very recently, many efforts have been made towards the fabrication of small Ni nano particles with high thermal stability, which can retain their initial high reactivity and coke-resistance during long-term operation of DRM reaction.

The main scope of this mini-review is to discuss recent progress in developing supported Ni catalysts for DRM. The overview of DRM reaction is provided in the first part of this review (Section 2), which includes the thermodynamics nature of DRM, possible side reactions, and impacts of operating conditions on the performance DRM reactions. Then, recent scientific findings on supported Ni catalyst for DRM are covered in the second part (Section 3). A variety factors including parameters of DRM operation have been proved to have influence on catalytic performance of Ni-based catalysts. Catalytic activity and stability of Ni catalyst can be altered by chemical nature of supports, e.g., acidity, basicity, oxygen storing ability, and reducibility [23]. Recently, small Ni nanoparticles (<~10 nm) have been extensively studied as DRM catalyst and it has been suggested that chemical and geometrical structures of underlying supports play an important role in dispersion and thermal stability of Ni nanoparticles. In this mini-review, the influence of chemical and physical nature of metal-oxide supports on the catalytic performance of supported Ni catalysts will be mainly discussed. In addition, recent scientific findings showing the merit of utilization of Ni nanoparticles will be summarized together with the recently proposed synthetic methods of stable Ni nanoparticles.

2. Overview of DRM

DRM can be expressed as follow,

\[
\text{CH}_4 + \text{CO}_2 \leftrightarrow 2 \text{CO} + 2 \text{H}_2 \quad \left( \Delta H_{298K}^\circ = +247 \text{ kJ mol}^{-1} \right)
\] (1)

Since DRM is a highly endothermic reversible reaction, it requires a large amount of heat energy to drive the reaction in the forward direction to achieve high conversion ratio of two green house gases (\( \text{CH}_4 \) and \( \text{CO}_2 \)) into syngas (\( \text{CO} \) and \( \text{H}_2 \)). Figure 1 shows the influence of operating temperature on equilibrium conversion of DRM reaction [39].

Besides the main reaction (Equation (1)), there are a number of other reactions that can occur during the DRM process. Those possible reactions were well documented previously by Wang et al. [40] and Nikoo et al. [39] and recently revisited in the review paper by Aramouni et al. [41]. Among the possible side reactions, following 4 reactions (Equations (2)–(6)) have been noticed as important ones by most of researchers, which are responsible for the carbon formation on catalysts surface during DRM reaction [39].

\[
\text{CH}_4 \leftrightarrow \text{C} + 2 \text{H}_2 \quad \left( \Delta H_{298K}^\circ = +74.9 \text{ kJ mol}^{-1} \right), \text{methane decomposition}
\] (2)
The temperature range of 870 to 1040 °C. Thus, considering the thermodynamic natures of main and aforementioned side reactions of DRM, the rapid carbon formation is a major cause of easy deactivation of Ni catalysts during DRM reaction. Surface can be suppressed at high temperature (>700 °C) (Figure 2) [39]. Among above four reactions, only the methane decomposition (Equation (2)) is an endothermic reaction that favored at high temperatures, whereas other reactions are exothermic disfavored at high temperature. Carbon formation is an undesired process during DRM process, which may lead to catalytic deactivation either by deactivating catalytic active sites or blocking the reactor [42]. The thermodynamic nature of DRM, it is intuitive that operating DRM over Ni-based catalysts at high temperature is not only beneficial for obtaining higher syngas yield, but also minimizing carbon formation during DRM reaction. The temperature range of 870 to 1040 °C was suggested as an optimal temperature range where the deactivation of catalyst by carbon (coke) formation can be minimized [40].

\[
2\text{CO} + \text{C} + \text{CO}_2 \left( \Delta H^{298K}_{298K} = -172.4 \text{kJ mol}^{-1} \right), \text{ Boudouard reaction} \quad (3)
\]

\[
\text{CO}_2 + 2\text{H}_2 \leftrightarrow \text{C} + 2 \text{H}_2\text{O} \left( \Delta H^{298K}_{298K} = -90 \text{kJ mol}^{-1} \right) \quad (4)
\]

\[
\text{H}_2 + \text{CO} \leftrightarrow \text{C} + \text{H}_2\text{O} \left( \Delta H^{298K}_{298K} = -131.3 \text{kJ mol}^{-1} \right) \quad (5)
\]

