A Comprehensive Review on Improving Combined Steam and CO_2 Reforming of Methane over Ni-based Catalysts

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Abstract

The global energy requirement has been significantly increased for several decades because of rising global population and economic development. This would lead to huge emissions of greenhouse gases, GHG (e.g. methane and carbon dioxide) into the atmosphere, thus posing a threat to the environment and leading to the undesirable effect of climate change. One sustainable solution to curb on emissions of GHGs into the atmosphere, is a utilization of CO_2 with methane to produce syngas via catalytic reforming. A comprehensive review has been performed on the performance of Ni-based catalysts in combined steam and dry reforming of methane (also known as bi reforming of methane, BRM). Due to the low cost and favorable activity, Ni-based catalysts have been extensively used for BRM. However, carbon deposition on the metal surface serves a major issue with Ni-based catalyst in BRM, which turns the catalyst inactive. Catalyst supports that have a strong metal-support interaction created during the catalyst preparation exhibit higher stability, higher thermal resistance and high coke resistance. This review covers recent progresses in the design of Ni-based catalysts along with mechanistic and kinetic aspects of the BRM reaction. Also, the impact of two-dimensional few-layered transition-metal nitrides and carbides, called

MXenes, have attracted a great interest given their large surface areas and their unique physicochemical properties.

Keywords:

Catalyst development; Greenhouse gases; Syngas; catalyst; methane bi reforming

1.0 Introduction

The global consumption of energy has been significantly increased over last few decades because of rising global population and emergence of new economic powers (i.e. China, Russia, Brazil, India etc.). Major chunk of the world energy requirement is still met from the Fossils fuels, including oil, coal and natural gas. Power production and treating of fossil fuels cause an intense increase in the amount of pollutants and significant emissions of GHGs, including mainly CH_4 and CO_2, which may cause temperature rise at global stage and related environmental damages [1,2].

In view of the present global adverse environmental situation, reduction in the release of GHGs into the atmosphere is a top priority. Thus, there is a need to develop efficient technologies to transform methane and carbon dioxide into valuable products. Presently, many proposals involve carbon dioxide capture and sequestration (CCS), whose prime instance relates to the sequestration processes of oil and gas reservoirs [3]. Nevertheless, such methods may encounter several issues, as well as having technical constraint in achieving practical significance. Hence, capturing CO_2 with subsequent transforming it to generate useful products, can become economically viable solution [4]. Due to the anticipated rise in CO_2 and CH_4 emissions, it may become more significant to develop efficient methods to capture and utilise these GHGs. One of the preeminent processes is to convert them into a synthesis gas, which is a versatile intermediate feedstock for liquid fuel and value-added chemical synthesis [5–8]. The major fields of utilising synthesised gas are methanol formation, hydrogen production and Fischer Tropsch process. The composition of the synthesis gas can widely vary, depending on the synthesis processes and the composition of the raw material, i.e. their hydrogen-to-carbon ratios (H_2/CO) and their reactivity. Among the various primary feedstocks, namely, natural gas, coal, biomass, petroleum coke and others, being utilised for production of Syngas, natural gas has proved to be the most economical route [9].

Syngas can be commonly produced by reforming processes which are the most conventional and cost-effective technologies for generating syngas from methane in industrial applications [2,10]. The operating conditions, strength and weakness of the recent advanced reforming approaches, including, dry reforming of methane (DRM), steam reforming of methane (SRM), partial oxidation of methane (POM), and bi reforming of methane (BRM), are compared in Table 1. The characteristics of reforming methods as well as their outcomes, depend on the selection of oxidant, energetics and kinetics of the reaction and the end H_2/CO product ratio. In practice, the catalytic route used in SRM reaction, is the most common route to form syngas. SRM faces drawbacks due to the higher H_2:CO ratio (i.e. over 3) and a huge quantity of CO_2 formed. Also, due to the endothermic nature of the SRM process, there is a need to inject rigorous energy that makes the method excessively expensive [11]. In the case of DRM, both unwanted greenhouse gases (CH_4 and CO_2) are utilized to yield the valuable syngas, but having the ratio less than unity for the final H_2/CO is unsuitable for Fischer-Tropsch synthesis (FTS) because stoichiometric H_2/CO ratio of 2 is required to generate methanol [12,13]. Hence, by employing these two approaches the implementation of supplementary separation and refinement measures for the downstream processes are enforced, which may raise the capital cost [14,15]. Even though, the POM possesses numerous advantages including considerably short residence time, generation of desirable H_2/CO ratio of 2 and others, however, local hot spots on catalyst bed due to its exothermicity is the major setback in adopting to a safe industrial operation as having possible explosion risks [16]. Recently, BRM, involving both dry and steam reforming of methane, gave impetus in raising interest of the scientific and academic community to accrue benefits while mitigating drawbacks associated with each of the three basic routes. Bi reforming is an alternate process to produce syngas with suitable H_2:CO ratio that avoids no additional costs for O_2 removal from air and/or CO_2 separation from biogas. BRM utilizes carbon dioxide, steam, and methane and converts them into carbon monoxide and hydrogen gas known as synthesis gas (syngas). Matter of fact, BRM presents a more prospective method than other reforming processes, owing to the high stability of its catalyst in the harmonization of CO_2 and H_2O as oxidizing reactants and adaptable adjustment of H_2/CO ratios by optimising composition of feedstock [9,17].

The significance of a catalyst lies in its vitality to reform methane with proper transformation of the reactants. Metals belonging to Noble group, including Pd, Ru, Rh, and Pt as well as Ni and Co have been used for catalytic purposes in case of BRM reaction due to their high selectivity, catalytic activity and high resistance to carbon formation [18–21]. While, Ni-based catalysts are in substantial use in industrial operations, it has been known that they are susceptible to coke formation that initiates their deactivation, which leads to severe industrial operating issues [22–24]. Hence, the development of efficient, economic and stable catalyst is crucial to implement BRM on industrial scale. Over a decade or so, extensive work has been into the preparation of an active and stable catalyst for BRM, however, there is no evidence if anyone has tried to gather these hard earned contributions to generate a document as a useful guide for others to follow research on the topic for possible further enhancement in BRM process. We plan to write a review article on the topic and in this review, our main object is to emphasize the development of Ni-based catalysts, including effect of support and promoters during last decade in the field of BRM. We hope that this contribution will be a good addition to the existing literature and will provide useful information to academicians and researchers in the area of catalysis relating to BRM process or other similar fields of catalysis.

Table 1. Comparison between different methane reforming processes

Process	**SRM**	**POM**	**DRM**	**BRM**
Reaction	$CH_4 + H_2O \rightarrow CO + 3H_2$ (ΔH^{o}_{298K} = 206 kJ mol^{-1})	$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$ (ΔH^{o}_{298K} = - 38 kJ mol^{-1})	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ (ΔH^{o}_{298K} = 248 kJ mol^{-1})	$3CH_4 + CO_2 + 2H_2O \rightarrow 4CO + 8H_2$ (ΔH^{o}_{298K} = +712 kJ mol^{-1})
Advantages	• High efficiency and no oxygen required • Industrially established technology with large-scale production • Highest H_2 selectivity	• Short residence time • No requirement of feedstock desulfurization • A fast and exothermic reaction	• Efficient greenhouse gases utilization • Favourable H_2/CO ratio for long-chain hydrocarbon production via Fischer-Tropsch synthesis • Green process	• Environmentally friendly • Flexible H_2/CO ratios via easy adjustment of feedstock composition • Negligible carbon deposition and prolonged catalyst lifespan
Disadvantages	• High emission of greenhouse gas (CO_2) emissions • Corrosion issues and requires a desulphurization unit • Endothermic nature and severe heat duty	• High explosion risk • Hot spots formation on the catalyst bed owing to exothermic nature. • The cryogenic unit is necessary for the separation of oxygen from the air	• Quick deactivation of the catalyst because of carbon deposit and metal sintering • Highly endothermic and energy intensive	• High reaction temperature requirement • Unavailable large-scale production
Operating conditions	Temperature (°C): 700–1000 Pressure (bar): 3–25 Feedstock ratio: CH_4/H_2O = 1/1	Temperature (°C): 950–1100 Pressure (bar): 100 Feedstock ratio: CH_4/H_2O = 2/1	Temperature (°C): 650-850 Pressure (bar): 1 Feedstock ratio: CH_4/H_2O = 1/1	Temperature (°C): 500-1000 Pressure (bar): 1 Ratio: $CH_4/H_2O/CO_2$ = 3/2/1
H_2/CO ratio	>3	2	<1	2

2.0 Thermodynamics Aspects

The BRM process involves occurrence of many side reactions [25-27], thus combination of all these reactions can be expressed as,

Bi reforming of methane (BRM)

$3CH_4 + CO_2 + 2H_2O \rightarrow 4CO + 8H_2$ $(\Delta H^{o}_{298K} = +712\ kJ\ mol^{-1})$ (1)

Steam reforming of methane (SRM)

$CH_4 + H_2O \rightarrow CO + 3H_2$ $(\Delta H^{o}_{298K} = +206\ kJ\ mol^{-1})$ (2)

Dry reforming of methane (DRM)

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ $\Delta H^{o}_{298K} = +247\ kJ\ mol^{-1})$ (3)

Water gas shift reaction (WGS)

$CO + H_2O \rightarrow CO_2 + H_2$ $(\Delta H^{o}_{298K} = -\ 41\ kJ\ mol^{-1})$ (4)

Reverse water gas shift reaction (RWGS)

$CO_2 + H_2 \rightarrow CO + H_2O$ $(\Delta H^{o}_{298K} = +41\ kJ\ mol^{-1})$ (5)

Methane decomposition

$CH_4 \rightarrow C + 2H_2$ $(\Delta H^{o}_{298K} = +75\ kJ\ mol^{-1})$ (6)

Boudouard reaction

$2CO \rightarrow C + CO_2$ $(\Delta H^{o}_{298K} = -\ 172\ kJ\ mol^{-1})$ (7)

The thermodynamics behaviour of BRM reaction is vital to establish the most optimum reaction conditions such as temperature, pressure and feed ratio to achieve a high yield of syngas [19,25]. However, the complexity of BRM reaction is due to the occurrence of simultaneous multiple reactions, namely SRM and DRM (Eq 2 and 3) as well as several side reactions (Eq 4 and and 5) and coke forming reactions (Eq 6 and 7). These side reactions play a significant role to determine the yield and lifespan of the catalyst.

