

Syngas production via combined dry and steam reforming methane over Ni-based catalyst: A review

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Abstract. Global energy consumption has eventually increased as a result of the growing world population. Various problems arise as a result. The accumulation of greenhouse gases (GHGs), which led to a shift in the world's climate, is the most problematic. Combined dry and steam reforming of methane (CDRSRM) is a highly advantageous method since it uses two of the most significant GHGs, CH₄ and CO₂, to produce syngas, an intermediate product to produce valuable fuels. Ni-based catalysts are inexpensive, compared to many noble metals, and exhibit good reaction activity. However, deactivation, coking, and sintering of catalysts continue to be the major obstacles to commercialization. Due to better and more stable catalytic structure, which is both coke and sintering resistant at high temperatures, bimetallic catalysts have established increased activity and prolonged durability when compared to monometallic catalysts. This review highlights recent advancements in Ni-based catalysts for CDSRM by emphasizing factors such as catalyst support, bimetallic catalyst, promoters, and strong metal-support interactions (SMSI).

Introduction

Advancement in the quality of life, which is directly related to the amount of energy consumed, has accelerated the increase in global energy consumption. The industrialization has transformed the power generation scenario over the years due to rising energy demand [1]. Many of the world's energy needs are currently met by burning fossil fuels (natural gas, coal, petroleum products, etc.). They have become a pivotal and fundamental element of modern society, relying on them more and more ever since industrialization, although the oil and gas prices are much higher than in the past [2]. Wind, geothermal, solar, and other renewable energy sources contribute only a small fraction of the total energy demand. It is also likely that energy consumption will increase further in the future since it has been increasing in recent years [3]. The current reliance on fossil fuels such as coal, natural gas (NG), and oil to meet energy demand has resulted in the production of hazardous greenhouse gases (GHGs), which has caused environmental problems [4]. GHGs with the highest abundance are methane and CO₂, and they are the key contributors to the present climate challenges. In recent decades, CH₄ emissions in the atmosphere have increased, making it a major contributor to increased global warming [5]. Earth System Research Laboratory (ESRL) [6] data show that worldwide methane and carbon dioxide concentrations rose from 1650 parts per billion and 345.36 parts per million in 1985 to 1884.7 parts per billion and 412.31 parts per million, respectively, in September 2021 [7]. These two gases boost the greenhouse effect by absorbing and radiating the energy. GHG emissions will affect the Earth's climate and degrade natural ecosystems, resulting in huge socio-economic losses [8]. Hence, reducing GHG emissions into the

atmosphere and synthesizing a clean fuel is a main priority. Furthermore, efficacious technologies for converting CH₄ and CO₂ into useful products, mainly syngas, are required [9].

For the creation of clean fuel, like hydrogen, natural gas needs to undergo a catalytic process described as reforming. Reforming is the most usual method for producing syngas, which is the intermediate product to produce liquid fuels, in the industry and it involves one of three reforming processes. Steam reforming (SRM), partial oxidation (POM), and dry reforming of methane (DRM) are the most frequent methods used in industry to make syngas [10]. But every process produces a different ratio of syngas 3, 2, and 1 respectively [11]. The stoichiometric ratio required for the Fischer Tropsch synthesis to produce methanol is 2 [12]. Only, POM produces syngas with a ratio of 2. However, it has various disadvantages like hotspot formation, high explosion risk, and the requirement of cryogenic unit [13]. Among all other processes, combined dry and steam reforming methane, which includes both SRM and DRM, has recently sparked interest within the research and educational communities in gaining benefits while minimizing the disadvantages of each of the three fundamental methods [14].

CDSRM has ability to decrease the formation of carbon deposition, easier modification of the H₂/CO ratio by varying the feed composition and high catalytic stability in the coexistence of CO₂ and H₂O oxidizing reactants [15]. It will help to reduce the coke formation by the oxidation of the carbon deposited on the surface. CDSRM, on the other hand, is a complicated reaction since it involves two reforming reactions, secondary reactions, and coke production reactions all at the same time [16]. The reaction pathway is highly dependent on reaction variables such temperature, feed composition, and pressure [17]. Excess steam has been shown to be useful in preventing the formation of coke, but it also raises the expense of the operating process. Due to endothermicity, CDSRM requires elevated reaction temperatures and catalyst helps in reducing the reaction's activation energy and increases the conversion rate [18]. However, the deposition of carbon on the catalyst's surface deactivates it to a large extent, causing harm to the catalyst's stability. The sintering of the active catalyst phase, the production of inactive metal oxide, and the unfavorable interaction with oxide support are all factors that affect catalyst performance [19].