Among above four reactions, only the methane decomposition (Equation (2)) is an endothermic reaction that favored at high temperatures, whereas other reactions are exothermic disfavored at high temperature. Carbon formation is an undesired process during DRM process, which may lead to catalytic deactivation either by deactivating catalytic active sites or blocking the reactor [42]. The rapid carbon formation is a major cause of easy deactivation of Ni catalysts during DRM reaction. Thus, considering the thermodynamic natures of main and aforementioned side reactions of DRM, it is intuitive that operating DRM over Ni-based catalysts at high temperature is not only beneficial for obtaining higher syngas yield, but also minimizing carbon formation during DRM reaction. The temperature range of 870 to 1040 °C was suggested as an optimal temperature range where the deactivation of catalyst by carbon (coke) formation can be minimized [40]. The thermodynamic equilibrium analysis conducted by Nikoo et al. also showed that the carbon formation on catalyst surface can be suppressed at high temperature (>700 °C) (Figure 2) [39].

Figure 1. Equilibrium conversion of (a) CH₄ and (b) CO₂ as a function of temperature and CO₂/CH₄ ratio at atmospheric pressure for n(CH₄ + CO₂) = 2 mol. Reprinted with permission from Ref. [39]. Copyright (2011) Elsevier.
Many of recent studies on the catalytic DRM reaction have been performed at high temperature (>700 °C) and methane decomposition (Equation (2)) is a main pathway of carbon formation at such a high temperature whereas other reactions (Equations (3)–(5)) are less likely to proceed at the high temperature [24].

The dissociation of methane (Equation (2)) over Ni surface is sensitive to structure of Ni surface [43], and it leaves carbon atoms (Cα and Cβ) on Ni surface. Cα species are reactive that can be easily gasified by interacting with H2O, CO2, O, or H2, whereas Cβ atoms are not reactive [44]. The less reactive Cβ atoms can dissolve in Ni surface generating Ni3C species which may resulted in the growth of whisker carbon or nucleate forming coke layers on Ni surface. For the formation of coke layers, a large ensemble of Ni surface covered with carbon atoms is needed since carbon layers over more than ~80 atoms are thermodynamically stable [45–48].

The small Ni nanoparticles do not offer these large ensembles, therefore the deactivation of catalytic active Ni surface due to the coke formation can be suppressed by using small Ni nanoparticles as DRM catalysts. However, these small Ni nanoparticles are easily aggregated to each other forming larger particles at harsh operating conditions of DRM (>700 °C), which results in an increased carbon formation and catalyst deactivation [49].

There is another important side reaction which can be expressed as follows,

\[ CO_2 + H_2 \leftrightarrow CO + H_2O \left( \Delta H_{298K}^\circ = +41 \text{ kJ mol}^{-1} \right), \text{ reverse water gas shift} \tag{6} \]

This process is often referred as reverse water gas shift (RWGS) and it lowers the syngas ratio of H2/CO produced by the main reaction of DRM less than 1. Generally, the main reaction of DRM takes place with RWGS. However, RWGS is less endothermic than the main reaction of DRM, therefore its influence on syngas ratio is less significant with an increasing operating temperature of DRM. It has been reported that the produced syngas ratio (H2/CO) gets higher as temperature of DRM operation increased and approaches to 1 above 800 °C [39,40,50].

In addition to the temperature, operating pressure also has influence on the equilibrium conversion of reagents and products, the produced syngas ratio (H2/CO), and on the carbon formation. Nikoo and Amin performed thermodynamic analysis on DRM process based on direct minimization of Gibbs free energy method [39]. They reported that the equilibrium conversion of main reagents (CH4 and CO2) and products (H2 and CO) were reduced as the operating pressure increased from the atmospheric pressure in the temperature range of 700–1000 °C [39]. This can be explained by Le Chatelier’s principle; please note that the main reaction of DRM (Equation (1)) convert two equivalent
reagents (CH$_4$ + CO$_2$) into four equivalent products (2CO + 2H$_2$). In addition, the amount of carbon deposition on catalysts surface during DRM became larger at higher pressure.

The CO$_2$/CH$_4$ feed ratio also affect to equilibrium conversion of reagents and the syngas yields [50,51]. It has been reported that higher CO$_2$/CH$_4$ ratio resulted in higher CH$_4$ conversion and H$_2$ production, but lower CO$_2$ conversion and CO generation at high temperature above 700 °C. Furthermore, the feed ratio influenced not only on the amount of deposited carbon, but also on the production of other side products, including water. 800 °C and ambient pressure with reagent mixture of CH$_4$, CO$_2$, O$_2$ (feed ratio of 1:1:0.1) was suggested as an optimal operating conditions of DRM [39]. There are also other operating parameters that can influence on the performance of catalytic DRM reaction, including a reactor design and gas hourly space velocity (GHSV), thus one should be careful when comparing activity of catalysts reported in various literatures.

