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Latest trends in Syngas production employing compound catalysts for methane dry reforming

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Abstract. The rise in the global population has ultimately steered to increase in global energy consumptions. This masqueraded several challenges worldwide. The most troublesome being the accumulation of greenhouse gases (GHGs) that induced a global climatic change. The utilization of fossil fuels like petroleum, coal and natural gas on the copious scale has led to the elevated levels of carbon dioxide (CO₂) and methane (CH₄) in the global environment. Dry reforming of methane (DRM) is a highly favorable technique as it utilizes two of the prominent GHGs, CH₄ and CO₂ to generate a useful and valuable product viz. syngas. However, the deactivation, coking and sintering of catalysts are still the main hurdles in the commercialization of the process. The compound metal catalysts have shown enhanced activity and prolonged durability when compared with monometallic catalysts due to enhanced morphology, improved and stable catalytic structure, i.e., both coke and sintering resistant at high temperatures. This brief review spotlights the recent developments in DRM by emphasizing parameters such as the effects of catalyst support, bimetallic catalyst, promoters and strong metal-support interaction (SMSI) in the last decade.

1. Introduction

The increase in the world population has led to a number of challenges on a global scale. The year 2013 observed a rapid rise in the growth of global consumption of energy, the growth of nearly 100 % over the past decades [1]. One of these challenges is the accumulation of GHGs that prompt a worldwide variation in climatic conditions, which is the reason for many natural havocs such as acute flooding in some areas whereas protracted droughts in others. These changes in the environment across the world are the root causes of adverse effects and pressure on ecosystems, triggering to a major harm of biodiversity. In the latest report by the Climate Council, the international panel on climate change emphasized the impact of various fossil fuels on the concentration of CO₂ in the atmosphere. Several millions of tons of CO₂ is being released into the environment due to burning huge volume of natural gas (i.e. 140 billion cubic meters) globally [2]. To overcome the devastating effects of global warming, the Paris Agreement was approved by 195 countries under the flag of the United Nations Framework Convention on Climate Change (UNFCCC) in December 2015. The aim of this has been to restrict the growth of average worldwide temperature under 2 °C, and to track down the measures adopted to check the increase in temperature even further to 1.5 °C by 2100. The pact was signed internationally to reduce



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the emission of global greenhouse gases (GHGs) and suggested major changes in energy production and consumption domain [3]. The reliance on the fossil fuels including petroleum, coal and natural gas to meet energy demand is making the situation worse for the future, as the burning of fossil fuel produces GHGs (i.e. mainly CO_2 & CH_4), which are the main culprits behind global warming in the present scenario [4]. Although CH_4 fraction in the atmosphere is smaller than CO_2 [5], however, it still causes about 20% global warming [6], since it is 81 times more effective for trapping the infrared radiations than CO_2 . The main sources for methane production and its escape into the atmosphere are the natural marshy lands, cattle, grasslands, wildfires and human interference including oil-gas treating, coal mining, landfills etc. [7]. The atmospheric CO_2 concentration (ppm) and averaged CH_4 abundance (ppb) especially in the last four decades, has displayed a dramatic rise as shown in Figure.1. Hence, due to the urgent necessity to protect the global environment and climate transformations, capture and storage of CO_2 was encouraged to decrease its concentration and discharge in the atmosphere [8]. Likewise, to reduce the dependency on fossil fuels and eliminate its harmful consequences on nature, another source of clean and renewable energy is needed [9]. Gas reforming is the conventional synthesis technique, which is a useful method to generate syngas. The methane can be reformed following any of the three directions, steam reforming of methane (SRM), DRM and partial oxidation of methane (POM) [10].

DRM is the most promising and favorable technique because it utilizes two main greenhouse gases (i.e. carbon dioxide and methane) to generate a useful and valuable product viz. syngas. Syngas has been extensively used as a starting material for synthesizing hydrogen, methyl ethers, methanol and Fischer-Tropsch synthesis [11] likewise it is an encouraging way to reduce the emissions of the GHGs into the environment [12]. DRM process produces syngas with the ratio of H_2/CO as unity, and hence can certainly be consumed both for the preparation of oxygenated value-added chemicals and long-chain hydrocarbons through Fischer-Tropsch synthesis [13]. Moreover, the feedstocks for DRM include but are not confined to that of biogas and natural gas (comprising of CO_2 , CH_4) for the production of clean and eco-friendly fuels [14]. DRM is an endothermic process; hence it involves operation at elevated reaction temperatures. Nonetheless, the catalyst can help in lowering the temperature and hence the energy constraint and optimize the reaction significantly [15].