A lot of studies have been done for the development of an efficient catalyst for the CDSRM [20] that has good selectivity and catalytic performance and is resistant to coke formation. Noble metals (Ru, Rh, Pd, Ir, and Pt) are enormously active and resistant to the development of carbon whiskers, however, carbon deposition can be reduced most effectively by Ru and Rh, according to researchers. However, apart from their high activity, noble metals are not used industrially because of their high cost [21]. There are a number of existing catalysts, but Ni-based catalysts are currently the most commonly used in industrial processes. The CDSRM process will require a highly active catalyst that has improved metal support interactions and is resilient to carbon formation in order to be commercialized [22]. The goal of this review is to highlight recent new developments in the synthesis of appropriate catalysts for CDSRM done in the last ten years. A comprehensive analysis of numerous emerging methods and measures used to stabilize catalysts is presented, along with associated data revealing activity and stability levels.

Ni-based catalysts for CDSRM reaction

Nowadays, the use of nickel as an active site rather than noble metals is the main focus of catalyst development due to its high intrinsic activity, lower cost, and abundance. [23]. However, the stability of Ni-based catalysts in harsh conditions is a significant problem because coke deposition and thermal sintering on the catalyst's surface encourage deactivation [24]. Laosiripojana et al. [25] suggest that poisonous chemicals in reactants or products cause a rapid decrease in reforming potential over time. There have been various investigations performed so far that have investigated the nature of the support, the methods for preparing it and the addition of catalysts[26]. It is

therefore essential to develop catalysts that resist carbonation, oxidative environments, and high temperatures in order to commercialize the process.

Irrespective of the fact that Ni-based catalysts are cheap and exhibit better performance that is comparable to expensive metallic catalysts, still thermal sintering and coke formation promote the deactivation of catalysts [27]. Since, the generation of carbon deposits is dependent on the operating conditions, namely the utilization of surplus steam or not during reactor feeding, and the nature of the catalyst and CDSRM uses low steam-carbon ratios in order to achieve the required the H₂/CO ratio, hence Ni-based catalyst deactivates due to carbon deposition [28]. In high-temperature CDSRM reactions, using a nickel-based catalyst with a high oxygen capacity or oxygen mobility is a useful strategy to prevent coke formation and improve catalytic performance. A lot of research emphasizes the use of a catalyst that has strong interaction between metal and support (MSI), redox properties and small particle size (<2 nm), and excellent metal dispersion, so as to prevent coke formation and catalyst sintering due to high temperature [29].

Effect of Catalyst Support. Catalysts typically consist of multiple components, which are constructed into the desired shape and structure. Materials embedded with active metal usually support metal catalysts. There are several functions that these support materials play in the catalyst's activity [30]. Metallic compounds can disperse over a large surface area, maximizing the surface area of active sites, which allows the coarse geometry of the catalyst to be tailored to the reactor [31]. Because of their interactions with active metal sites, these supports are typically inactive on their own but participate in the whole process when involved in a reaction [32]. Using Ni-Co in combination with supports containing strong Lewis basicity can limit the accumulation of carbon on metal active sites, resulting in an enhanced ability for the catalyst to absorb CO₂, resulting in a decrease in carbon generation by reverse Boudouard reaction, thereby altering the equilibrium concentration [33]. During the reforming reaction, catalyst-support interactions significantly influence carbon deposition over metal-support catalysts. According to a study by Roh et al. [34], adding La₂O₃ to Ni/Al₂O₃ improved the dispersion of Ni particles over the CDSRM's support surface. It proved advantageous to add La₂O₃ to Ni catalysts supported by SiO₂. The inclusion of La₂O₃ improved Ni dispersion, increasing its interaction with the support, and so promoting CO₂ activation.