3. Ni Catalysts for DRM

A lot of scientific studies have been done on transition metal-based catalysts for DRM reaction and Ni catalysts supported on metal-oxides are most frequently investigated among them. Highly dispersed Ni nanoparticles supported on metal-oxide supports has been considered as a promising candidate as DRM catalyst since it can exhibit high catalytic activity and good long-term stability under the harsh operating conditions of DRM (>700 °C). Utilization of appropriate metal-oxide supports for Ni nanoparticles can not only increase thermal stability and coke-resistance of Ni nanoparticles at high temperature, but it can also promote the catalytic DRM reaction.

3.1. Reaction Mechanism of DRM over Supported Ni Catalysts; Influences of Metal-Oxide Supports

The DRM reaction over supported Ni catalyst mainly proceed via two steps: (1) decomposition of methane; and, (2) CO$_2$ dissociation. It is generally agreed that dissociation of methane on Ni surface is the rate determining step of DRM reaction. Dissociated CH$_3$ species are adsorbed on a top of Ni atom, whereas CH$_2$ species prefer to be adsorbed between two adjacent Ni atoms. The dissociative adsorption of CH$_4$ on Ni atoms is favored at step sites than that on terrace Ni atoms and this can explain higher catalytic activity of small Ni nanoparticles compared to bigger counterparts, which possess less amount of step Ni atoms per unit mass of Ni. Decomposition of a methane molecule leaves carbon atoms (atomic carbon, or CH$_x$ species) on Ni surface and these carbon atoms need to be oxidized into carbon monooxide that will be desorbed from Ni surface regenerating active Ni surface. The oxidation of the carbon atom on Ni surface is mainly proceeded by interaction with an atomic oxygen either on the surface of Ni or supports. Dissociate adsorption of CO$_2$ is a major route for the generation of atomic oxygen on Ni surface during DRM and is generally considered as a fast process. When Ni particles are supported on inert metal-oxides, such as SiO$_2$, the CO$_2$ dissociation takes place on the surface of Ni particles. On the other hands, on the other active metal-oxide supports (e.g., MgO, La$_2$O$_3$, Ga$_2$O$_3$), chemisorption, and dissociation of CO$_2$ can take place on the surface of supports or Ni-supports interfaces [29,52,53]. It has been suggested that higher basicity of metal-oxides supports can facilitate CO$_2$ dissociation on the supports surface [26,54]. Some metal-oxides, such as CeO$_2$ and ZrO$_2$, can provide their lattice oxygen to oxidize carbon atoms on Ni surface into carbon monooxide [55–57]. The oxidation of carbon species from the Ni surface can also proceed via an interaction with hydroxyl groups on the surface, but this process has been suggested only significant at low temperature (<800 °C) [41,44].

3.2. Adjustment of Acidity and Basicity of Catalyst Surface

It has been generally believed that acidic supports (e.g., SiO$_2$, Al$_2$O$_3$) facilitate the dissociation of methane leading to predominant methane cracking reaction over CO$_2$ dissociation, which produce atomic oxygen and this, in turn, resulted in carbon formation on catalyst surface. In contrast, metal-oxide supports, such as MgO, La$_2$O$_3$ with high basicity promote dissociative adsorption of CO$_2$, which can result in the suppression of carbon formation by producing higher number of oxygen
atoms near the catalytic active metal surface [26–28,30,50]. The DRM reaction proceeds via three major step reactions (CH₄ cracking, CO₂ dissociation, and oxidation of carbon species on Ni surface) over Ni particles supported either by acidic metal-oxide (e.g., SiO₂) or basic metal-oxides (e.g., MgO) are schematically described in Figure 3.

Figure 3. Schematic description of DRM reaction proceeds via three major steps (CH₄ cracking, CO₂ dissociation, and oxidation of carbon species) over Ni particles supported by either acidic (e.g., SiO₂) or basic metal-oxide supports (e.g., MgO).

