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Current advances in syngas (CO + H2) production through bi-reforming of methane using various catalysts: A review

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Review Article

Current advances in syngas (CO + H₂) production through bi-reforming of methane using various catalysts: A review

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HIGHLIGHTS

• Addition of dopants to the catalysts increased the stability, coke resistance & catalytic activity.
• Ni–MgO–Al₂O₃ catalyst depicts higher CH₄ conversion than other Ni based catalysts at 700–800 °C.
• Co-precipitation technique depicts higher catalytic activity than wetness impregnation method.
• Conversion of H₂O and CH₄ were greatly affected by the feed ratio of CO₂/H₂O.

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ABSTRACT

Today, bi - reforming of methane is considered as an emerging replacement for the generation of high-grade synthesis gas (H₂:CO = 2.0), and also as an encouraging renewable energy substitute for fossil fuel resources. For achieving high conversion levels of CH₄, H₂O, and CO₂ in this process, appropriate operation variables such as pressure, temperature and molar feed constitution are prerequisites for the high yield of synthesis gas. One of the biggest stumbling blocks for the methane reforming reaction is the sudden deactivation of catalysts, which is attributed to the sintering and coke formation on active sites. Consequently, it is worthwhile to choose promising catalysts that demonstrate excellent stability, high activity and selectivity during the production of syngas. This review describes the characterisation and synthesis of various catalysts used in the bi-reforming process, such as Ni-based catalysts with MgO, MgO–Al₂O₃, ZrO₂, CeO₂, SiO₂ as catalytic supports. In summary, the addition of a Ni/SBA-15 catalyst showed greater catalytic reactivity than nickel celites; however, both samples deactivated strongly on stream. Co-promoted catalysts were more found to more favourable than Ni/MgAl₂O₄ catalyst alone in the bi-reforming reaction due to their inherent capability of removing amorphous coke from the catalyst surface. Also, Lanthanum promoted catalysts exhibited greater nickel dispersion than Ni/MgAl₂O₄ catalyst due to enhanced interaction between the metal and...
support. Furthermore, La₂O₃ addition was found to improve the selectivity, activity, sintering and coking resistance of Ni implanted within SiO₂. Non-noble metal-based carbide catalysts were considered to be active and stable catalysts for bi-reforming reactions. Interestingly, a five-fold increase in the coking resistance of the nickel catalyst with Al₂O₃ support was observed with incorporation of Cr, La₂O₃ and Ba for a continuous reaction time of 140 h. Bi-reforming for 200 h with Ni–γ-Al₂O₃ catalyst promoted 98.3% conversion of CH₄ and CO₂ conversion of around 82.4%. Addition of MgO to the Ni catalyst formed stable MgAl₂O₄ spinel phase at high temperatures and was quite effective in preventing coke formation due to enhancement in the basicity on the surface of catalyst. Additionally, the distribution of perovskite oxides over 20 wt.% silicon carbide-modified with aluminium oxide supports promoted catalytic activity. NdCOO₃ catalysts were found to be promising candidates for longer bi-reforming operations.

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Introduction

Due to increasing evidence of global warming in the present century, scientists at the UN Intergovernmental Panel on Climate Change have reached a consensus for reduction of greenhouse gas emissions, especially carbon dioxide, to the atmosphere [1–8]. This has also prompted steering committees of industrialized countries to assess their energy strategies based on mitigation of greenhouse gas emissions [9–14] (see Table 1).

Extensive literature has covered on the various alternatives for cleaner energy sources [15,16,227–229], smart drilling techniques [17–20], efficient fracturing technologies [21–25,230–232], usage of nanoparticles [26–31,233], their economic aspects and advantages to mitigate CO₂ emissions and reduce environmental pollution [234–241]. Among the list of proposed alternative energy sources, hydrogen appears to be the most promising large-scale fuel due to its efficient storage over time and clean combustion [2,244]. Recent, there has been enormous interest in hydrogen and it’s been increasing rapidly due to its potential applications in fuel cells. They also serve as an excellent replacement to batteries in the field of portable electronics, internal combustion engines as well as power plants. The demand for hydrogen in the
Table 1 – Conversion efficiencies of CH₄ and CO₂ obtained for various catalysts.