Because of its high surface area, which makes it possible for metallic particles to be easily and uniformly dispersed on either internal or external surfaces, alumina is frequently used as a catalytic carrier in practically all reforming reactions [35]. Additionally, despite being chemically and physically stable, Al₂O₃ has a moderately acidic pH, which tends to encourage a side-reaction called methane breakdown that is more likely to occur on acidic sites, which tends to increase carbon deposition [36]. In a study conducted by Nakoua and Naas [37], the authors tested Ni/Al₂O₃ in a detachable reactor. The author noted that during the dry reforming of methane at 700°C, 1 atm, rapid carbon deposition was seen. However, a decrease in carbon deposition on the surface was seen when CO₂ reforming was carried out in conjunction with steam reforming reaction in thinner channels deposited with a thinner layer of catalyst.

Roh et al. used various supports for the Ni catalyst including Ni/ZrO₂, Ni/MgO, Ni/MgO-Al₂O₃, Ni/CeO₂, and Ni/Al₂O₃. The authors tested these catalysts for CCSRM to produce syngas with a ratio of 2.0. The catalyst was prepared by the wetness impregnation method. The feed ratio H₂O: CO₂: CH₄ of 2.4:1.2:3 was used at the temperature of 800 °C [38]. A study on zirconia-supported nickel (Ni/ZrO₂) catalysts with less than 2% metal content demonstrated that they were exceptionally durable at the stoichiometric ratio of CO₂ to CH₄. According to research by Bae et al. [39], co-impregnating Ni and mixed CeO₂-ZrO₂ oxides onto MgAl₂O₄ surfaces is significantly more important than post-impregnating Ni on CeO₂-ZrO₂-coated MgAl₂O₄ surfaces. Rezaei [40] presented similar findings by synthesizing Ni catalyst over nano-crystalline ZrO₂ using a

surfactant-based method that produced high levels of CH₄ transformation. A strong interaction between the catalyst and the support plays a significant role in determining activity, stability and performance, as evidenced in the literature presented here.

Effect of Promoters. It is reported that the anti-coking and anti-sintering ability of the catalyst can be improved by using support along with promoters. The coke-resistance properties can be increased by introducing promoters such as alkali, alkaline earth, and metal oxides of rare-earth elements, such as lanthanum, magnesium, cerium, and calcium, and also diminish the active site's thermal sintering. In their study of Boron-doped Ni/SBA-15, Siang et al found that Boron promoted CO₂ adsorption by donating electrons to nearby Ni. This results in enhanced catalytic activity [41]. They concluded that for Ni/SBA-15, 3 wt.% boron was optimum. Moreover, Ni-SiO₂-MgO catalysts showed better catalytic activity having 80% of methane and 60% of CO₂ conversion. The operating temperature was 750°C and the produced syngas ratio of 2. Stroud et al., tested Sn modified Ni/Al₂O₃ and dual oxide support Ni/CeO₂-Al₂O₃ catalyst. It showed promising activity, as it occupies the C nucleation sites near the Ni atom. As a result, it decreases the coke formation rate during reaction [42].

Li et al. [43] have found that Ni/ZrO₂ promoted by Mo₂C for CDSRM enhanced the Ni dispersion and it significantly increased the activity. Moreover, various authors develop Ni-based catalysts that have high stability and reactivity which are supported by the Ce-ZrO₂, MgO, ZrO₂, and MgO-ZrO₂ for CDSRM. They studied the effect of the support and promoters on the activity of the nickel catalyst [26]. Furthermore, a study conducted by Jabbour et al. [44], in which they used Ni/Al₂O₃ promoted by 5 wt.% Mg and Ca. And gives the conclusion that the addition of Ca and Mg as a promoter significantly increased the Ni catalyst activity. Moreover, various authors develop Ni-based catalysts that have high stability and reactivity which are supported by the Ce-ZrO₂, MgO, ZrO₂, and MgO-ZrO₂ for CCSRM. They studied the effect of the support and promoters on the activity of the nickel catalyst [45].