Numerous researchers have studied and developed the catalyst having high activity along with substantial resistance to the coke formation for the DRM process [16]. The most commonly studied catalysts supporting the DRM method are noble metals, for example, Pt, Rh and Ru, supported on alumina, magnesia or other commercially available supports and transition metal including Ni and Co-based catalysts [17]. Noble metals such as Pt, Rh and Ru comprise excellent resistant to coke, extended durability compared to the transition metals; however, they are inadequate and have a low economy [18]. Amongst the existing catalysts, the most commonly used catalysts are Ni-based catalysts, being employed at industrial scales [19]. Hence to commercialize DRM, it is essential to develop an economic catalyst that is highly active, resistant to carbon formation and possesses improved SMSI (solid metal support interaction). The present review study highlights the developments in the compound catalysts i.e. being done in the last five years for DRM. It focuses on the effect of promoters, bimetallic catalysts, bimetallic supported catalysts and various catalyst support interactions for Ni-based catalysts in DRM, with the purpose of highlighting the existing research gap in developing a novel catalyst.

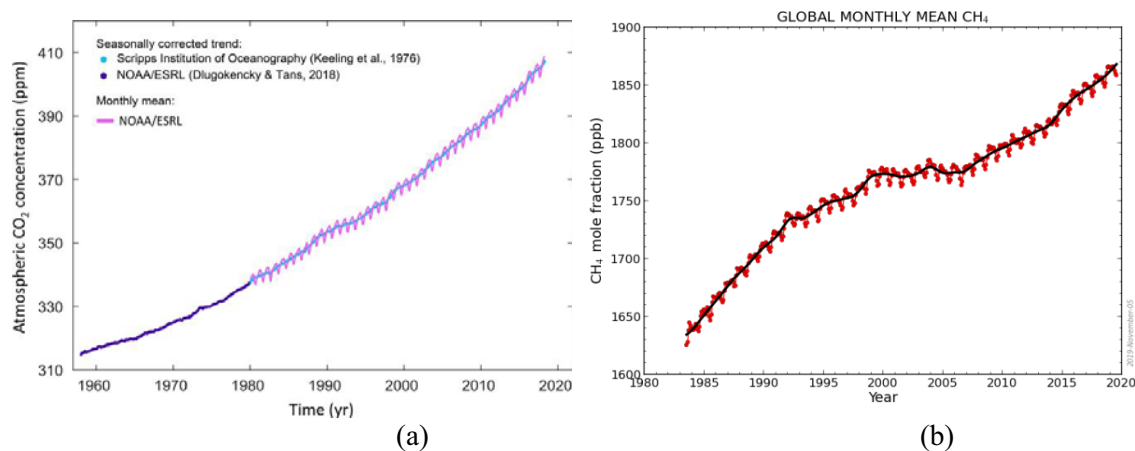


Figure 1. (a) Surface average atmospheric CO₂ concentration (ppm) [20], (b) Globally-averaged, monthly mean atmospheric CH₄ abundance [21].

2. Effect of various parameters on the catalyst

2.1. Effect of catalyst support and preparation technique

Generally, a catalyst contains a combination of elements. The active part of the catalyst is entrenched within the catalyst metal oxide support. The catalyst support serves to maximize the surface area on which the active metal is dispersed throughout. The catalyst support also provides the appropriate geometry and anchorage to the active metal so as to provide resistance towards sintering and prolonged durability [22]. Recently Chong *et al.* [23] synthesized a distinctive and durable Ni-based catalyst with dendritic fibrous SBA-15 as support. They observed that the DRM is greatly influenced by Ni metal loading (varied from 3-15%) on the support. It has been reported that for the sturdy DFSBA-15 support, 10% Ni loading proved out to be optimum due to the synergistic effect between Ni and the support. It has also been found that for 15% Ni loaded catalyst extreme sintering, accumulation of Ni particles and maximum coke formation occurred.