Ozkara-Aydinoglu [19] found that the H_2/CO ratio of synthesis gas depends on the comparative concentration of H_2O and CO_2, as well as the temperature and pressure of the reaction. Kumar et al. [26] reported that the kinetics seemed to constraint the reaction of carbon removal (i.e. reverse Boudouard reaction, Eq 6) and steam gasification of deposited carbon at reaction temperature below 800°C. In addition, the amount of carbon formed with the presence of steam is significantly reduced as shown in Figure 1. Jabbour et al. [14] performed thermodynamic simulations to determine the best conditions for conducting BRM reaction. As stated before, the BRM is a complex reaction consisting of multi reactions network occurring simultaneously, however, possibility of any reaction depends on the BRM reaction temperature. Table 2 summarizes the possible reactions as well as their favourable temperature regions. All reforming reactions predominantly occur at reaction temperature beyond 600°C due to their endothermic nature. Meanwhile, the presence of side reaction also significantly emerges with a rise in reaction temperature, particularly the CH_4 decomposition involves formation of the undesired carbon and subsequently forms the graphitic carbon resulting in the severe catalytic deactivation.

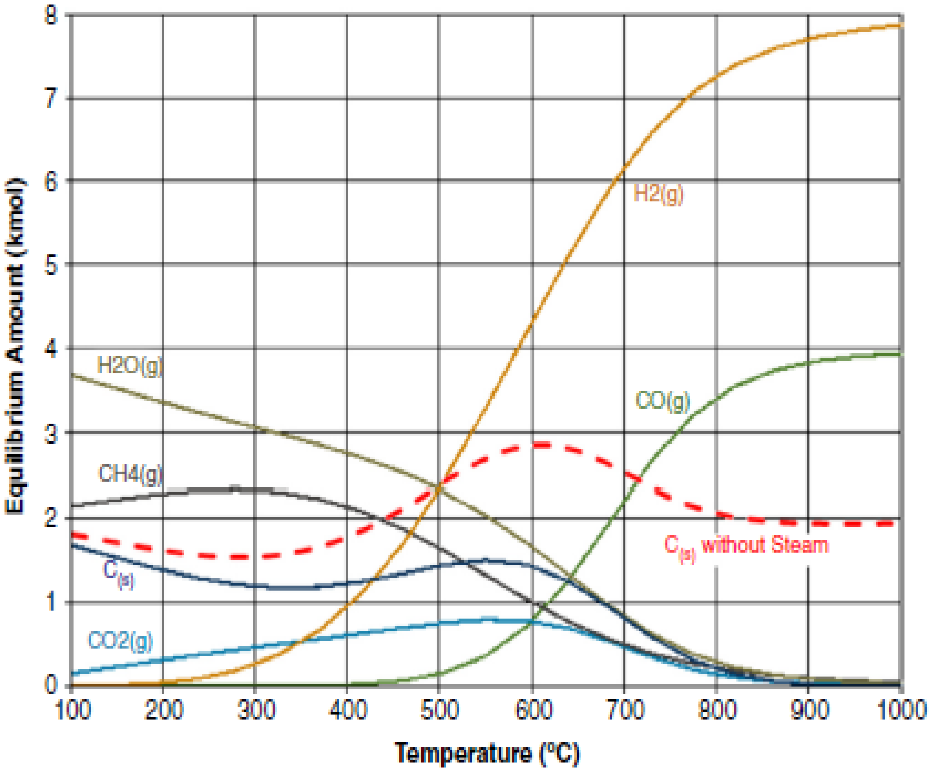

Figure 1: Equilibrium composition of BRM reaction at atmospheric pressure for different temperatures [26]

Table 2: List of main and side reactions possibly occurring during CSCRM and probability of occurrence as assessed by thermodynamic calculations by Gibbs free energy change [14]

Reactions		Equations	Temperature range (°C)			
			100-400	**400-600**	**600-800**	**800-1000**
Reforming reactions	Steam reforming of methane (SRM)	$CH_4 + H_2O \longrightarrow CO + 3H_2$	N.F. – F.	F.	F.	F.
	Dry reforming of methane (DRM)	$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$	N.F.	N.F. – F.	F.	F.
	Bi reforming of methane (BRM)	$3CH_4 + CO_2 + 2H_2O \longrightarrow 4CO + 8H_2$	N.F.	N.F.	N.F. – F.	F.
Side reactions (non-coke forming)	Water gas shift (WGS)	$CO + H_2O \rightarrow H_2 + CO_2$	F.	F.	F. – N.F.	N.F.
	Reverse water gas shift (RWGS)	$CO_2 + H_2 \rightarrow CO + H_2O$	N.F.	N.F. - F	F.	F. – N.F.
	CO_2 Methanation	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	F.	F. – N.F.	N.F.	N.F.
Side reactions (coke forming)	CO_2 hydrogenation	$CO_2 + 2H_2 \rightarrow C_{(s)} + 2H_2O$	F.	F. – N.F.	N.F.	N.F.
	CH_4 decomposition	$CH_4 \rightarrow C_{(s)} + 2H_2$	N.F.	N.F. – F.	F.	F. – N.F.
	Boudouard reaction	$2CO \rightarrow CO_2 + 2H_2O$	F.	F.	F. – N.F.	N.F.
	CO dehydrogenation	$CO + H_2 \rightarrow C_{(s)} + H_2O$	F.	F. – N.F.	N.F.	N.F.

where F. = favoured reaction: N.F. = not favoured reaction; N.F. – F. (or F. – N.F.) = from not favoured to favoured (or vice versa)

For determining the thermodynamic analysis of CH_4 , CO_2 and H_2O mixtures, FactSage software can be used for the computations [27].

The principle of this computations is based on the minimization of Gibbs free energy [27]. The percentage of reactant conversions, X_i (with i being CH_4 and CO_2), syngas ratio (H_2/CO) and coke content are computed according to the following equations,

$$X_i(\%)=\frac{Q_i^{In}-Q_i^{Out}}{Q_i^{In}}\times 100 \tag{8}$$

$$H_2/CO=\frac{Q_{H_2}^{Out}}{Q_{CO}^{Out}}\times 100 \tag{9}$$

$$\text{Coke content} = \frac{C_{out}}{CH_4^{In}-CO_2^{Out}}\times 100 \tag{10}$$

Won-Jun et al [28], studied the equilibrium analysis of the BRM, which can be seen in Figure 2 that exhibits the effects of $(CO_2+H_2O)/CH_4$ ratio and temperature on the CH_4 and CO_2 conversion, as well as H_2, CO, and coke yield, and H_2/CO ratio in CSDRM reaction. Figure 2a shows the profiles of methane conversion against temperature under atmospheric pressure. Also, due to the endothermic nature of the SRM (Eq. 2) and DRM (Eq. 3), conversion of CH_4 increases with raising the temperature for all range of $(CO_2+H_2O)/CH_4$ ratios. Nearly 100% CH_4 transformation is achieved above 850°C except for the lowest $(CO_2+H_2O)/CH_4$ ratio of 0.9. Figure 2b illustrates the CO_2 conversion as a function of reaction temperature for different initial mixtures. In all cases, CO_2 conversion decreases up to around 550°C because of the WGS reaction (Eq. 4) which causes formation of CO_2. Alternatively, for the $(CO_2+H_2O)/CH_4$ ratios, ranging between 2.0 and 2.9, CO_2 conversion has a negative value with temperature ranging between 500°C-600°C. This owes to the WGS reaction, which is strongly favoured by large amounts of water in the initial mixture. These findings agree well with those found by Ozkara-Aydinoglu and Nikoo [19,29]. Above 560°C, CO_2 conversion increases because of its participation at other equilibriums which are favoured at higher temperatures.

Figure 2c exhibits H_2 yield against temperature for a range of $(CO_2+H_2O)/CH_4$ ratios. Also, yield in H_2 increases when the temperature raises for the lower $(CO_2+H_2O)/CH_4$ ratios (i.e. 0.9, 1.2 and 1.4), formation of H_2 is supported by SRM (Eq. 2), DRM (Eq. 3) and WGS (Eq. 4). For the higher $(CO_2+H_2O)/CH_4$ ratios (i.e. 2.0 and 2.9), H_2 yield increases at the temperature up to 750°C. Figure 2c also shows that the yield of H_2 drops slightly at 800°C, owing to the occurrence of RWGS (Eq. 5). Figure 2d illustrates CO yield against temperature with a range of $(CO_2+H_2O)/CH_4$ ratios. CO's yield rises sharply with increasing the temperature due to the favourable circumstances for the reforming reactions at elevated temperatures. There is no CO formation until around 500°C because of the WGS reaction (Eq. 4). The production of CO is preferred at high temperature (>700°C) and high oxidant (i.e. CO_2 and H_2O) amounts in the initial reaction mixtures. Coke yield decreases with increasing the temperature and $(CO_2+H_2O)/CH_4$ ratio as shown in Figure 2e. Coke is strongly favoured by the Boudouard reaction and CH_4 decomposition which are firmly endothermic. This shows the close relation of the coke yield with CH_4 conversion and CO yield. Typically, the excess oxidizing substance can initiate a higher CH_4 conversion by means of the reforming reaction [30]. At temperature above 700°C, coke's selectivity is highly limited and depends strongly on the composition of the initial mixtures. Figure 2f depicts the dependence of H_2/CO ratio with reaction temperature. High H_2/CO ratios were obtained in the low temperature range (500-600°C). This is due to H_2 production, CH_4 decomposition and the consumption of CO by WGS reaction (Eq. 4) and Boudouard reaction (Eq. 7).

As a partial conclusion, the thermodynamic equilibrium of the syngas production from the BRM can be predicted by FactSage software. The process is preferred at high reaction temperature (>700°C), high oxidants to CH_4 ratio, and steam content in the feedstock mixtures. These parameters are of crucial importance to control the CH_4 conversion, H_2/CO molar ratio, and coke formation.