Farooqi et al. [46] studied the production of syngas over Ni/ZrO₂-MgO by comparing the performance of Ni/ZrO₂-MgO with the Ni-MgO. The authors observed that coke deposition varies with the type of catalyst used. Ni/MgO had significant carbon deposition on its active sites, and the carbon was in the form of sheets having a negative influence on the activity of the reaction and resulting in catalyst deactivation. However, Ni/ZrO₂-MgO generated a different type of carbon, which was in the form of filamentous carbon having structures like nanotubes and the intensity was insignificant. Moreover, Ni/ZrO₂-MgO exhibited better stability and activity for CDSRM reaction at 800 °C by using a stoichiometric feed ratio, and carbon deposition amount and type strictly depend on the catalyst [47]. Ji et al. [48] investigated Ce-promoted Ni/SBA-15 catalysts for CDSRM in an analogous manner. Based on the findings, the Ce-promoted catalyst supported on SBA-15 demonstrated a higher surface area, longer stability, higher activity, and higher oxygen storage capacity. In addition to alkaline earth metals, noble metals doping metal catalysts resulted in encouraging results that improved coke resistance and stability. Catalysts can be greatly improved with even a minute amount of noble metals[49].

In a study, Khani et al. [50] concluded that ZnLaAlO₄ catalyst with a 3 wt.% Ru promoter produced the best results due to increased catalytic activity and reduced coke deposition. As a result, the promoters boosted dispersion, which also lowered the temperature required in order to achieve optimal performance through synergistic interactions. Since the actual reaction mechanism pathway must be identified before selection can begin, choosing an appropriate co-metal may be challenging.

Effect of Bimetallic Catalyst. Apart from designing monometallic Ni-based catalysts with different support variations and altering their properties by adding metals with redox or basic properties,

alloying a second metal (whether noble or transition) with the existing Ni metal, which acts as co-metal helps in the modification of various catalytic properties via a synergistic effect between each other [51]. As, the second metal offers various advantages including high activity, and stability [52].

Zhang et al. [53] perform a stability test for the Ni-Co bimetallic catalyst and it shows minute deactivation for 2000 hrs. TOS. Due to the technological impacts, bimetallic catalysts are receiving a lot of attention from researchers for CDSRM-based processes [54]. When these catalysts are used along with oxide support, they generate bi-functional capabilities as a result of the change in metal-oxygen bond strength, which subsequently reflects variations in their performances and catalytic properties [55]. Introducing a minute amount of noble metal modifies the Ni environment. Garcia et al. [56] studied the effect of 0.04% Rh₂O₃ and found the enhanced CDSRM performance. Furthermore, Shakouri et al. [57] studied the effect of Ni-Co bimetallic catalyst and compared its performance with monometallic Co and Ni catalyst. Authors concluded that Ni-Co bimetallic exhibits better performance than the monometallic ones as it converts 70% more CO₂ and the respective H₂/CO ratio was 1.8-2.

Therefore, from the above studies, it was observed that as compared to monometallic catalysts, the bimetallic catalyst demonstrated improved performance. As, bimetallic catalysts significantly activated both metals via a synergistic effect and a stable alloy was formed that prevented the catalyst from sintering at high temperatures. Also, the use of suitable promoters helps in better metal dispersion, reduced coke formation, increased oxygen storage capacity, and better stability. Hence, co-metal and promoters should be selected carefully as they vary the main reaction mechanism.