| Catalyst Support | Catalytic Composition | CH₄ Conversion (%) | CO₂ Conversion (%) | H₂/CO | Remarks |
|------------------|-----------------------|--------------------|--------------------|-------|---------|
| MgO Ni/MgO–Al₂O₃ | 91                    | 77                 | 2.0                |       |         |
| MgO Ni/MgO–Al₂O₃ | 83                    | 71                 | 2.0                |       |         |
| MgO Ni/MgAl₂O₄   | 62                    | 50                 | 2.0                |       |         |
| Cr, Ba, La Ni/Al₂O₃ | 50                  | 15                 | 2.0                |       |         |
| Cr, Ba, La Ni/Al₂O₃ | 50–75               | 20–60              | 2.0                |       |         |
| MgO–Al₂O₃ Ni/La/MgAl₂O₄ | 83.1         | 57.4               | 2.0                |       |         |
| MgO–Al₂O₃ Ni/La/MgAl₂O₄ | 80.6           | 58.0               | 2.0                |       |         |
| MgO–Al₂O₃ Ni/La/MgAl₂O₄ | 83.9           | 59.0               | 2.0                |       |         |
| MgO–Al₂O₃ Ni/La/MgAl₂O₄ | 98.3           | 82.4               | 2.0                |       |         |
| MgO–Al₂O₃ Ni/MgAl₂O₄ | 83.1           | 57.4               | 2.0                |       |         |
| MgO–Al₂O₃ Ni/MgAl₂O₄ | 80.6           | 58.0               | 2.0                |       |         |
| MgO–Al₂O₃ Ni/MgAl₂O₄ | 77.7           | 54.8               | 2.0                |       |         |
| α-Al₂O₃ Ni/Co/Al₂O₃ | 90.9           | 69.2               | 2.0                |       |         |
| α-Al₂O₃ Ni/Co/Al₂O₃ | 88.6           | 68.9               | 2.0                |       |         |
| α-Al₂O₃ Ce/Co/Al₂O₃ | 86.6           | 57.0               | 2.0                |       |         |
| α-Al₂O₃ Ce/Co/Al₂O₃ | 89              | 73                 | 2.0                |       |         |
| Al₂O₃ Ni/Ce/Al₂O₃ | 78                    | 56                 | 2.4                |       |         |
| Al₂O₃ Ni/Ce/Al₂O₃ | 70                    | 40                 | 2.6                |       |         |
| Al₂O₃ Ni/Ce/Al₂O₃ | 60                    | 53                 | 2.5                |       |         |
| MgAl₂O₄ Ni/Ce/Al₂O₃ | 79.8           | 47.4               | 2.23               |       |         |
| MgAl₂O₄ Ni/Ce/Al₂O₃ | 85.3           | 47.5               | 2.27               |       |         |
| MgAl₂O₄ Ni/Ce/Al₂O₃ | 85.5           | 53.8               | 2.20               |       |         |
| MgAl₂O₄ Ni/Ce/Al₂O₃ | 77.0           | 35                 | 2.2                |       |         |
| MgAl₂O₄ Ni/Ce/Al₂O₃ | 80.0           | 41                 | 2.3                |       |         |
| MgAl₂O₄ Ni/Ce/Al₂O₃ | 81.0           | 44                 | 2.2                |       |         |
| SBA-15 Ni/MgO/SBA-15 | 98.9          | 84                 | 1.85               |       |         |
| 'CaO Ni/Co/Al₂O₃ | 98.5                    | 2.0                |         |       |         |

20 wt% MgO demonstrated maximum CH₄ conversion and exhibited stable activity for 20 h due to increase in CO₂ adsorption. Magnesium oxide addition to Ni/Al₂O₃ catalyst resulted in suppression of coke formation and prevented NiAl₂O₄ formation. Enhanced activity and stability of the catalyst was caused due to powerful interaction between Ni and the support enhanced steam adsorption. The coking resistance increased with addition of Ba, Ca and La for a continuous reaction of 140 h. Aged Ni/2.5La/MgAl₂O₄ catalyst exhibited maximum activity and sinter stability due to efficient Ni dispersion and higher surface area. TPR and XPS established stronger metal-support interaction after the reforming process. Coking resistance of the catalyst as well as the long term stability increased significantly. Lanthanum (La) promotion enhanced the sinterability of Ni-XLa/MgAl₂O₄ (aged) catalysts during the ageing treatment. The Co-impregnation method promoted enhanced interaction between CO₂ and Ni thereby resulting in stronger interaction between nickel and CeO₂. Thermodynamic equilibrium state was established at 265,000 mL h⁻¹ g⁻¹ at a temperature of 800 °C for the catalyst with 6 wt % Ce. Nevertheless, lowest conversion of CH₄ was noticed for the catalyst without Ce as promoter. High Ni dispersion along with high resistance towards coke formation for 40 h of catalytic run. Superior catalytic activity exhibited by Cerium oxide catalyst with Ni/ MgAl₂O₄ as the promoter. Co-precipitation method is the most recommended precipitation method for obtaining high catalytic performance in Ni/CeO₂–ZrO₂/MgAl₂O₄ catalyst. The molar ratio of H₂/CO underwent increase from 1.74 to 1.84 after reaction for 620 h and there was a drop in percentage of CO₂ from 92 to 77%, while the CH₄ conversion was 96.7%. Interaction of the Ni containing catalyst with MgO promoter enhanced the dispersion of Ni species. Drastic reduction in the carbon deposition.
most important sector of road transport is depicted in Fig. 1, which illustrates that the annual hydrogen demand is projected to surge from 25 tons in 2020 to 945.5 thousand tons in 2045.