Influence of basicity of supports on catalytic performances have been studied either by comparing Ni catalyst supported by various metal-oxides or by comparing supported Ni catalysts with different promoters. Zhang et al. prepared a variety of Ni catalysts that are supported by SiO₂, TiO₂, ZrO₂, Al₂O₃, MgO-modified Al₂O₃ (MA) [52]. In the presence of each catalyst inside a tubular fixed-bed continuous quartz reactor, DRM reaction was performed at 750 °C at ambient pressure with a reagent feed ratio of 1:1 (CH₄:CO₂). Ni catalyst supported by MA exhibited the best catalytic performances in terms of catalytic activity, stability, and anti-coking capability among them. They attributed the enhanced catalytic performances of MA-supported Ni catalysts to the promotion of dissociative CO₂ adsorption on basic MgO sites, which led to the suppression of carbon formation. However, one should note that those supports studied by Zhang et al. also exhibited various degree of metal-support interaction which can affect size, dispersion, and reducibility of Ni particles, as authors also discussed in detail [52].

It has been demonstrated that utilization of alkali or alkaline metal oxides, such as Na, K, Mg, and Ca, onto the supported Ni catalyst, as promoters can suppressed the carbon formation by promoting dissociative CO₂ adsorption on the basics sites of catalyst surface [58]. Recently, Pan et al. investigated promotion effects of Ga₂O₃ onto SiO₂ supports on CO₂ adsorption and catalytic DRM performance of supported Ni catalysts [53]. DRM was performed at 700 °C under ambient pressure with a feed ratio of 1:1:2 (CH₄:CO₂:Ar) over Ni/SiO₂ and Ni/SiO₂-Ga₂O₃, and they analyzed the states of adsorbed CO₂ by means of Fourier transformation infrared spectroscopy (FT-IR) [53]. The results showed that
Ga$_2$O$_3$ activated adsorbed CO$_2$ on its surface, whereas CO$_2$ only physically adsorbed on SiO$_2$ surface, which resulted in the enhanced resistance of Ni/SiO$_2$-Ga$_2$O$_3$ catalyst towards carbon formation during DRM reaction [53].

However, the promotion of CO$_2$ dissociation on catalysts surfaces by increasing basicity can also cause the deactivation of catalysts. The Boudouard reaction (Equation (3)) can be facilitated even at high temperature due to increased amount of reagents (CO), generating larger numbers of carbon atoms on catalysts surface. In addition, an excess amount of atomic oxygen can oxidize neighboring Ni atoms into NiO, which are not catalytically active towards DRM reaction. Very recently it has been demonstrated that excessive surface basicity led to catalyst deactivation by carbon formation and formation of metal-oxides [59]. The excessive surface acidity also caused the catalytic deactivation by carbon deposition through the promoted decomposition of methane. Das et al. suggested that the moderate acidity and basicity on catalyst surface is important factor, together with their homogeneous distribution that determines catalytic conversion ratio of DRM reaction and long-term stability of supported metal catalysts (Figure 4) [59].

![Figure 4](https://via.placeholder.com/150)

**Figure 4.** Suggested mechanism of deactivation of Ni catalysts supported by metal-oxides with excessive acidity or basicity. Reprinted with permission from Ref. [59]. Copyright (2017) Elsevier.

La$_2$O$_3$ has been also used either as a basic support or a basic promoter for supported Ni catalysts [60]. On the surface of Ni/La$_2$O$_3$ catalyst, methane dissociation takes place on Ni nanoparticles, whereas CO$_2$ dissociation occurs on the surface of La$_2$O$_3$ supports. Interaction of La$_2$O$_3$ supports with CO$_2$ can result in the formation of La$_2$O$_2$CO$_3$ species that can oxidize carbon deposits on adjacent Ni atoms producing CO and regenerating active species (Ni and La$_2$O$_3$), as follows,
La$_2$O$_2$CO$_3$ + C − Ni → La$_2$O$_3$ + 2CO + Ni

This positive effects of the formation of La$_2$O$_2$CO$_3$ on the removal of carbon deposits has been confirmed by previous transient studies performed using isotopic molecules ($^{13}$CH$_4$, $^{13}$CO$_2$, $^{13}$CO, and C$^{18}$O) [28]. Recently, it has been demonstrated that addition of Co on Ni/La$_2$O$_3$ catalyst facilitated the La$_2$O$_2$CO$_3$ formation during DRM reaction, which resulted in enhanced catalytic activity and stability [61].