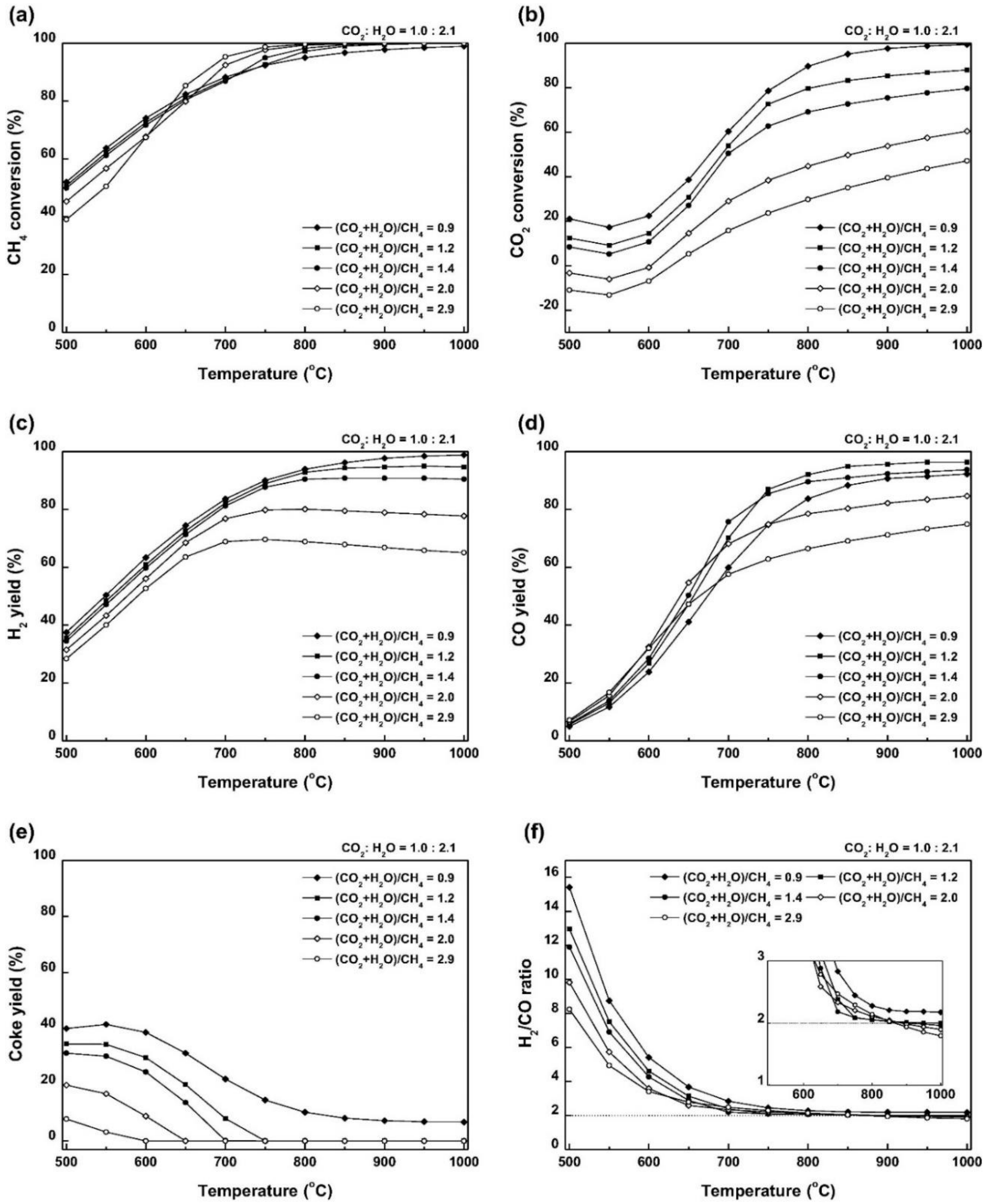

Figure 2. Effect of $(CO_2 + H_2O)/CH_4$ ratio as a function of temperature at a fixed CO_2: H_2O ratio of 1.0:2.1: (a) CH_4 conversion, (b) CO_2 conversion, (c) H_2 yield, (d) CO yield, and (e) Coke yield, and (f) H_2/CO ratio [28].

3.0 Ni-based catalysts for BRM

Several investigations were conducted for the preparation of active and coke resistant catalysts favouring BRM reactions. The performance of a catalyst for BRM reaction relies on the features of support, and the intensity of interaction between metal and support. The common catalysts widely used in BRM are transition metal-based catalysts including Ni-based catalysts [31–43] and Co-based catalysts [12,44,45]. Ni-based catalysts have been broadly tested for BRM owing to their availability, low price and high activity. However, the formation of coke leads to the fast deactivation which is a major drawback for these catalysts to be applied in the industrial sector. The poisonous chemicals in the reactants or products are the main factors causing the rapid decrease in potential of reforming activity with time as suggested by Laosiripojana et al. [46]. The poisoning of the catalyst can be mainly categorized into three groups: (i) poisoning to the intrinsic activity, (ii) poisoning to the activity of single pellets and (iii) poisoning of the complete reactor. Thus, in order to reduce the poisoning of the catalyst, several studies were conducted to highlight the crucial role of the support materials owing to the improvement in stability and the activity of the catalyst. Several transition metals such as Ni, Co, Pt Ru, Rh were studied and employed as a catalyst in the development of reforming reaction.

3.1 Catalyst Support

A catalyst unit is a multicomponent assembly, whose components are normally built into the required shape and structure. The active metal is normally inserted within the support material to form a support-metal sandwich catalyst. The selection of support’s material is important as it signifies several important functions to enhance the catalyst activity. For instance, the support metals may serve a large surface area, where metallic compounds may disperse. The support’s material may act to enhance the surface area of the active sites which becomes a significant part of the overall geometry of the catalyst for the reactor. Usually, supports are non-reactive on their own, however, they can contribute in the total reaction when positioned beside the active metal sites (i.e. bi-functional mechanism) [47].

Deposition of carbon on the metal active sites can be constrained when Ni-Co being used in conjunction with supports containing strong Lewis basicity [ref ??]. The ability of the catalyst to absorb CO_2 improves with raising Lewis basicity, which leads to the decreases in carbon formation by reverse Boudouard reaction through shifting the equilibrium concentration. Further, during reforming reaction, metal-support interaction and metal particle size contribute significantly towards carbon deposition over supported metal catalysts [48]. Also, the addition of basic supports such as CaO, MgO, K_2O and lanthanum oxide (La_2O_3) can enhance both catalyst performance and coke resistance [49]. Roh and Jun [50] discovered that the addition of La_2O_3 to Ni/Al_2O_3 can improve the dispersion of Ni particles on the supports during the reforming reaction. Also, La_2O_3 can also react subsequent to absorbing CO_2 to form $La_2O_2CO_3$ on the surface of a catalyst which can accelerate the conversion of surface CH_x species (x = 0-3)[ref??]. As reported in the literature, NiO/MgO [16], Ni/CeO_2 [17], and Ni/ZrO_2 [51] have good activity for BRM reaction with CO_2 conversion of 71.3%, 55.7% and 92.3% with temperature of 830°C, 800°C, and 850°C respectively. Gao *et al*. [52] showed the advantages of modifying the SiO_2 supported Ni catalysts by La_2O_3. They showed that the presence of La_2O_3 improved the dispersion of Ni, enhanced its interaction with the support and promoted the activation of CO_2. Verykios and co-workers [53] have proposed that the association between nickel and lanthanum species generates a unique type of collegial active sites at the Ni-La2O3 interface that boosts the activity and stability of the catalyst. Martinez *et al*. [54] reported that the addition of La within a certain bound increased the Ni dispersion within a catalyst which in turn improved the conversion percentage and enhanced the catalyst stability. Apart from single oxide supports, mixed oxide supports such as $MgO-Al_2O_3$

was also reported in other studies for BRM reaction with CH_4 conversion of 85% and 65% for Mg/Al ratios of 0.5 and 3.5 respectively at the temperature of 850°C [55].

The potential of a metal carbide-based catalyst also has been explored in literature for BRM. The interesting feature of the molybdenum carbide (Mo_2C) as the catalyst in reforming reaction is related to its capability to inhibit coke deposition without requiring an excess of oxidant because of its unusual mechanism that consists of competing carburization and oxidation reactions [56]. Brush and co-workers explored the performance of Ni/Mo_2C for bi-reforming reaction with CH_4 and CO_2 conversion of 70.5% and 99.8% respectively. They also observed no signs of coking despite conducting the reaction with excessive methane at high temperature [57].

A study [58] related to the zirconia-support nickel catalysts was conducted that emphasised the stability of the catalysts and reported that Ni/ZrO_2 catalyst with lower metal loading (<2%) was very stable for a stoichiometric CO_2/CH_4 ratio. But the stability of Ni/ZrO_2 catalyst also depends largely on the preparation method of the support. Wei et al. [59] reported very high conversion of CH_4 as well as CO_2 and stable catalytic performance over 600 h using Ni catalyst over $Zr(OH)_4$ ultra-fine support. While, Ni-based catalyst over $Zr(OH)_4$ was prepared using co-precipitation method, however, the method performed well for 50 h, deactivation started afterwards. The similar results were reported by Rezaei et al. [60], who showed that the Ni catalyst over nano-crystalline ZrO_2 being synthesized using surfactant-assisted method, rendered high CH_4 conversion.

As evident from the literature presented here, catalyst support holds a vital role in contributing towards activity, stability and performance because of its strong interaction with the metal. Table 3 summarizes the catalytic performance of Ni-based catalysts with various supports for BRM reaction.