Zhu *et al.* [24] worked on the DRM method and studied the effect of Mg:Al ratio on mixed Ni:MgAl oxide catalyst, which was obtained from hydrotalcite. Their study concluded that Ni/MgAlO₄ mixed oxides were having a higher ratio of Mg:Al, were found to have higher catalytic activity and coke resistance, whereas the finest performance was demonstrated by Ni:MgAl having Mg:Al ratio of unity. Sokolov *et al.* [25] synthesized various supported Ni catalysts (i.e. Ni:Al₂O₃, Ni:MgO, Ni:TiO₂, Ni:SiO₂, Ni:ZrO₂, Ni:La₂O₃-ZrO₂ and also Ni on mixed metal oxides supported catalyst such as Ni:doped alumina Siral10 and Ni:promoted magnesium oxide PuralMG30) and observed the consequence of the support materials on the activity of the catalyst at low temperatures (400°C) for DRM. It has been found that Ni/La₂O₃-ZrO₂ displayed maximum stability (180 h) and produced a CO/H₂ ratio in proximity of equilibrium. The enhanced stability of Ni/La₂O₃-ZrO₂ catalyst was due to the strong interaction between metal and the support, which owed to the caging of metal on the pores of the support.

Chaudhary *et al.* [26] investigated Ni metal-based catalyst (10% w/w) supported on Al₂O₃ and MgAl₂O₄. They observed strong metal support interactions for Ni/Al₂O₃ and Ni/MgAl₂O₄ but comparatively improved distribution of Ni metal for mixed metal (MgAl₂O₄) support. It has also been found that conversion of CH₄ and CO₂ during DRM is higher for Ni:MgAl₂O₄ than Ni:Al₂O₃ with equivalent coke deposition for both the catalysts.

Djaidja *et al.* [27] synthesized Ni/MgO catalyst for DRM for testing in DRM. It has been observed that without Mg, a marginal rise in coke formation takes place. Hence this finding supports that on raising the Mg concentration in the catalyst support, carbon generation can be minimized. The noticeable basicity of magnesia and consonant crystal structure is highly beneficial for Ni-based catalysts.

Improved Ni particle size and CO₂ adsorption is observed due to the strong interface across metal-support, which has been observed among NiO and MgO resulting into a basic solid solution (Ni_xMg_(1-x)O).

Li *et al.* [28] devised a novel coke resilient Ni@Ni phyllosilicate@SiO₂ core shell hollow sphere catalysts through the facile synthesis route for DRM. The catalyst showed incredibly good performance with no coke formation at low reaction temperatures, for duration of 600 h of reaction time, while maintaining SMSI. Independent but similar research was conducted by Lu *et al.* [29], they formed a novel yolk-shell Ni at hollow silica spheres (Ni@HSS) catalyst. The Ni nanoparticles were highly dispersed in the interior surface of silica voids. However, the Ni particle size was remained constant due to the confinement effect and hence no sintering of the catalyst is observed. The catalyst showed outstanding catalytic activity and stability with zero coke formation during 55 h of reaction.

Fauteux-lefebvre *et al.* [30] carried out research on the Ni-Al spinel phase (NiAl₂O₄) supported on Al₂O₃-ZrO₂. The results showed that the NiAl₂O₄:Al₂O₃-YSZ-1 and NiAl₂O₄:Al₂O₃-YSZ-2 catalysts presented enhanced conversions and elevated concentrations of H₂. Moreover, minor coke deposition has been seen even at severe conditions on the active catalyst sites. The effect of catalyst support on metal catalysts has been summarized in table 1. Thus, it can be concluded that catalyst support and method of catalyst preparation contribute a key role in the outcome of the catalyst. Hence, a deep understanding of MSI is needed to enhance the performance and durability of the catalyst by taking this parameter into consideration.

2.2. Effect of promoters

The doping of catalyst belonging to group 1 or group 2 metals enhances the efficiency of the catalyst. Depending upon the catalytic system for the DRM, a promoter may alter and stabilize catalyst structure, enhance its reducibility, increase the oxygen storage capacity and reduce the coke formation [31].