3.3. Enhancement of Dispersion and Thermal Stability of Ni Nanoparticles

It has been demonstrated that the size of Ni particle plays an important role in its resistance towards carbon formation as well as catalytic activity. Very recently, Aramouni et al. studied the size effect of catalytic metal particles on carbon formation during DRM by performing thermodynamic analysis [62]. They used Gibbs energy minimization method taking into account the Gibbs energy deviation of carbon formation during DRM on metal surface with different particle sizes from the thermodynamics of graphite formation [62]. It was found that the formation of carbon depends on the particle sizes; larger metal particles are more prone to yield higher amount of carbon at moderate operating conditions. High conversion of CH$_4$ and CO$_2$ with an optimal ratio of H$_2$/CO (close to unity) can be achieved at higher temperature of 827−927 °C, however at this condition carbon formation can limit the efficiency of DRM process [62]. This highlighted the importance of developing highly dispersed small Ni nanoparticles (<5 nm) which possessing high resistance of carbon formation. This is in line with numerous experimental results previously performed by many researchers, indicating that the carbon formation on Ni surface during DRM reaction can be minimized by reducing the size of Ni particles [37,38,63,64].

Kim et al. reported the relationship between the carbon formation and size of Ni particles by performing DRM reaction over alumina supported Ni particles that were prepared via a sol-gel method and a subsequent supercritical drying process [63]. The average diameter of Ni particles drastically increased with increasing metal loading over 0.2 in Ni/Al mole ratio, while only the marginal change was found in the surface composition (Figure 5). This large increase of particle size with increasing metal loading attributed to the re-dispersion or aggregation of metal Ni particles during the thermal treatment. It was strongly correlated to the higher amount of filamentous carbon that formed on the surface Ni particles during DRM, as confirmed by TEM analysis performed after the DRM reaction at 773 °C for 30 h [63].

The thermal sintering of small Ni nanoparticles under harsh conditions of DRM operation (>700 °C) is a major problem that prevents the realization of their application as DRM catalysts. Many scientific results pointed that the size of Ni nanoparticles need to be below at least 8 nm to exhibit high resistance towards carbon formation [37,38,63,64]. However, those small Ni nanoparticles are prone to forming larger particles by the aggregation at high temperature (>700 °C).

The choice of metal oxides supports not only alters the catalytic activity of supported Ni particles towards DRM, but also influence on thermal stability of Ni nanoparticles. Strong metal-support interaction can stabilize the small Ni nanoparticles preventing them from thermal sintering, as well as enhance the catalytic activity by altering the electronic structure of Ni. The geometrical structure of metal-oxide supports is another parameter that can affect the catalytic performance of Ni nanoparticles; dispersion of Ni nanoparticles inside porous structure of metal-oxides supports has been demonstrated as a promising way to retain the size of small Ni nanoparticles.

The interaction between Ni and Al$_2$O$_3$ supports can lead to the formation of NiAl$_2$O$_4$ spinel structure, which can provide stable and highly dispersed metallic Ni particles via reduction [65]. The microstructural evolution of Ni-alumina catalyst at elevated temperature under reducing atmosphere has been investigated by in-situ XRD and TEM analysis [65]. Braidy et al. proposed the 3-step process of Ni particles formation from γ-Ni$_6$Al$_4$O$_7$; (1) the formation of NiAl$_2$O$_4$ spinel structure from the Ni-rich zone generated by the diffusion of Ni atoms from γ-Ni$_6$Al$_4$O$_7$, (2) the
which reduced the metal-support interaction between Ni and Al [65]. Guo et al. reported the higher activity and better stability of Ni particles on MgO-\(\gamma\)-Al\(_2\)O\(_3\) when compared to those on \(\gamma\)-Al\(_2\)O\(_3\) supports and it was attributed to the enhanced stability of the small Ni crystallites on MgAl\(_2\)O\(_4\) spinel structure [66]. Very recently, Chamoumi et al. demonstrated a highly active and stable Ni catalysts supported by an upgraded slag oxide (UGSO), which were prepared by an improved solid-state reaction [67]. The mining residue consisting of various metal (Fe, Mg, Al, Ca, Mn, and etc.) oxides was used as a support material. The high catalytic activity and stability of the Ni/UGSO catalyst was attributed to the high dispersion of Ni particles resulted from the formation of the NiAl\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\) spinel structure, and the presence of various elements, including basic promoters, such as (MgO, CaO, and MnO) [67].