Table 3: A Bibliographic listing of catalytic performance of Ni-based catalysts in BRM reaction

				Initial Performance				**Final Performance**				
Catalysts	**CH_4/H_2O /CO_2 ratio**	**T (^{0}C)**	**GHSV (L gcat^{-1} h^{-1})**	**CH_4 Conversion (%)**	**CO_2 Conversion (%)**	**H_2/CO Ratio**	**TOS (h)**	**CH_4 Conversion (%)**	**CO_2 Conversion (%)**	**H_2/CO Ratio**	**D* (%)**	**References**
Ni/MgO/SBA-15	1/0.75/0.5	850	27	98.6	92.3	1.74	600	95.6	76.0	1.82	3.0	[61]
Ni/MgO-Al_2O_3 (Mg/Al = 3.5)	1/0.8/0.4	700	1060	65.0	---	---	15	60.0	---	---	7.7	[55]
Ni/MgO-Al_2O3 (Mg/Al = 0.5)	1/0.8/0.4	700	1060	85.0	---	---	15	78.0	---	---	8.2	[55]
Ni/CeO_2	1/0.8/0.4	800	26.5	55.7	---	---	20	47.4	---	---	14.9	[17]
Ni/$MgAl_2O_4$	1/1/0.4	850	5	77.4	35.9	---	24	75.6	32.0	---	2.3	[62]
Ni/MgO	1/0.8/0.4	830	60	71.3	73.8	2.0	320	70.8	73.4	2.0	1.0	[16]
Ni/ZrO_2	1/0.8/0.4	850	60	92.3	71.4	1.98	20	82.4	54.3	2.0	11.0	[51]
Ni/MgO-Al_2O_3	1/1.2/0.4	900	4680	92.3	62.0	---	5	89.6	64.9	---	2.9	[63]
Ni/Mo_2C	1/0.375/0.375	950	n.m	57.6	99.8	1.26	250	7.9	13.0	1.40	86.3	[57]

Ni/Al_2O_3	1/0.8/0.4	800	69	80.9	81.9	2.03	40	82.5	77.0	2.09	---	[64]
Ni/SBA-15	1/0.5/0.5	800	36	67.3	---	0.93	10	64.5	---	1.17	4.2	[65]
Ni-Ca/Al_2O_3	1/0.8/0.4	800	138	64.0	58.0	2.09	40	65.0	58.0	2.05	---	[14]
Co-Pt/Al_2O_3	1/0.2/1	800	---	99.5	73.7	---	---	---	---	---	---	[44]
Ni-La/$MgAl_2O_4$	1/1.2/0.4	900	4680	77.7	54.8	3.10	5	68.1	44.7	3.10	12.4	[66]
Ni/ZrO_2-Mo_2C	1/0.8/0.4	850	60	97.7	79.2	1.95	20	96.5	73.2	1.89	1.3	[51]
Ni/Ce-SBA-15	1/0.5/0.5	800	36	77.7	---	1.60	10	71.3	---	1.65	8.2	[65]
Ni-Ce/$MgAl_2O_4$	1/0.8/0.4	700	530	81.3	65.9	2.10	20	---	---	---	---	[36]
Ni-Ce-Fe/Al_2O_3	1/1.3/0.8	900	24.6	90.3	65.6	---	50	87.8	64.0	---	2.8	[67]

TOS: time on stream. n.m: not mentioned. D* = Degree of catalyst deactivation = D* (%) = [1 – (final CH_4 conversion/initial CH_4 conversion)] × 100%.

3.2 Effect of Catalyst Promoters

According to the available literature [14,25,36,37] doping metal catalysts (Ni based) with another suitable metal may diminish the coke formation on the active sites of the catalyst thereby enhancing its overall activity and performance for methane bi reforming. Adding promoters basically interferes with the reaction mechanism of BRM process to facilitate the reduction of metal oxides (NiO), thus, escalating the quantity of basic spots on catalysts and easing formation of active sites at reduced temperature conditions. The promoters used in methane reforming reaction may be classified into three groups: (I) alkali or alkaline earth metals, such as K, Li, Mg, Ca, Ba, (II) rare earth metals, such as Ce, Zr, La and (III) other metals, such as Au, Ag, Sn, Bi, As, Pb and Cu.

Refashioning the Ni-metal based catalyst by alkaline and alkaline-earth metals can be a promising solution for catalyst deactivation [68]. These promoters generally stimulate the triggering of CO_2 and its subsequent reactions with carbonaceous build-ups in proximity. Alkaline earth metal oxide can avoid sintering, which is the major reason of deactivation of catalyst [69]. The similar trend can be seen in the research due to Mehdi et al., 2015 [70], which emphasizes strong metal-support interaction, leading to a narrower particle size distribution and more uniform dispersion without agglomeration are found in case of MgO nano-catalyst. Also, higher surface area was observed with promoter using 25 wt% MgO, unlike other samples. Moreover, Ni dispersion over catalyst surfaces increases in the presence of Tin [71], which may act to reduce sintering, and therefore, enhancing long-term catalytic performance.

The addition of Mg or Ca proved beneficial in enhancing performance for Ni-based catalyst in a study conducted by [14]. They studied with 5 wt% Ca & Mg promoted Ni-alumina catalysts and concluded that promoted catalysts were highly active and extremely stable. It was also found in the study that the morphology of the catalyst and the dispersion of active phase were not disturbed by the addition of the promoters. In another study, the addition of vanadium as a promoter can lower carbon deposition and a sharp increase in BET surface area is found by adding 0.8 wt.% V. It was also concluded from this study that vanadium has changed the microstructure by resisting aluminate spinel phase formation on the Ni/Al_2O_3 catalyst [72].

Rare earth metals such as La_2O and CeO_2 have grabbed significant attention because of their advantageous attributes. Park and co-workers [73] studied La promoted Ni/Mg Al_2O_4 catalyst for BRM. They found that La-promoted catalysts showed better Ni dispersion due to the presence of smaller crystallite sizes than nonpromoted catalyst. Also, the La promoted catalyst exhibited better, sintering resistance, resistance to agglomeration of Ni particles, metal-support interactions, and surface area. A similar investigation was carried out by Ji et al. [65] on Ce promoted Ni/SBA-15 catalyst for BRM. The results showed better surface area, prolonged stability, better activity and high oxygen storage capacity for Ce promoted catalyst supported on commercial SBA-15 support.

Besides the rare earth metals, non-precious transition metals have also gained considerable interest because of their excellent bulk properties. Recently, Ji et al. [65] determined the effect of boron (B) as promoter on Ni/SBA-15 catalyst in case of bi-reforming of methane. The experimental study deduced to the findings that 3wt.% of boron was optimum for Ni/SBA-15 catalyst for BRM in view of the conversion of the feed reactants, hydrogen yield and reduction of graphitic coke formation to almost four times [13].

The modification of metal catalysts by doping with noble metals provided encouraging results involving advances in the coke resistance and steadiness of the catalyst, besides the alkaline earth metals. Even a minute quantity of noble metals can bring a huge improvement in the performance of the catalyst. Khani and co-workers [74] used 3wt.% Ru as promoter for $ZnLaAlO_4$

catalyst contributed the best performance due to the enhanced catalytic activity and reduced coke deposition.

The discovery of a new family of low-dimensional transition metal nitrides and carbides in 2011 [75] provides a completely new scenario for such materials with unforeseen applications [76], opening new possibilities for the use of carbides in catalysis. Inspired by the isolation of graphene [77], these new two-dimensional (2D) materials were termed MXenes [75]. Only few studies have been reported on the catalytic activity of MXenes at relatively high temperatures, such as the ammonia perchlorate decomposition [78], water gas shift reaction [79], ethyl benzene dehydrogenation [80], and propane dehydrogenation [81].

In conclusion, adding promoters boost the main metal dispersion by synergistic interactions and also drops the needed temperature to obtain the optimized performance. However, selecting a suitable co-metal may be difficult and their actual reaction mechanism pathway is still needing to be determined.

4.0 Kinetics and Mechanistic of BRM

The main area of concern for both academia and industrial domain, to develop a suitable reaction rate model i.e. principally resulting from the fundamental reaction path is the kinetic studies of the reactions. The derived kinetic model should have extensive capability of fitting of experimental data in it and must apprehend the rate of reactants consumed and the respective products formed. The study of reaction mechanisms and kinetics of bi-reforming of methane is essential and advantageous for optimization of bi-reforming process, catalyst and reactor design from the respective deduced kinetic models. However, there are only a few studies being devoted into the kinetic study of methane bi-reforming process as compared to dry reforming, steam reforming and partial oxidation of methane. Therefore, the kinetic studies of methane bi-reforming process could be of great significance for the development of the optimum BRM kinetic and mechanistic model.

Qin and co-workers [82] proposed a reaction pathway for BRM over magnesia supported catalysts. They studied an in situ labelled CO_2 transient experiment which showed that carbon was formed by decomposition of CO_2 or CO was comparatively less reactive than CHx species being adsorbed, which was generated by decomposition of methane. They also uncovered that SRM and DRM reaction can undergo in parallel reaction mechanism. Both steam and CO_2 dissociation reaction also shared the same intermediate. Since, both SRM and BRM undergo the same reaction mechanisms, their kinetics are perhaps similar. The atomic oxygen (O_{ad}) i.e. adsorbed oxygen reacts with respective carbon species to form the activated methane. Hence, the transitional specie is spent to form CO and cutbacks the amount of CO_2 and steam. The entire BRM process can be elucidated as follows (M is the active metal site of the catalyst, which is the same for various adsorbing species in the formulas) [26],

Activation of CH_4:

$CH_4 + 2M \rightarrow CH_3\text{–}M + H\text{-}M$
$CH_3\text{-}M + 2M \rightarrow CH\text{-}M + 2\ H\text{-}M$
$CH\text{-}M + M \rightarrow C\text{-}M + H\text{-}M$
Decomposition of H_2O and CO_2:

$H_2O + 3M \rightarrow O\text{-}M + 2\ H\text{-}M$
$CO_2 + 2M \rightarrow O\text{-}M + CO\text{-}M$
Reaction of adsorbed species:

$CHx\text{-}M + O\text{-}M + (x-1)M \rightarrow CO\text{-}M + xH\text{-}M$

Production of CO and H_2:

$CO\text{-}M \rightarrow CO + M$
$2H\text{-}M \rightarrow H_2 + 2M$

The main reaction is that of the adsorbed species, which is the rate determining step, and is suggested as Langmuir–Hinshelwood mechanism [82].