Zhang *et al.*, [32] synthesized Ni/ZrO₂ catalyst and doped it by rare earth metals (Ce, La, Sm and Y) to observe the effects for DRM. The outcome verifies that the surface adsorbed oxygen species were surprisingly advantageous to improve methane dissociations and CO₂ activation as well. The Y-doped catalyst showed the best surface adsorbed oxygen catalyst activity followed by Sm, La, Ce and non-doped catalysts.

Alipour *et al.* [33] conducted another study in which they prepared Ni supported on alumina and promoted with alkaline earth metals (CaO, BaO and MgO) for DRM. The results showed that by adding the above metal oxides as promoters, enhanced the catalytic activity and the reducibility of Ni/Al₂O₃ as well as reduced the coke formation. Magnesia doped catalyst exhibited best results in the above-mentioned aspects of catalyst performance.

Mattos and Noronha [34] investigated the effect of dopant (Nb, Pr and Zr) on Pt metal supported on CeM/Al₂O₃ (M = Nb, Zr and Pr) for DRM. The conclusion drawn from the research was that, doped ceria to Pt/Al₂O₃ catalyst showed superior stability, reduced coke formation due to oxygen storage capacity of ceria and absence of sintering for Pt, which was also responsible for better durability. Amongst all catalyst, Pt/CePr/Al₂O₃ catalyst showed best performance in the above-mentioned parameters of catalyst performance.

Enrique *et al.* [35] studied the working of modified mixed oxide (Ni/Al-Mg) catalyst by varying the concentration of promoter (Ce as 0, 1, 3, 5, and 10 wt%). They observed that the weight percentage of the promoter is a vital parameter to hinder coke formation. For instance, the catalyst with 3wt% doped with Ce, showed elevated conversions and better stability (up to 100 hours) as compared to the one with 1wt% of Ce. The effect of promoters on catalyst has been briefed in the tabular form in table 1. Thus, it can be concluded that largely the performance and durability of the catalyst have been enhanced by adding promoters to the reference catalyst due to improved structure and stable configuration of the metallic framework.

2.3. Effect of bimetallic catalysts

The fundamental aspect of the exceptional performance of bi/duo-metallic catalysts is its preparation technique. SMSI is observed in the catalysts calcined at elevated temperatures, giving rise to the

formation of stable spinel-type structures [36]. Recently, Abdulrasheed *et.al.*[37] synthesized Ni-La bimetallic catalyst supported on fibrous silica KCC-1 (KAUST Catalysis Centre 1) by employing the one-pot hydrothermal route. The addition of La to the Ni catalyst resulted in superior activity as well as selectivity of the bimetallic catalyst, then monometallic (Ni) catalyst comparatively. Likewise, the MSI enhanced and the basic site has been strengthened then monometallic Ni catalyst in a similar fashion. The predicted response was obtained by modeling fitted with the experimental value of 98.2% conversion of methane.

Aybuke and Ramazan [38] investigated the effect of different structured bimetallic (Ni-Co) catalysts supported on magnesia over monoliths. Catalytic activity was tested for DRM at 600°C-800°C. It has been observed that the performance of the catalyst is greatly affected by its structure; and Ni (8 wt%) and Co (2 wt.%) supported on magnesia wash-coated monolith showed higher catalytic stability and activity and reduced coke deposition at low O₂ supplies.

Liu *et al.*[39] synthesized a novel core-shell catalyst, consisting of Ni nano-particles with ZrO₂ (as core) supported on mesoporous silica (as a shell) denoted as Ni-ZrO₂@SiO₂. This catalyst displayed prolonged durability, stability under drastic conditions (at 800°C) with no coke formation even after a 240 hours experimental run. The catalyst competently restrained the sintering of Nickel nano-particles and hence reduced the coke formation; because of special core-shell structure and activated oxygen by the enhancement of ZrO₂.

Zhang *et al.* [40] proposed a bimetallic Ni₁₇W₃ alloy supported on SiO₂ for the DRM reaction. They observed α -WC formation which aided in CO₂ activation in DRM. The alloy stabilized the catalyst and resulted in better coke resistance and Ni dispersion in the catalyst, as compared to the monometallic Ni/SiO₂ catalyst.