Table 1 Recent developments of catalyst used in CDSRM for syngas

Catalyst	T (°C)	P (bar)	Feed Ratio (H ₂ O:CO ₂ :CH ₄)	GHSV ¹ (Lgcat ⁻¹ hr ⁻¹)	TOS ² (hrs)	CH ₄ %Con.	CO ₂ %Con.	H ₂ /CO	Ref
Ni/MgO-ZrO ₂	800	1	2:1:3	36	20	82.5	81.5	1.70	[46]
Ni/MgO-Al ₂ O ₃	850	1	2:1:3	-	-	61.8	59.8	2	[58]
13XZnO-Ni-u	800	1	2:1:3	-	6	90	58	-	[59]
Ni-Co/AlMgOx	850	1	2:1:3	110	15	80.3	89.1	1.68	[57]
Ni/CeO ₂ -SrO ₂	800	1	1.5:2.4:3	-	250	91	78	1.9	[26]
Ni-K/LDH	800	1	2:1:3	-	-	90	64.6	2	[60]
Ni-Sn/Ce-Al	700	1	1:1:1	60	24	70	40	1.6	[42]
Ni/Al ₂ O ₃	800	1	0.8:0.4:1	69	3	71	56	2.5	[44]
Ni/MgO	830	1	0.8:0.4:1	60	160	71	73	1.92	[61]
Ni/SBA-15	800	1	2:1:3	36	-	61.6	58.9	2.14	[62]
Ni-Ce/MgAl ₂ O ₄	850	1	1:0.4:1	-	20	83	52	2.2	[34]
Ni/SiO ₂ MgO	750	1	2:1:3	160	140	80	60	2	[63]
Ni/SBA-15 3%B-Promoter	800	1	2:1:3	36	24	71.4	70	2.5	[14]
Ni-Mg/Al ₂ O ₃	800	1	0.8:0.4:1	138	40	80	74	2.10	[44]
Ni-Ce-Fe/Al ₂ O ₃	900	20	1:0.8:1	25	50	89	70	2	[2]

¹GHSV stands for Gas hourly space velocity

²TOS stands for Time on stream

Conclusions and recommendations

Considering the future's increasing demand for fossil fuels, CDSRM offers an environmentally friendly alternative. The use of CO₂ and CH₄ as feedstock might also make this a useful technology for mitigating GHG emissions. Despite this, a few obstacles prevent it from becoming widely commercialized. Economic considerations force the employment of Ni-based catalysts in the majority of situations. However, these materials can degrade through the creation of coke and sintering. The commercialization of CDSRM consequently requires the creation of a commercially viable catalyst that is highly active, immune to carbon formation, resistant to sintering, and has enhanced SMSI (metal support interaction). Researchers found that adding promoters and catalyst supports to Ni-based catalysts decreased the generation of coke. Improved performance can be achieved by doping metal-based active catalysts with alkali, alkaline earths, or noble metals. It results from improved stability, oxygen storage capacity, and enhance catalytic structure. Furthermore, since the preparation of catalysts affects both their structural behavior and performance, it is vital to examine this process. Bimetallic catalysts have been discovered to operate pretty well in comparison to the monometallic catalysts at high temperatures because of stable alloy formation. However, there is still a need for a coke-resistant, highly active bimetallic catalyst that uses less energy by operating at lower temperatures and has a longer lifespan for the CDSRM process. Interactions between metals and supports, along with dispersion of metals in supports, are also important future considerations. A number of variables, including as the composition of feedstock gases, reaction temperature, and gas hourly space velocity (GHSV) also influences the catalytic activity of CDSRM. It is essential to establish a reliable relationship between the process variables and the performance of CDSRM catalysts.

Future outlook

In order to comprehend the mechanism of the CDSRM reaction, numerous experiments on Ni-based catalysts have been carried out during the past few decades. These investigations have helped to develop new strategies to stop the creation of coke in addition to identifying the causes of coke formation. To lessen the likelihood of coke generation employing Ni-based catalysts, several strategies have been used. This entails choosing the right method for effective and viable catalyst formation, picking the right metal for improved SMSI, keeping the support material alkaline, doping with the right promoter to increase oxygen storage capacity, and choosing the right bimetallic catalyst to improve mutual synergies.

Future research should concentrate on creating suitable bimetallic and trimetallic catalysts based on Ni, as this catalyst has demonstrated significant and encouraging evidence of enhanced activity. However, carbon deposition continues to be a constraint. Future studies should concentrate on metal dispersion and active metal particle size for improved catalyst durability. A major factor in the performance of the catalyst is also its preparation method. The proper technique for catalyst synthesis can enhance Ni dispersion on the support, stability, activity, SMSI, and resistance to coke formation. Future studies should pay particular attention to these factors in order to create the optimum catalyst.

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