To the best of our knowledge, there are no reported kinetic BRM models derived from inherently mechanistic steps. Most attempts for expressing reactant consumption and product formation rates were based on the established kinetic models of SRM and DRM reaction models. Challiwala *et al.* [83] conducted the BRM kinetics by combininh together the kinetics for SRM and DRM proposed by Froment [84] and Verykios [53] respectively . They joined the Langmuir-Hinshelwood reaction mechanism with Hougen-Watson reaction mechanism to label it as LHHW reaction mechanism in which they studied the kinetic modelling for steam reforming of methane along with water-gas shift reaction on a Ni-based catalyst ($Ni/MgAl_2O_4$) [53] to form a single kinetic model so as to analyze its behaviour in predicting the distribution of the product gases during combined DRM/SRM process for the kinetic analysis. Eqs. 11 – 14 show the LHHW model relations representing reactions involved in DRM and SRM,

$$R_{CH4} = \frac{k_1\, k_2 k_3 k_4 P_{CH4} P_{CO2}}{k_1\, k_2 k_3 k_4 P_{CH4} P_{CO2} + k_1\, k_2 P_{CH4} + k_3 k_4 P_{CO2}}^2 \qquad \text{DRM model} \qquad (11)$$

$$r_{I,SRM} = \frac{k_5 (P_{CH4} + P_{H2O} - \frac{P_{H2^3}\ P_{CO}}{k4})}{P_{H2}^{2.5}\left(1 + K_{CO}\, P_{CO} + K_{H2}\, P_{H2} + K_{CH4}\, P + \frac{K_{H2O}\, P_{H2O}}{P_{H2}}\right)^2} \qquad \text{SRM model} \qquad (12)$$

$$r_{II,SRM} = \frac{k_6 (P_{CO} + P_{H2O} - \frac{P_{H2}\, P_{CO2}}{k5})}{P_{H2}\left(1 + K_{CO}\, P_{CO} + K_{H2}\, P_{H2} + K_{CH4}\, P_{CH4} + \frac{K_{H2O}\, P_{H2O}}{P_{H2}}\right)^2} \qquad \text{SRM model} \qquad (13)$$

$$r_{III,SRM} = \frac{k_7 (P_{CH4} + P_{H2O} - \frac{P_{H2^4}\ P_{CO2}}{k6})}{P_{H2}^{3.5}\left(1 + K_{CO}\, P_{CO} + K_{H2}\, P_{H2} + K_{CH4}\, P_{CH4} + \frac{K_{H2O}\, P_{H2O}}{P_{H2}}\right)^2} \qquad \text{SRM model} \qquad (14)$$

The thermo-kinetic study performed by Challiwala *et al.*, 2017 [ref?] that concluded the effect of various reaction parameters on the behaviour of reforming reactions. To almost nullify the coke formation and abate the energy requirements the optimized conditions i.e. 1 bar pressure, a temperature of 750°C and a feed ratio as CH_4: H_2O: O_2: CO_2 of 1:0.4:0.3:1 was found to be justified at % conversion of CO_2 as 47.84% , with energy requirement as 180.26 kJ. This comparison provided the evaluation of the applicability of the different kinetic models and hence to recognize the most appropriate one as the reformer reactor model [83].

Park et al., (2015) used a power law model (Eq. 15) to capture CH_4 consumption rate and estimate the corresponding reactant reaction order for BRM over unpromoted and Co or La promoted Ni/Al_2O_3 catalysts. BRM runs with various feedstock composition (CH4/CO2/H2O/Ar) under temperature ranging from 600°C to 850°C were conducted support the power law model, where r_{CH4} and k_{CH4} are CH_4 reaction rate and CH_4 rate constants respectively [85], expressed as,

$$r_{CH_4} = k_{CH_4} \left(P_{CH_4}\right)^{\alpha} (CO_2)^{\beta} (H_2O)^{\gamma} \tag{15}$$

The partial pressure of CH_4, CO_2 and H_2O are denoted as P_{CH4}, P_{CO2} and P_{H2O} respectively while α, β and γ are the corresponding reaction orders for CH_4, CO_2 and H_2O reactants. (Omata *et al.*, 2012) [86] investigated the effects of preparation conditions such as calcination temperature during catalyst synthesis, the Ni content and loading of K for a K–Ni/α-Al_2O_3 catalyst by the L_9 orthogonal array. The impregnation method was used to synthesize the catalyst. For carrying out the activity tests, various parameters such as gas contact time are varied by changing the gas feed velocities and conversion was achieved when O_2 conversion was below 30%. The selectivity of syngas and the conversion were employed for curve fitting by natural algorithm. The kinetic parameters of the high-pressure reforming of methane were then determined by using the algorithm. Hence, every kinetic rate constant seems to be expected as function of method of catalyst preparation. The conclusion drawn from the study was that, the reason for low selectivity of syngas was the continual oxidation of syngas. Also, the hydrogen oxidation was affected by NiO content and didn’t had any accelerating effect on the oxidation of CO.

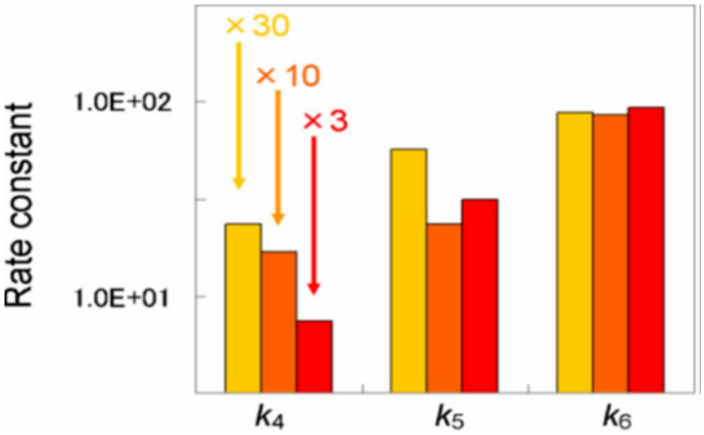

Figure 3: Logarithmic graph of rate constants (k4, k5, k6) of catalytic partial oxidation of CH4 over 14Ni–3K/1200 diluted 3–30 times with α-Al_2O_3 [86]

The evaluation of the reaction system indicates that the rate constant of total oxidation of H_2 and CO is only marginally affected by the diluent (as shown in figure 3), and the reduction of the rate constant of total oxidation of CH_4 is the main factor of the syngas selectivity improvement. Therefore, total oxidation of methane and hot-spot formation, can be hindered by high selectivity of syngas, provided the correct inert material is used in place of α-Al_2O_3.

5.0 Catalyst Deactivation

The use of the catalyst in BRM reaction is vital to enhance the formation of syngas. However, catalyst deactivation is a major drawback for Ni-based catalysts that affects the catalytic performance during the BRM reaction. This is also the case in the heterogeneous catalysis that impairs the reactivity of the reaction. The time scale of the catalyst deactivation can vary depending on the type of catalyst, type of process and operation conditions such as pressure, temperature and reactants [87].

Table 4 shows a summary of the major mechanisms of catalyst deactivation [88]. Two major causes of catalyst deactivation in BRM reaction are the carbon deposition (fouling) at lower temperatures (773.15 - 973.15 K) and sintering (thermal degradation) at higher temperatures (973.15 - 1073.15 K).

Table 4: Mechanisms of catalyst deactivation [88]

Mechanism	Type	Description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites resulting in blocked sites
Fouling	Mechanical	Physical deposition of species from fluid phase onto catalytic surface and pores
Thermal degradation	Thermal	`Thermally induced loss of catalytic surface area, support area, and active phase-support reactions
Vapor formation	Chemical	The reaction of gas with the catalyst phase to produce a volatile compound
Vapour-solid and solid-solid reactions	Chemical	The reaction of fluid, support or promoter with catalytic phase to produce inactive phases
Attrition/Crushing	Mechanical	Loss of internal surface area from the mechanical induced crushing of catalyst.

5.1 Carbon Deposition

Carbon deposition or coking is the major drawback in BRM reaction. Side reactions may lead to the formation of carbonaceous material especially in a catalytic reaction that involves hydrocarbons. Coking deactivates the catalysts by blocking the pores or active sites of the catalyst. Coke deposition is a main problem for the BRM reactions and takes place during the methane cracking and/or the Boudouard reaction which leads to the termination of adsorption sites for the reactants [89].

Based on the thermodynamic analysis, it is recommended that operation at high CO_2/CH_4 ratios and high temperatures may prevent carbon formation [90]. However, it is preferable for the chemical industry to operate close to stoichiometric ratios and at low temperatures. Hence, it is significant to understand the mechanisms of carbon formation and develop more carbon-resistant catalysts. The main source of carbon deposition for the CH_4 reforming reactions are from CO disproportionation reaction and CH_4 deposition [91].

The formation of carbon leading to metal dislodgement and consequently deactivation has been suggested to proceed by the following steps [92–94],

i. Formation of carbon at the surface of Ni embedded in the support
ii. Diffusion of carbon through the Ni particle
iii. Segregation at the rear of Ni particle
iv. The eventual lifting of Ni particle from the support by a growing carbon filament

Strong metal-support interactions (SMSI) can prove useful method to prevent the coke formation to enhance the catalyst functioning. It may prevent dislodgement of metal particles during the growth process of carbon filaments [94,95]. On the other hand, increasing the catalyst basicity will also suppress the carbon deposition because of the increased ability of the catalyst to chemisorb CO_2 [96]. Another way of controlling carbon deposition is to control the metal particle size as the ensemble size required for carbon formation is larger than that of reforming reactions.

5.2 Sintering

Sintering or thermal degradation refers to the reduction of catalytic as well as support surface area, and also loss of active phase-support reactions due to structural modifications. Excessive temperatures will cause the sintering of catalyst which may occur at all stages of the catalyst's life cycle. Studies reported that sintering of active sites was affected by several factors such as the well-defined catalyst structure, porosity, and nature of the support and metal-support interaction [97,98]. Sintering may take place in supported metal catalyst through loss of active surface area because of crystallite growth. For the crystallite's migration, the whole crystallite will migrate over the surface of the support before colliding. Whereas, in case of the atomic migration, atoms being involved in migration over the support's surface, are captured by larger crystallites [88].

Based on the study by Bartholomew and Sorenson [99], the loss of surface area for Ni/SiO_2 exposed to H_2 for 50 hours at 1,023 K was 70%, while surface area loss at 923 K for the same duration was 25%. Hence, the selection of suitable reaction temperature is important to prevent the sintering of catalyst. In addition, the sintering of catalyst can be prevented by the presence of strong metal-support interactions and use of promoters in the catalyst may increase the resistance towards sintering [30].