Dou *et al.* [41] synthesized sandwiched SiO₂@Ni and SiO₂@Ni@ZrO₂ catalysts through the wet chemical method; and verified for the DRM process. The results revealed that Ni catalyst coated with ZrO₂ exhibited elevated activity (6 times high), superior coke resistance (since no coke formation is seen for 20 h run) at 700 °C for DRM than SiO₂@Ni catalyst. In other recent studies, Ruocco et al. [42] designed ternary perovskite-type oxides (AZrRuO₃) catalysts synthesized by the auto-combustion technique. The results showed better reducibility, increased surface area, and upgraded overall performance for DRM. SrZrRuO₃ provided the finest performance in terms of percentage conversion and catalyst durability (for 66 h run).

Apart from the above-mentioned parameters and catalysts, recent developments in catalysts have been done besides the conventional co-precipitation and sol-gel techniques for catalysts preparations. Moura-Nickel et al. [44] prepared lyophilized nickel catalysts and compared it with commercially available catalysts. The lyophilization process proved out to be quite agreeable with the LNi10 catalyst giving the highest syngas production (82% H₂, 95%CO, H₂/CO = 0.87) at 800°C.

Hoyos et al. [43] prepared and studied the Ni-based mesoporous MCM-41(obtained from Rice Husk Ashes (RHA)) by employing a one-pot synthesis and microwave heating method. They concluded that Ni-MCM catalyst persisted high activity, maintained a stable morphology, and a negligible amount of coke was deposited even after 100 h of DRM reaction. A concise form of the literature has been shown in table 1 for the effect of using bimetallic catalyst gas reforming processes.

Furthermore, a comparative study has been done by Bagheri-Mohagheghi [45] concluding that the catalyst preparation route effectuates in the functioning and performance of the catalyst as a key factor. For example, they showed that amongst catalysts synthesized by conventional co-precipitation and sol-gel methods at 750°C, the catalyst synthesized by co-precipitation showed higher BET surface area and generated almost spherical and hexagon α -powder. Therefore, from the above studies, it can be established that the bimetallic catalyst showed improved performances then the corresponding monometallic catalysts, comparatively. This is because the bimetallic catalyst worked synergistically with one another and formed a stable alloy, which hindered the catalyst sintering at large temperatures.

Table 1. Performance of some recently developed catalysts reported in literature during last 5 years at different GHSV and temperatures for reforming reactions.

Catalyst Used	Reaction Conditions	Major finding/Conclusions	References
Ni/DFSBA-15	Effect of catalyst support and preparation technique 800°C, GHSV = 15,000 mL/geat h, 1atm.	DFSBA-15 support with 10% Ni loading proved out to be optimum performance and most sturdy catalyst due to the synergistic effect between Ni and the support.	[23]
Ni/SBA-15	800°C, 10-45 kPa, CH ₄ :H ₂ O:CO ₂ =3:2:1	Ni(10wt%)/SBA-15 was found resistant to coke deposition and better stability after BRM. H ₂ /CO ratio decreased from 2.14 to 1.83 with reducing H ₂ O/(CH ₄ /CO ₂) ratio from 0.5 to 0.25 due to the growing parallel RWGS reaction in the water-scarce feed.	[16]
Ni/Mg-Al	800°C, CH ₄ :CO ₂ = 1:1, WHSV = 80,000 mL/g h	Ni/Mg-Al mixed oxides with higher Mg/Al ratio are superior for coke resistance and activity, Ni/ Mg-Al with a Mg/Al ratio equal to one displays the best activity and stability.	[24]
Ni/Al ₂ O ₃ and Ni/MgAl ₂ O ₄	600-750°C, CH ₄ :CO ₂ :N ₂ = 1:1:1 for the DRM, CH ₄ :CO ₂ :O ₂ :N ₂ = 1:1:0.08:0.92 for ODRM, Gas flow rate = 60ml/min 600°C and 700°C, CO ₂ :CH ₄ :Ar=1:1:1, 1 atm, flow rate = 30 mL/min 500-800 °C, CH ₄ :CO ₂ =1:1, GHSV= 35,800 h ⁻¹	SMSI for Ni/Al ₂ O ₃ and Ni / MgAl ₂ O ₄ , improved Ni metal dispersion for MgAl ₂ O ₄ support. With similar coke formation, the conversion of CH ₄ and CO ₂ is higher for Ni/MgAl ₂ O ₄ than for Ni/Al ₂ O ₃ .	[26]
Ni-MCM *MCM=mesoporous silica		Even after 100 hours of DRM response, the Ni-MCM catalyst remained very active and structurally stable, with negligible coke deposition.	[43]
BaZr _{0.8649} Ru _{0.1351} O ₃ , CaZr _{0.91087} Ru _{0.08913} O ₃ and SrZr _{0.88729} Ru _{0.11271} O ₃		Catalysts synthesized by the auto-combustion technique showed advanced reducibility, improved surface area, excellent thermal stresses, and improved DRM efficiency. SrZrRuO ₃ performed best as per long durability and conversion (66 hrs test).	[42]
Lyophilized nickel catalysts [5 wt% (LNi5)- 20 wt% (LNi20)]	600 °C, 700 °C and 800 °C, WHSV=168,000 mL/h.geat	At 800 °C LNi10 catalyst has delivered the highest syngas production (82% H ₂ , 95%CO, H ₂ /CO = 0.87)	[44]
Sandwiched SiO ₂ @Ni@ZrO ₂ and SiO ₂ @Ni	500-900 °C, CO ₂ :CH ₄ :N ₂ = 1:1:1, WHSV=180,000 mL/geat ¹ h ⁻¹	The ZrO ₂ coated Ni catalyst showed more than 6 times higher activity, better coke resistance at 700 °C for DRM than that of SiO ₂ @Ni catalyst.	[41]
Ni-ZrO ₂ @SiO ₂	800 °C, CH ₄ :CO ₂ = 1:1, (WHSV)= 15 mL min ⁻¹ ,	Ni-ZrO ₂ @SiO ₂ showed extremely high anti-sintering and anti-coking property.	[39]