It was also found that poor dispersion of metal particles on La\(_2\)O\(_3\) supports due to weak metal-support interaction can be improved by partial substitution of La with other metals such as Ca, Ce, Sr, etc. [60]. Chen et al. suggested that presence of small amount of Cu can also prevent deactivation of Ni particles due to aggregation or loss of Ni crystallites [67]. On the other hands, Dias et al. showed that addition of CaO could reduce the thermal stability of Ni particles that are supported by \(\gamma\)-Al\(_2\)O\(_3\). Cu atoms competed with Ni atoms in interaction with Al\(_2\)O\(_3\) supports, which reduced the metal-support interaction between Ni and Al\(_2\)O\(_3\) supports. It, in turn, decreased the sintering resistance of the Ni particles although it improved the reducibility of Ni particles [68]. The degree of metal-support interactions was often measured by conducting temperature-programmed

![Figure 5](image_url)
reduction (TPR) analysis with a constant flow of reduction gas (e.g., H₂, CO₂). The shift of TPR peak position to higher temperature is an indication of stronger interaction between metal and support, i.e., higher temperature or longer time is needed to activate the Ni particles prior to DRM reaction with increasing metal-support interactions. It is also worth to mention that metal-oxides exhibiting a strong interaction with metals can cover the surface of metal particles either by the diffusion of oxides over the metal particles or diffusion of metal particles into the supports, resulting in a decrease of the number of active Ni atoms exposed to the reagent gas. These results pointed that there is an appropriate level of metal-support interaction for optimum catalytic performance of supported Ni nanoparticles. It was reported that the strong capability of CeO₂ supports for metal-support interaction can lead to the reduced catalytic activity of metal particles [69,70].

Geometrical structure of metal-oxide supports also have a significant impact on the dispersion and sintering resistance of Ni nanoparticles. La₂O₃ supports derived from peroskite LaNiO₃ precursors have been extensively studied recently and it has been proved that Ni dispersion on those supports can be significantly improved. X. Li et al. also reported that La₂O₃ nanorod can not only improve dispersion of Ni nanoparticles but also stabilize Ni nanoparticles (Figure 6) [60]. Recently, it has been demonstrated that Ni particles fabricated by exsolution from parent perovskite structures exhibited better dispersion and thermal stability when compared to the respective ones prepared by a conventional deposition method [71]. It is attributed to the stronger interaction between exsolved Ni particles and supports to their nano-socket structure [71]. Singh et al. reported that the shape of parent perovskites affected the degree of exsolved Ni/supports interactions and the defective anisotropic perovskites were suggested as ideal parent perovskite presursors [72]. The Ni particles that were exsolved from LaNiO₃ spheres and rods were highly dispersed on the supports and exhibited high catalytic activity and stability towards DRM reaction [72]. Recently, the fabrication Ni particles alloyed with Re and Fe by exsolution method has been also demonstrated [73]. The exsolved Ni-alloy particles were firmly ‘socketed’ into a La₂O₃/LF supports and they exhibited high catalytic activity towards DRM reaction without showing carbon accumulation and particles sintering over 70 h of operation [73].

Recently, mesoporous silica and alumina has been received much attention as supports of Ni nanoparticles since Ni nanoparticles that are embedded in pores of those supports can exhibit good sintering resistance at high temperature [74–79]. Zhang et al. demonstrated that mesoporous structure of SBA-15 can prevent sintering of monometallic Ni particles by confining their size inside the pores [74].

Xu et al. prepared the ordered mesoporous alumina via improved evaporation-induced self-assembly (EISA) strategy and the synthesized mesoporous alumina exhibit large specific surface area, big pore volume, uniform pore size, and excellent thermal stability [80]. Ni particles were embedded inside the pores of the alumina via an incipient wetness impregnation method and their catalytic performances towards DRM reaction was investigated. The catalytic conversion of CH₄ and CO₂ at 700 °C reached the thermodynamic equilibrium conversion values and its high initial activity was retained for 100 h without a notable deactivation [80]. These results highlighted that the merit of utilization of mesoporous framework that can stabilize active Ni nanoparticles by the “confinement effect” and provide more accessible Ni active centers during DRM reaction [80].