Conclusion:

BRM is a propitious green technology to address the rising energy demand of the future and mitigation of GHGs for syngas production in future, since it utilizes two GHGs as feed reactants (i.e. CO_2 and CH_4). Though, there are still certain hurdles which limit its commercialization. Thermodynamic studies reveal that BRM reaction is favorable at high temperatures, this affects the economy of the process due to the deposition of the carbon over catalyst surface. Ni- based catalysts have been extensively studied over last decade due to its superior activity and better economy when compared to noble metal catalysts. However, the coke formation and sintering at high temperatures remains a hurdle in the commercialization of the BRM process. Various parameters have been studied using the Ni- based catalysts such as metal-support interaction since every metal solution has a unique lattice arrangement, which makes it amongst key factor to decide the stability of catalyst against sintering. Effect of promoters along with the few of the bimetallic catalysts have also been investigated to limit the coke formation, enhance the oxygen storage capacity and basicity of the catalyst. However, there is still a need for more refined work on the bimetallic catalysts in future, since bimetallic catalysts showed superior results and seems to be a promising alternative to monometallic catalysts. Adding promoters boost the main metal dispersion by synergistic interactions and drops the needed temperature to obtain the optimized performance. The various operating conditions such as the composition of feedstock gases, the reaction temperature, and gas hourly space velocity (GHSV) have a vital role on the catalytic performance of methane bi-reforming process. Hence it is a necessary to develop a correct correlation which could give a better association between the process parameters and performance of catalyst, for BRM. Since, there is only a limited amount of work that has been performed on reaction mechanism of BRM, therefore, latest techniques such as DFT simulations, also for characterization cutting-edge techniques including TPD, in situ adsorption spectroscopy, and chemisorption should be employed to understand the fundamental insight of catalyst surface interaction and to develop the kinetics model for BRM process.

Outlook

Over last few decades, several studies have been carried out for BRM reaction, using Ni-based catalysts, for better understanding of its reaction mechanism and find the key factors responsible for coke formation and methods to improve its resistance for coke formation. Numerous methods have been implemented to lessen the tendency of coke formation involving Ni based catalysts, which include application of appropriate method for catalyst synthesis, selection of suitable metal for support for enhanced SMSI, maintaining proper basicity of the catalyst support, doping with apposite promoter for boosted oxygen storage capacity and choosing a proper bimetallic catalyst for better mutual synergistic interactions.

The future research work should be focused on designing of ideal Ni based complex catalysts (bimetallic and trimetallic); since Ni have exhibited significant stability and high activity. However, coke formation is still its constraint. Since BRM is highly endothermic reaction and require high activation energy to cross the energy barrier; a suitable bimetallic and trimetallic catalyst that can work on lower ranges of temperatures and provide considerable CO_2 and CH_4 conversion, needs to be studied. Fundamental studies focused on enriched metal dispersion and metal catalyst particle size, which is also a crucial component, needs to be studied further in the future research for better endurance of catalyst. However, further work needs to be done for synthesis of 2-D materials such as MXenes, boron nitride sheets and graphene oxide nano-catalysts which may be economic and possess superior catalytic performance in BRM reaction. Moreover, the method of catalyst preparation contributes a vital influence in the catalyst performance. The suitable catalyst synthesis method can provide enhanced Ni dispersion on catalytic support, improved SMSI, prolonged stability, superior activity and endurance against coke formation. Regarding kinetics and mechanistic of reaction the imminent research should focus on DFT modeling of complex catalysts beforehand and proceeded with the synthesis and experimental segment, to save material and time spent in hit and trial approach. Hence the future research work should also focus on these parameters to contribute effectively for development of an efficient catalyst system.

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References:

[1] Mozammel T. Catalyst development and process intensification towards syngas production through methane reforming 2017.

[2] Abdullah B, Abd Ghani NA, Vo DVN. Recent advances in dry reforming of methane over Ni-based catalysts. J Clean Prod 2017;162:170–85. https://doi.org/10.1016/j.jclepro.2017.05.176.

[3] Olajire AA. A review of mineral carbonation technology in sequestration of CO2. J Pet Sci Eng 2013. https://doi.org/10.1016/j.petrol.2013.03.013.

[4] Maxwell D, Zhu Z. Natural gas prices, LNG transport costs, and the dynamics of LNG imports. Energy Econ 2011. https://doi.org/10.1016/j.eneco.2010.06.012.

[5] Penkova A, Bobadilla L, Ivanova S, Domínguez MI, Romero-Sarria F, Roger AC, et al. Hydrogen production by methanol steam reforming on NiSn/MgO-Al2O3catalysts: The role of MgO addition. Appl Catal A Gen 2011;392:184–91. https://doi.org/10.1016/j.apcata.2010.11.016.

[6] De Freitas Silva T, Dias JAC, MacIel CG, Assaf JM. Ni/Al2O3 catalysts: Effects of the promoters Ce, la and Zr on the methane steam and oxidative reforming reactions. Catal Sci Technol 2013;3:635–43. https://doi.org/10.1039/c2cy20573d.

[7] Al-Swai BM, Osman NB, Abdullah B. Catalytic performance of Ni/MgO catalyst in methane dry reforming. AIP Conf Proc 2017;1891. https://doi.org/10.1063/1.5005361.

[8] Santos J., Reina TR, Odriozola JA, Centeno MA, Smith TJ, le Saché E, et al. Multicomponent Ni-CeO 2 nanocatalysts for syngas production from CO 2 /CH 4 mixtures. J CO2 Util 2018;25:68–78. https://doi.org/10.1016/j.jcou.2018.03.012.

[9] Ghoneim SA, El-Salamony RA, El-Temtamy SA. Review on Innovative Catalytic Reforming of Natural Gas to Syngas. World J Eng Technol 2016;4:116–39. https://doi.org/10.4236/wjet.2016.41011.

[10] Nieva MA, Villaverde MM, Monzón A, Garetto TF, Marchi AJ. Steam-methane reforming at low temperature on nickel-based catalysts. Chem Eng J 2014;235:158–66. https://doi.org/10.1016/j.cej.2013.09.030.

[11] Usman M, Wan Daud WMA, Abbas HF. Dry reforming of methane: Influence of process parameters - A review. Renew Sustain Energy Rev 2015;45:710–44. https://doi.org/10.1016/j.rser.2015.02.026.

[12] Olah GA, Goeppert A, Czaun M, Mathew T, May RB, Prakash GKS. Single Step Bi-reforming and Oxidative Bi-reforming of Methane (Natural Gas) with Steam and Carbon Dioxide to Metgas (CO-2H<inf>2</inf>) for Methanol Synthesis: Self-Sufficient Effective and Exclusive Oxygenation of Methane to Methanol with Oxygen. J Am Chem Soc 2015;137:8720–9. https://doi.org/10.1021/jacs.5b02029.

[13] Siang TJ, Pham TLM, Cuong N Van, Phuong PTT, Phuc NHH, Truong QD, et al. Combined steam and CO2reforming of methane for syngas production over carbon-resistant boron-promoted Ni/SBA-15 catalysts. Microporous Mesoporous Mater 2018;262:122–32. https://doi.org/10.1016/j.micromeso.2017.11.028.

[14] Davidson A, Casale S, Jabbour K, El Hassan N, Massiani P. Ordered mesoporous "one-pot" synthesized Ni-Mg(Ca)-Al 2 O 3 as effective and remarkably stable catalysts for combined steam and dry reforming of methane (CSDRM). Appl Catal B Environ 2016;201:527–42. https://doi.org/10.1016/j.apcatb.2016.08.009.

[15] Asencios YJO, Assaf EM. Combination of dry reforming and partial oxidation of methane on NiO-MgO-ZrO2 catalyst: Effect of nickel content. Fuel Process Technol 2013. https://doi.org/10.1016/j.fuproc.2012.08.004.

[16] Olah GA, Goeppert A, Czaun M, Prakash GKS. Bi-reforming of methane from any source with steam and carbon dioxide exclusively to metgas (CO-2H2) for methanol and hydrocarbon synthesis. J Am Chem Soc 2013;135:648–50. https://doi.org/10.1021/ja311796n.

[17] Roh HS, Koo KY, Yoon WL. Combined reforming of methane over co-precipitated Ni-CeO2, Ni-ZrO2and Ni-Ce0.8Zr0.2O2catalysts to produce synthesis gas for gas to liquid (GTL) process. Catal Today 2009;146:71–5. https://doi.org/10.1016/j.cattod.2009.01.001.

[18] Gangadharan P, Kanchi KC, Lou HH. Evaluation of the economic and environmental impact of combining dry reforming with steam reforming of methane. Chem Eng Res Des 2012;90:1956–68. https://doi.org/10.1016/j.cherd.2012.04.008.

[19] Özkara-Aydnolu Ş. Thermodynamic equilibrium analysis of combined carbon dioxide reforming with steam reforming of methane to synthesis gas. Int J Hydrogen Energy 2010;35:12821–8. https://doi.org/10.1016/j.ijhydene.2010.08.134.

[20] He S, Wu H, Yu W, Mo L, Lou H, Zheng X. Combination of CO2 reforming and partial oxidation of methane to produce syngas over Ni/SiO2 and Ni-Al2O3/SiO2 catalysts with different precursors. Int J Hydrogen Energy 2009;34:839–43. https://doi.org/10.1016/j.ijhydene.2008.10.072.

[21] Safariamin M, Tidahy LH, Abi-Aad E, Siffert S, Aboukaïs A. Dry reforming of methane in the presence of ruthenium-based catalysts. Comptes Rendus Chim 2009;12:748–53. https://doi.org/10.1016/j.crci.2008.10.021.

[22] Guo J, Lou H, Zhao H, Chai D, Zheng X. Dry reforming of methane over nickel catalysts supported on magnesium aluminate spinels. Appl Catal A Gen 2004;273:75–82. https://doi.org/10.1016/j.apcata.2004.06.014.

[23] Montoya J. Methane reforming with CO2 over Ni/ZrO2–CeO2 catalysts prepared by sol–gel. Catal Today 2000;63:71–85. https://doi.org/10.1016/S0920-5861(00)00447-8.

[24] Hally W, Bitter JH, Seshan K, Lercher JA, Ross JRH. Problem of coke formation on Ni/ZrO2 catalysts during the carbon dioxide reforming of methane. Stud Surf Sci Catal 1994;88:167–73.

[25] Elsayed NH, Maiti D, Joseph B, Kuhn JN. Precious Metal Doped Ni – Mg / Ceria – Zirconia Catalysts for Methane Conversion to Syngas by Low Temperature Bi-reforming. Catal Letters 2018;148:1003–13. https://doi.org/10.1007/s10562-018-2310-y.

[26] Kumar N, Shojaee M, Spivey JJ. Catalytic bi-reforming of methane: From greenhouse gases to syngas. Curr Opin Chem Eng 2015;9:8–15. https://doi.org/10.1016/j.coche.2015.07.003.