Catalyst Used	Reaction Conditions	Effect of promoters	Major finding/Conclusions	References
Pt/Al ₂ O ₃ , Pt/CePr/Al ₂ O ₃ , Pt/CeNb/Al ₂ O ₃ , Pt/CeZr/Al ₂ O ₃	800 °C, CH ₄ :CO ₂ =1:1, total flow rate = 100 mL/min, 1 atm		Adding CeO ₂ doped with Pr, Zr and Nb to Pt/Al ₂ O ₃ catalyst substantially hindered the loss of catalytic activity. Pr exhibited maximum reducibility of ceria (23%) and Pt/CePr/Al ₂ O ₃ exhibited the highest activity and stability.	[34]
Ni/ZrO ₂ catalyst doped with (Ce, La, Sm and Y)	700 °C, CH ₄ :CO ₂ =1:1, GHSV= 24000 mlcat ⁻¹ h ⁻¹		Improved methane dissociations and CO ₂ activation were observed with promoted catalysts at temperatures below 700 °C, with more coke deposition. The order of doped catalyst activities Y > Sm > La > Ce	[32]
Ni/Al ₂ O ₃ promoted with (3 wt.%) MgO, CaO, and BaO	650 °C, CH ₄ :CO ₂ from 1:2 to 4:1, GHSV = 12,000(ml/h geat).		The addition of MgO, CaO and BaO as promoters reduced SBET and improved the catalytic activity. MgO showed the highest activity, increased the Ni catalyst reducibility and decreased the NiO species reduction temperature	[33]
Ce doped Ni/Mg–Al catalysts	700 °C, CH ₄ :CO ₂ = 1:1, flow rate = 24-90 L g ⁻¹ h ⁻¹ , 1 atm		With Ce, the Ni – Mg-Al catalyst showed a steady output for 100 h of the reaction time corresponding to the CO ₂ feed ratio: CH ₄ : He = 10:10:80 at 24 L / gh. And for 20 h of reaction time, corresponding to the CO ₂ : CH ₄ = 20:20 feed ratio at 48 L / g.h.	[35]
Effect of the bimetallic catalyst				
Ni-La/KCC-1	550-850 °C, CH ₄ :CO ₂ :N ₂ =2:2:8, GHSV= 30,000 mlg ⁻¹ h ⁻¹ , 1 atm		Ni-La bimetallic catalyst showed improved activity and selectivity with strengthened basic sites of the catalyst comparatively. The actual CH ₄ conversion reached 98.2% as predicted by response simulations.	[37]
Ni-Co/MgO over monoliths	600-800 °C, CH ₄ :CO ₂ =1:1, GHSV= 42000 and 84000 mlcat ⁻¹ h ⁻¹		Catalyst Ni(8 wt%) – Co (2wt.%) /MgO wash-coated monolith showed elevated activity, stability (48 hours), reduced coke formation (at 3% O ₂ feed)	[38]
Ni-M/MgO and (Ni-M-Mg) ₂ Al (M= Cu or Fe)	800°C, CH ₄ :CO ₂ = 1:1, 1atm		An increase in the Mg amount in the support hindered the coke formation. Suitable Ni particle size and CO ₂ adsorption is observed due to SMSI.	[27]
Ni ₁₇ W ₃ /SiO ₂	800°C, CH ₄ :CO ₂ = 1:1, F/W = 96,000 ml.g ⁻¹ h ⁻¹ , 1atm		W stabilized Ni in the bimetallic catalyst during DRM reaction and α-WC is created on the catalyst which aided the dissociation of carbon dioxide.	[40]