Effective incorporation of Ni nanoparticles inside pores of mesoporous silica and alumina supports is a major key for the utilization of the confinement effect to retain the size of Ni nanoparticles. Xie et al. proposed a modified incipient wet process using polyols as new conveyors and removable carbon templates [77]. Polyl (ethylene glycol, EG) coordinated Ni²⁺ species can be effectively delivered into small channels of SBA-15 and polyl acted as carbon template during a subsequent pyrolysis process. As a result, highly dispersed Ni nanoparticles with an average diameter of 3.6 nm was synthesized inside the microchannel of silica SBA-15. The Ni/SBA-15-EG showed superior catalytic activity than Ni/SBA-15-H₂O towards DRM reaction and its activity did not change significantly during long-term operation of DRM at 750 °C. This attributed to high dispersion and thermal stability of Ni nanoparticles of Ni/SBA-15-EG samples, which was confirmed by TEM images of spent Ni/SBA-15-EG [77].
were prepared via a “two solvent” method where aqueous Ni precursor solution is mixed into DRM at 750 ◦C [82]. The prepared catalysts showed stable catalytic activity towards impregnation processes. It resulted in better dispersion of small Ni nanoparticles with narrower size distribution of Ni nanoparticles of “two solvent”-prepared Ni/SBA-15 than the classically-prepared ones, as evidenced by TEM and XRD analysis [81]. It was explained by better dispersion of Ni nanoparticles at interior of the mesoporous structure of SBA-15 silica [81]. Ni/SBA-15 catalysts have been studied recently, as 5Ni/La2O3 perovskites have high activity for DRM [73]. Ni/SBA-15 catalysts over supports via a wet impregnation method (denoted as 5Ni/La2O3-C in Ref. [60]) before DRM reaction. TEM image of (c) Ni nanoparticles on La2O3 nanorod (denoted as 5Ni/La2O3-LOC in Ref. (denoted as 5Ni/La2O3-C in Ref. [60]) Insets of (c,d) present the size distribution of Ni particles on each support. Reprinted with permission from Ref. [60]. Copyright (2017) Elsevier.

Kaydouh et al. demonstrated that the “two solvent” method resulted in much selective dispersion of Ni nanoparticles at interior of the mesoporous structure of SBA-15 silica [81]. Ni/SBA-15 catalysts were prepared via a “two solvent” method where aqueous Ni precursor solution is mixed into silica suspended hydrophobic solvents and they exhibited superior catalytic performances when compared to Ni/SBA-15 prepared by a classical impregnation method [81]. It was explained by better dispersion of Ni nanoparticles of “two solvent”-prepared Ni/SBA-15 than the classically-prepared one, as evidenced by TEM and XRD analysis [81].

Recently, some research groups presented the modified impregnation method using various chelating ligands to immobilize Ni nanoparticles in mesoporous silica. Kang et al. used a polyethylenimine (PEI) as a chelating ligand of Ni precursors during impregnation processes [82]. Ni-PET complexes were well distributed inside the pores and strongly bound the SBA-15 silica surface through the strong interaction between NH2 terminal groups of PEI and surface silanol groups of silica. Moreover, steric hindrance of PEI ligands prevented the aggregation of Ni-PEI complexes during the impregnation processes. It resulted in better dispersion of small Ni nanoparticles with narrower size distributions compared to the respective one prepared by classical impregnation method without using chelating ligands (Figure 7) [82]. The prepared catalysts showed stable catalytic activity towards DRM at 750 ◦C for 40 h and the size of Ni particles inside pores of SBA-15 silica was confined by pore structures of parent supports [82].
Zhang et al. studied the promoting impacts of various chelating ligands during modified impregnation methods on the dispersion of Ni nanoparticles [83]. Three ligands (ethylenediamine, citric acid, and acetic acid) were tested as chelating agents of Ni precursors during impregnation methods. Utilization of each ligand resulted in the formation of smaller Ni nanoparticles with better dispersion compared to non-ligand assisted impregnation methods. The catalysts prepared via ligands assisted method exhibit higher catalytic activity and stability than the respective one that was prepared via a classical impregnation method, which was attributed to better dispersion of Ni nanoparticles inside the pores of SBA-15 silica [83].

Although utilization of ligand during the impregnation method can improve dispersion of Ni nanoparticles inside the pore structure of supports, it has been reported that the formation of some Ni particles outside of pores during wet-chemical processes is still not avoidable, which are subject to aggregation during the DRM reaction [82,83]. Alternatively, small Ni nanoparticles can be embedded inside pores of porous supports using dry-methods. It can be more advantageous for preparation of small metal nanoparticles on porous supports since incorporation of gas phase precursor into the
pore structure is much easier than aqueous precursors. Especially, atomic layer deposition (ALD) has been considered as a suitable technique for the preparation of small metal nanoparticles inside the pore structures of various supports. ALD is a self-limiting and self-terminating deposition technique where two gas phase precursors (metal precursor and oxidizing/reducing precursor) are injected onto the surface of substrates separately in a sequential manner. Gould et al. synthesized highly dispersed small Ni nanoparticles (particle size of ~4 nm) on alumina supports by ALD processes. The ALD-prepared Ni catalysts exhibited higher catalytic activity and carbon-formation resistance when compared to one prepared via incipient wetness (IW) process, which is attributed to smaller size of Ni particles with better dispersion of ALD-prepared sample than IW-prepared one [84]. Shang et al. prepared small Ni nanoparticles (mean diameter: ~3.6 nm) supported either by a porous γ-Al2O3 support using ALD process. The prepared catalysts showed high catalytic reactivity and exceptionally high stability towards DRM reaction performed in the range of 700 and 850 °C for 300 h (Figure 8) [85]. They also suggested that stronger bonding force between Ni nanoparticles and alumina supports was established for ALD-prepared sample than IW-prepared based on the larger size and lower catalytic performance of Ni nanoparticles that were prepared by IW method [86].