[27] Bale CW, Bélisle E, Chartrand P, Decterov SA, Eriksson G, Hack K, et al. FactSage thermochemical software and databases - recent developments. Calphad Comput Coupling Phase Diagrams Thermochem 2009. https://doi.org/10.1016/j.calphad.2008.09.009.

[28] Jang WJ, Jeong DW, Shim JO, Kim HM, Roh HS, Son IH, et al. Combined steam and carbon dioxide reforming of methane and side reactions: Thermodynamic equilibrium analysis and experimental application. Appl Energy 2016;173:80–91.

https://doi.org/10.1016/j.apenergy.2016.04.006.

[29] Nikoo MK, Amin NAS. Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation. Fuel Process Technol 2011. https://doi.org/10.1016/j.fuproc.2010.11.027.

[30] Soria MA, Mateos-Pedrero C, Guerrero-Ruiz A, Rodríguez-Ramos I. Thermodynamic and experimental study of combined dry and steam reforming of methane on Ru/ ZrO2-La2O3catalyst at low temperature. Int J Hydrogen Energy 2011;36:15212–20. https://doi.org/10.1016/j.ijhydene.2011.08.117.

[31] Kumar N, Wang Z, Kanitkar S, Spivey JJ. Methane reforming over Ni-based pyrochlore catalyst: deactivation studies for different reactions. Appl Petrochemical Res 2016;6:201–7. https://doi.org/10.1007/s13203-016-0166-x.

[32] Roh HS, Koo KY, Jeong JH, Seo YT, Seo DJ, Seo YS, et al. Combined reforming of methane over supported Ni catalysts. Catal Letters 2007;117:85–90. https://doi.org/10.1007/s10562-007-9113-x.

[33] Choudhary VR, Rajput AM. Simultaneous carbon dioxide and steam reforming of methane to syngas over NiO-CaO catalyst. Ind Eng Chem Res 1996;35:3934–9. https://doi.org/10.1021/ie960002l.

[34] Khani Y, Shariatinia Z, Bahadoran F. High catalytic activity and stability of ZnLaAlO4supported Ni, Pt and Ru nanocatalysts applied in the dry, steam and combined dry-steam reforming of methane. Chem Eng J 2016;299:353–66. https://doi.org/10.1016/j.cej.2016.04.108.

[35] Son IH, Lee SJ, Soon A, Roh HS, Lee H. Steam treatment on Ni/γ-Al2O3for enhanced carbon resistance in combined steam and carbon dioxide reforming of methane. Appl Catal B Environ 2013;134–135:103–9. https://doi.org/10.1016/j.apcatb.2013.01.001.

[36] Koo KY, Lee SH, Jung UH, Roh HS, Yoon WL. Syngas production via combined steam and carbon dioxide reforming of methane over Ni-Ce/MgAl2O4 catalysts with enhanced coke resistance. Fuel Process Technol 2014;119:151–7. https://doi.org/10.1016/j.fuproc.2013.11.005.

[37] Álvarez M A, Centeno MÁ, Odriozola JA. Ru-Ni Catalyst in the Combined Dry-Steam

Reforming of Methane: The Importance in the Metal Order Addition. Top Catal 2016;59:303–13. https://doi.org/10.1007/s11244-015-0426-5.

[38] Li W, Zhao Z, Ding F, Guo X, Wang G. Syngas Production via Steam–CO $_2$ Dual Reforming of Methane over LA-Ni/ZrO $_2$ Catalyst Prepared by <scp>l</scp> -Arginine Ligand-Assisted Strategy: Enhanced Activity and Stability. ACS Sustain Chem Eng 2015;3:3461–76. https://doi.org/10.1021/acssuschemeng.5b01277.

[39] Zhao Z, Ren P, Li W, Miao B. Effect of mineralizers for preparing ZrO2support on the supported Ni catalyst for steam-CO2bi-reforming of methane. Int J Hydrogen Energy 2017;42:6598–609. https://doi.org/10.1016/j.ijhydene.2016.11.144.

[40] Danilova MM, Fedorova ZA, Kuzmin VA, Zaikovskii VI, Porsin A V., Krieger TA. Combined steam and carbon dioxide reforming of methane over porous nickel based catalysts. Catal Sci Technol 2015;5:2761–8. https://doi.org/10.1039/C4CY01614A.

[41] Koo KY, Roh HS, Jung UH, Yoon WL. Combined H2O and CO2reforming of CH4over Ce-promoted Ni/Al2O3catalyst for gas to liquid (GTL) process: Enhancement of Ni-CeO2interaction. Catal Today 2012;185:126–30. https://doi.org/10.1016/j.cattod.2011.07.027.

[42] Stroud T, Smith TJ, Le Saché E, Santos JL, Centeno MA, Arellano-Garcia H, et al. Chemical CO2recycling via dry and bi reforming of methane using Ni-Sn/Al2O3and Ni-Sn/CeO2-Al2O3catalysts. Appl Catal B Environ 2018;224:125–35. https://doi.org/10.1016/j.apcatb.2017.10.047.

[43] Zhang QH, Li Y, Xu BQ. Reforming of methane and coalbed methane over nanocomposite Ni/ZrO2catalyst. Catal Today 2004;98:601–5. https://doi.org/10.1016/j.cattod.2004.09.015.

[44] Itkulova SS, Zakumbaeva GD, Nurmakanov YY, Mukazhanova AA, Yermaganbetova AK. Syngas production by bireforming of methane over Co-based alumina-supported catalysts. Catal Today 2014;228:194–8. https://doi.org/10.1016/j.cattod.2014.01.013.

[45] Itkulova SS, Nurmakanov YY, Kussanova SK, Boleubayev YA. Production of a hydrogen-enriched syngas by combined CO2-steam reforming of methane over Co-based catalysts supported on alumina modified with zirconia. Catal Today 2018;299:272–9.

https://doi.org/10.1016/j.cattod.2017.07.014.

[46] Laosiripojana N, Assabumrungrat S. Catalytic dry reforming of methane over high surface area ceria. Appl Catal B Environ 2005;60:107–16. https://doi.org/10.1016/j.apcatb.2005.03.001.

[47] Ferreira-Aparicio P, Rodríguez-Ramos I, Anderson J., Guerrero-Ruiz A. Mechanistic aspects of the dry reforming of methane over ruthenium catalysts. Appl Catal A Gen 2000. https://doi.org/10.1016/S0926-860X(00)00525-1.

[48] Hu YH, Ruckenstein E. Catalytic Conversion of Methane to Synthesis Gas by Partial Oxidation and CO2 Reforming. Adv Catal 2004;48:297–345. https://doi.org/10.1016/S0360-0564(04)48004-3.

[49] XU J, ZHOU W, WANG J, LI Z, MA J. Characterization and Analysis of Carbon Deposited during the Dry Reforming of Methane over Ni/La2O3/Al2O3 Catalysts. Chinese J Catal 2009. https://doi.org/10.1016/S1872-2067(08)60139-4.

[50] Roh HS, Jun KW. Carbon dioxide reforming of methane over Ni catalysts supported on Al 2O3 modified with La2O3, MgO, and CaO. Catal Surv from Asia 2008. https://doi.org/10.1007/s10563-008-9058-0.

[51] Li W, Zhao Z, Ren P, Wang G. Effect of molybdenum carbide concentration on the Ni/ZrO2 catalysts for steam-CO2 bi-reforming of methane. RSC Adv 2015;5:100865–72. https://doi.org/10.1039/c5ra22237k.

[52] Gao J, Hou Z, Guo J, Zhu Y, Zheng X. Catalytic conversion of methane and CO2 to synthesis gas over a La2O3-modified SiO2 supported Ni catalyst in fluidized-bed reactor. Catal Today 2008. https://doi.org/10.1016/j.cattod.2007.10.019.

[53] Verykios XE. Catalytic dry reforming of natural gas for the production of chemicals and hydrogen. Int J Hydrogen Energy 2003;28:1045–63. https://doi.org/10.1016/S0360-3199(02)00215-X.

[54] Martínez R, Romero E, Guimon C, Bilbao R. CO2reforming of methane over coprecipitated Ni-Al catalysts modified with lanthanum. Appl Catal A Gen 2004. https://doi.org/10.1016/j.apcata.2004.06.017.

[55] Koo KY, Roh HS, Jung UH, Seo DJ, Seo YS, Yoon WL. Combined H2O and CO2 reforming of CH4 over nano-sized Ni/MgO-Al2O3 catalysts for synthesis gas production for gas to liquid (GTL): Effect of Mg/Al mixed ratio on coke formation. Catal Today 2009. https://doi.org/10.1016/j.cattod.2009.02.002.

[56] Lamont DC, Thomson WJ. Dry reforming kinetics over a bulk molybdenum carbide catalyst. Chem Eng Sci 2005. https://doi.org/10.1016/j.ces.2005.01.021.

[57] Brush A, Evans EJ, Mullen GM, Jarvis K, Mullins CB. Tunable Syn-gas ratio via bireforming over coke-resistant Ni/Mo2C catalyst. Fuel Process Technol 2016;153:111–20. https://doi.org/10.1016/j.fuproc.2016.07.012.

[58] Hally W, Bitter JH, Seshan K, Lercher JA, Ross JRH. Problem of coke formation on Ni/ZrO2catalysts during the carbon dioxide reforming of methane. Stud Surf Sci Catal 1994;88:167–73. https://doi.org/10.1016/S0167-2991(08)62737-8.

[59] Wei J-M, Xu B-Q, Li J-L, Cheng Z-X, Zhu Q-M. Highly active and stable Ni/ZrO2 catalyst for syngas production by CO2 reforming of methane. Appl Catal A Gen 2000;196:L167–72. https://doi.org/10.1016/S0926-860X(99)00504-9.

[60] Rezaei M, Alavi SM, Sahebdelfar S, Bai P, Liu X, Yan ZF. CO2 reforming of CH4 over nanocrystalline zirconia-supported nickel catalysts. Appl Catal B Environ 2008. https://doi.org/10.1016/j.apcatb.2007.08.004.

[61] Huang B, Li X, Ji S, Lang B, Habimana F, Li C. Effect of MgO promoter on Ni-based SBA-15 catalysts for combined steam and carbon dioxide reforming of methane. J Nat Gas Chem 2008. https://doi.org/10.1016/S1003-9953(08)60055-9.