3. Conclusions and recommendations

Catalytic dry reforming of methane is a valuable technique not only for the sequestration of greenhouse gases (CO_2 and CH_4) but also for the syngas production. The commercialization of the DRM process still needs to be addressed due to certain limitations as discussed in this brief review. Due to economic constraints, Ni-based catalysts are most widely used, but they face problems such as deactivation by coke formation and sintering. Hence to commercialize DRM, it is essential to develop an economic catalyst that is both highly active, resistant to carbon formation, resistant to sintering and possess improved SMSI (solid metal support interaction) for the prolonged durability. Researchers have investigated the effect of adding promoters and different catalyst supports for Ni-based catalysts to reduce the coke formation. It has been accomplished that doping an active metal-based catalyst by alkaline, alkaline earth or noble metal enhances its performance. This is mainly due to increased stability, oxygen storage capacity (in case of Ce doped) and enhanced catalytic structure for DRM. The method of catalyst preparation also provides a crucial role in the structural characteristics and performance of the catalyst. Also, a recent attempt has been made to minimize the coke formation by synthesizing a multi-metal framework catalyst with improved anti-sintering properties. It has also been concluded that bimetallic catalysts performed quite well compared to the reference monometallic catalysts due to stable alloy formation giving rise to enhanced and stable morphology of the catalyst even at high temperatures. However, to overcome the remaining technical glitches, in prospects, research on bimetallic catalysts is still another milestone to synthesize a suitable catalyst, since bimetallic catalysts have shown quite improved properties. A bimetallic catalyst that is coke resistant, highly active, can work on a lower range of temperatures to save the energy intake for reaction and has prolonged durability for the DRM process is still missing. Another aspect that needs future consideration is the interaction among the metal and support as well as metal dispersion in the support. Every metal solution has a distinctive structure lattice, which is a very important parameter for the stability of catalysts to avoid its sintering. Hence, it needs a thorough understanding while choosing an appropriate metal for catalyst support to have an ideal solid solution for catalysts with prolonged durability.

Apart from the catalyst development, the production of syngas by DRM also depends on operating conditions, including reaction temperature and molar feed ratio of the feed gases (i.e. CH_4 and CO_2). This may be another parameter to be considered for future research.

4. Outlook

In the last five years, numerous studies have been conducted on CO_2 reforming of CH_4 to identify the root cause and techniques to upgrade the resistance towards coke formation. Several methods have been adopted to lessen the inclination of Ni-based catalysts towards carbon deposition; for example, using an appropriate method of catalyst synthesis, utilizing the basic metal oxide for catalyst support and doping with a suitable promoter to enrich the oxygen storing capability of the catalyst. The future research work should be aimed at designing and synthesis of ideal Ni-based bimetallic catalyst; as Ni has shown considerable and promising signs of raised activity and stability. But still, carbon deposition is its limitation yet. The investigations focused on metal dispersion and active metal catalyst particle size is also a key factor that needs to be investigated further in future research for better durability of the catalyst. The catalyst preparation route also portrays a vital role in the overall performance of the catalyst. The proper method of catalyst synthesis can provide enhanced Ni dispersion on the support, better SMSI, elevated stability, higher activity, and resistance to coke formation. Hence the future research work should also focus on this parameter to contribute towards the development of an ideal catalyst.

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