![Figure 8. CH₄ conversion of DRM catalyzed by atomic layer deposition (ALD)-prepared Ni nanoparticles on mesoporous alumina at different temperatures (700–850 °C) (denoted as ALD Ni/γ-Al₂O₃ in Ref. [85]). Reprinted with permission from Ref. [85]. Copyright (2017) Elsevier.](image)

4. Conclusions

Catalytic DRM reaction has been attracted much attention since its main reaction converts two major greenhouse gases (CO₂ and CH₄) into useful synthetic gas (H₂ and CO). Due to high endothermic nature of the main reaction, it needs be operated at high temperature (>700 °C) to achieve high equilibrium conversion. The high temperature conditions are also beneficial to reduce the formation of carbon on the surface of active metal catalyst during DRM, which possibly deactivates the catalytic DRM reaction, since most of side reactions relating to carbon formation are exothermic.

Among many non-noble metal catalysts, supported Ni catalysts have been extensively studied due to high initial catalytic activity, which is comparable to other noble-based catalysts, and economic viability. However, easy deactivation of supported Ni catalysts due to coke-formation during the DRM operation remains as a main obstacle of its real application. Coke formation on active Ni surface at high temperature (>700 °C) mainly proceeds via methane cracking on Ni atoms and it has been suggested that this issue can be addressed either by adjusting the acidity-basicity of catalyst surface or reducing the size of Ni particles below ~8 nm.
Metal-oxide supports with higher basicity can alleviate the deactivation of Ni surface due to coke formation by promoting the CO$_2$ dissociation at basic sites. It can provide oxygen atoms to neighboring Ni sites covered with carbon species, which can facilitate gasification of the carbon species from Ni surface regenerating catalytic active sites. Recent studies on the influence of chemical nature of supports on the catalytic performances of Ni catalyst pointed the importance of even dispersion of moderate acidic and basic sites near the Ni atoms.

It has been generally acknowledged that coke formation on Ni surface can be inhibited when the size of Ni catalyst is below ~8 nm since carbon atoms on more than ~80 atoms are not thermodynamically stable. Many experimental results indicated that small Ni nanoparticles are less prone to deactivated due to coke formation, and recent results of theoretical simulation also pointed the importance of small size of Ni nanoparticles. However, small Ni nanoparticles are prone to easy aggregation at such a high temperature (>700 °C) due to its thermodynamic instability. This low stability issue of small Ni nanoparticles can be addressed by increasing metal-support interaction or by immobilizing Ni nanoparticles inside porous metal-oxide supports, as pointed by recent studies. It has been demonstrated that small Ni nanoparticles can be highly dispersed on porous silica and alumina supports via modified wetness impregnation methods or atomic layer deposition and they exhibited high stability as well as high catalytic conversion of DRM.

Utilization of porous substrates is a promising strategy to develop highly active and stable Ni catalysts for DRM reaction with good economically viability. It is further desirable to investigate the synergic effect of “confinement effects” of porous supports and the optimized chemical nature of supports, e.g., even distribution of moderate acidic and basic sites. ALD process possesses high potential for this purpose since the various metals can be loaded into the nanopores and the amount of metal loading can be finely controlled by ALD. For instance, one may prepare Ni nanoparticles with basic MgO promoter, of which sizes are confined by porous structures via a subsequent ALD deposition of Ni and Mg elements inside the porous substrates. Besides, in order to fully exploit the advantages of Ni nanoparticles that are supported by porous substrates, it is also the desire to find the optimum pore structures (pore size, distribution, pore network) of support to maximize the accessibility of reagents to confined Ni nanoparticles inside the pores.

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