[62] Bae JW, Kim AR, Baek SC, Jun KW. The role of CeO2-ZrO2 distribution on the Ni/MgAl2O4 catalyst during the combined steam and CO 2 reforming of methane. React Kinet Mech Catal 2011;104:377–88. https://doi.org/10.1007/s11144-011-0371-7.

[63] Koo KY, Lee JH, Jung UH, Kim SH, Yoon WL. Combined H2O and CO2 reforming of coke oven gas over Ca-promoted Ni/MgAl2O4 catalyst for direct reduced iron production. Fuel 2015. https://doi.org/10.1016/j.fuel.2015.03.007.

[64] Jabbour K, El Hassan N, Davidson A, Casale S, Massiani P. Factors affecting the long-term stability of mesoporous nickel-based catalysts in combined steam and dry reforming of

methane. Catal Sci Technol 2016;6:4616–31. https://doi.org/10.1039/c6cy00032k.

[65] Siang TJ, Danh HTHT, Singh S, Truong QD, Setiabudi HD, Vo D-VNDND-VN, et al. Syngas production from combined steam and carbon dioxide reforming of methane over Ce-modified silicasupported nickel catalysts. Chem Eng Trans 2017;56:1129–34. https://doi.org/10.3303/CET1756189.

[66] Park JE, Koo KY, Jung UH, Lee JH, Roh HS, Yoon WL. Syngas production by combined steam and CO2 reforming of coke oven gas over highly sinter-stable La-promoted Ni/MgAl2O4 catalyst. Int J Hydrogen Energy 2015. https://doi.org/10.1016/j.ijhydene.2015.08.026.

[67] Li P, Park YH, Moon DJ, Park NC, Kim YC. Carbon deposition onto Ni-Based catalysts for combined steam/CO2reforming of methane. J Nanosci Nanotechnol 2016. https://doi.org/10.1166/jnn.2016.12006.

[68] Bian Z, Das S, Wai MH, Hongmanorom P, Kawi S. A Review on Bimetallic Nickel-Based Catalysts for CO2 Reforming of Methane. ChemPhysChem 2017;18:3117–34. https://doi.org/10.1002/cphc.201700529.

[69] Dias JAC, Assaf JM. Influence of calcium content in Ni/CaO/γ-Al2O3 catalysts for CO2-reforming of methane. Catal. Today, 2003. https://doi.org/10.1016/S0920-5861(03)00194-9.

[70] Sajjadi SM, Haghighi M, Rahmani F. Sol-gel synthesis of Ni-Co/Al2O3-MgO-ZrO2 nanocatalyst used in hydrogen production via reforming of CH4/CO2 greenhouse gases. J Nat Gas Sci Eng 2015. https://doi.org/10.1016/j.jngse.2014.11.014.

[71] Hou Z, Yokota O, Tanaka T, Yashima T. Surface properties of a coke-free Sn doped nickel catalyst for the CO2reforming of methane. Appl Surf Sci 2004. https://doi.org/10.1016/j.apsusc.2004.03.223.

[72] Valentini A, Carreño NLV, Probst LFD, Lisboa-Filho PN, Schreiner WH, Leite ER, et al. Role of vanadium in Ni:Al2O3 catalysts for carbon dioxide reforming of methane. Appl Catal A Gen 2003. https://doi.org/10.1016/S0926-860X(03)00560-X.

[73] Park JE, Koo KY, Jung UH, Lee JH, Roh HS, Yoon WL. Syngas production by combined steam and CO<inf>2</inf> reforming of coke oven gas over highly sinter-stable La-

promoted Ni/MgAl<inf>2</inf>O<inf>4</inf> catalyst. Int J Hydrogen Energy 2015;40:13909–17. https://doi.org/10.1016/j.ijhydene.2015.08.026.

[74] Shariatinia Z, Khani Y, Bahadoran F. Synthesis of a novel 3 %Ru/CeZr0.5GdO4 nanocatalyst and its application in the dry and steam reforming of methane. Int J Environ Sci Technol 2016. https://doi.org/10.1007/s13762-015-0907-x.

[75] Naguib M, Kurtoglu M, Presser V, Lu J, Niu J, Heon M, et al. Two-dimensional nanocrystals produced by exfoliation of Ti 3AlC 2. Adv Mater 2011. https://doi.org/10.1002/adma.201102306.

[76] Naguib M, Gogotsi Y. Synthesis of two-dimensional materials by selective extraction. Acc Chem Res 2015. https://doi.org/10.1021/ar500346b.

[77] Novoselov KS, Geim AK, Morozov S V., Jiang D, Katsnelson MI, Grigorieva I V., et al. Two-dimensional gas of massless Dirac fermions in graphene. Nature 2005. https://doi.org/10.1038/nature04233.

[78] Gao Y, Wang L, Li Z, Zhou A, Hu Q, Cao X. Preparation of MXene-Cu2O nanocomposite and effect on thermal decomposition of ammonium perchlorate. Solid State Sci 2014. https://doi.org/10.1016/j.solidstatesciences.2014.06.014.

[79] Li Z, Cui Y, Wu Z, Milligan C, Zhou L, Mitchell G, et al. Reactive metal-support interactions at moderate temperature in two-dimensional niobium-carbide-supported platinum catalysts. Nat Catal 2018. https://doi.org/10.1038/s41929-018-0067-8.

[80] Diao J, Hu M, Lian Z, Li Z, Zhang H, Huang F, et al. Ti3C2Tx MXene Catalyzed Ethylbenzene Dehydrogenation: Active Sites and Mechanism Exploration from both Experimental and Theoretical Aspects. ACS Catal 2018. https://doi.org/10.1021/acscatal.8b02002.

[81] Li Z, Yu L, Milligan C, Ma T, Zhou L, Cui Y, et al. Two-dimensional transition metal carbides as supports for tuning the chemistry of catalytic nanoparticles. Nat Commun 2018. https://doi.org/10.1038/s41467-018-07502-5.

[82] Qin D, Lapszewicz J, Jiang X. Comparison of Partial Oxidation and Steam-CO2Mixed Reformingof CH4to Syngas on MgO-Supported Metals. J Catal 1996;159:140–9. https://doi.org/10.1006/jcat.1996.0073.

[83] Challiwala MS, Ghouri MM, Linke P, El-halwagi MM, Elbashir NO. A combined thermo-kinetic analysis of various methane reforming technologies : Comparison with dry reforming. Biochem Pharmacol 2017;17:99–111. https://doi.org/10.1016/j.jcou.2016.11.008.

[84] Froment GF. Methane Steam Reforming , Methanation and Water-Gas Shift : 1 . Intrinsic Kinetics 1989;35:88–96.

[85] Park MH, Choi BK, Park YH, Moon DJ, Park NC, Kim YC. Kinetics for steam and CO2 reforming of methane over Ni/La/Al2O3 catalyst. J Nanosci Nanotechnol 2015;15:5255–8. https://doi.org/10.1166/jnn.2015.10403.

[86] Omata K, Kobayashi S, Horiguchi J, Kobayashi Y, Yamazaki Y. Applied Catalysis A : General Kinetic model of K – Ni / ¿ -Al 2 O 3 catalyst for oxidative reforming of methane determined by genetic algorithm. "Applied Catal A, Gen 2012;425–426:170–7. https://doi.org/10.1016/j.apcata.2012.03.014.

[87] Baktash E, Littlewood P, Schomäcker R, Thomas A, Stair PC. Alumina coated nickel nanoparticles as a highly active catalyst for dry reforming of methane. Appl Catal B Environ 2015. https://doi.org/10.1016/j.apcatb.2015.05.018.

[88] Bartholomew CH. Mechanisms of catalyst deactivation. Appl Catal A Gen 2001;212:17–60. https://doi.org/10.1016/S0926-860X(00)00843-7.

[89] Aramouni NAK, Touma JG, Tarboush BA, Zeaiter J, Ahmad MN. Catalyst design for dry reforming of methane: Analysis review. Renew Sustain Energy Rev 2018;82:2570–85. https://doi.org/10.1016/j.rser.2017.09.076.

[90] Gadalla AM, Bower B. The role of catalyst support on the activity of nickel for reforming methane with CO2. Chem Eng Sci 1988. https://doi.org/10.1016/0009-2509(88)80058-7.

[91] Wang S, Lu GQ, Millar GJ. Carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts: State of the art. Energy and Fuels 1996;10:896–904. https://doi.org/10.1021/ef950227t.

[92] Snoeck JW, Froment GF, Fowles M. Kinetic study of the carbon filament formation by methane cracking on a nickel catalyst. J Catal 1997. https://doi.org/10.1006/jcat.1997.1635.

[93] Snoeck JW, Froment GF, Fowles M. Steam/CO2 reforming of methane. Carbon filament formation by the Boudouard reaction and gasification by CO2, by H2, and by steam: Kinetic study. Ind Eng Chem Res 2002. https://doi.org/10.1021/ie010666h.

[94] Snoeck JW, Froment GF, Fowles M. Filamentous carbon formation and gasification: Thermodynamics, driving force, nucleation, and steady-state growth. J Catal 1997. https://doi.org/10.1006/jcat.1997.1634.

[95] Baker RTK. Catalytic growth of carbon filaments. Carbon N Y 1989. https://doi.org/10.1016/0008-6223(89)90062-6.

[96] Zhang ZL, Verykios XE. Carbon dioxide reforming of methane to synthesis gas over supported Ni catalysts. Catal Today 1994. https://doi.org/10.1016/0920-5861(94)80183-5.

[97] Zhang S, Muratsugu S, Ishiguro N, Tada M. Ceria-doped Ni/SBA-16 catalysts for dry reforming of methane. ACS Catal 2013;3:1855–64. https://doi.org/10.1021/cs400159w.

[98] Eltejaei H, Reza Bozorgzadeh H, Towfighi J, Reza Omidkhah M, Rezaei M, Zanganeh R, et al. Methane dry reforming on Ni/Ce0.75Zr0.25O 2-MgAl2O4 and Ni/Ce0.75Zr 0.25O2-γ-alumina: Effects of support composition and water addition. Int J Hydrogen Energy 2012. https://doi.org/10.1016/j.ijhydene.2011.11.128.

[99] Bartholomew CH, Sorensen WL. Sintering kinetics of silica- and alumina-supported nickel in hydrogen atmosphere. J Catal 1983. https://doi.org/10.1016/0021-9517(83)90152-5.