Furthermore, the soaring demand for hydrogen in Japan [33] can be illustrated in Fig. 2. This shows a gradual increase in hydrogen demand from 2015, which will increase rapidly to 21 million tons in 2035.

Additionally, electric engines in any vehicle are energised by electricity from fuel cells, which is generated by conversion of clean and environmentally friendly hydrogen (and oxygen from the air) in fuel cells. A schematic diagram representing hydrogen supply from various sources, and its applications, are illustrated in Fig. 3.

It has been established that CO₂ emission levels [35] to the atmosphere can be significantly decreased by substitution of traditional fuels such as diesel, gasoline and carbon with higher (H/C) ratio fuels such as natural gas or biomass, as shown in Fig. 3. Therefore, production of hydrogen from hydrocarbons is regarded as the most economic and efficient way of achieving a significant degree of reduction in the emissions of greenhouse gases. Natural gas is a non-renewable energy source; essentially a blend of lighter hydrocarbons existing in the basement of gas accumulations present in porous rock which might or might not be associated with oil. It is mainly constituted of saturated hydrocarbons, mainly methane, with butane and propane in insignificant quantities, and other compounds composed of inorganic gases. Production of synthesis gas comprising of a mixture of CO along with purified H₂ being obtained from natural gas by using various catalyst and is currently the most preferred choice (Table 1). With the advent of the hydrogen economy, there has been an increased focus on the transformation of petroleum gas into more ecologically friendly hydrogen fuel.

The Global carbon dioxide emissions from various industrial processes and fossil fuel combustion have been estimated to be around 35.7 billion tons [36] annually, which has contributed to increased global warming [242,243]. Therefore, it is imperative to develop clean technologies for the utilisation of fossil fuels [245–247] and to introduce alternative greener fuels for inhibiting the adverse effects of greenhouse gas emissions and subsequent climatic changes. Among various alternative fuels, hydrogen [37] is considered to be a sustainable energy carrier and offers near zero end-use emissions of greenhouse gases and pollutants [38].

For the creation of clean fuel, like hydrogen, natural gas needs to undergo a catalytic process described as natural gas reforming. Reforming is the most common technique used in industries for production of synthesis gas via through one of three reforming processes i.e., partial oxidation of methane (POM) [39], steam reforming of methane (SRM) [40–48] and CO₂ reforming of methane (DRM) [49–55]. SRM is a fully developed generation technique which utilises steam at high temperature (700–1000 °C) for the production of H₂ from natural gas. During SRM, CH₄ interacts with steam with pressures ranging from 3 to 25 bar using catalyst to produce H₂, CO and a moderate quantity of CO₂. Eventually during the water-gas shifting reaction, steam and CO₂ interact to generate CO and more H₂ using an efficient catalyst. Steam reforming of methane requires rigorous energy input because of its endo-thermicity.
and higher H₂O/CH₄ ratio which results in better yields of H₂, thereby making the SRM process energetically unfavourable [56–62] and accelerates the catalyst deactivation process [51]. On the other hand, DRM [63–69] can be utilized for the generation of syngas from methane and is valuable for the immediate transformation of CO₂ into different compounds, Equations 1 to 8

SRM: CH₄ + H₂O ↔ CO + 3H₂ = ΔH°₂₉₈ = −206 kJ/mol (1)

POM: CH₄ + 1/2O₂ ↔ CO + 2H₂ = ΔH°₂₉₈ = −38 kJ/mol (2)

DRM: CH₄ + CO₂ ↔ 2CO + 2H₂ = ΔH°₂₉₈ = −248 kJ/mol (3)

POM can deliver syn gas with a H₂/CO proportion of 2.0. Nonetheless, controlling this process is an arduous task due to the danger associated with explosions [70] and the presence of hot spots. Also, Partial oxidation of methane needs an air separation unit (ASU), which markedly impacts the expenses associated with the reforming plant. Because of these disadvantages associated with POM, combined steam and dry-reforming of methane (CSDRM), where H₂O is used in conjunction with CO₂, has been considered as a worthwhile strategy for the mass production of syn gas with a H₂/CO proportion of 2.0 [71,72]. The CSDRM can generate syn gas with flexible H₂/CO proportions, which can be effectively controlled by modifying the feed gas (H₂O, CO₂ and CH₄) composition. The utilized procedure is alternatively known as bi-reforming (BRM) where a 3/2/1 proportion of CH₄ along with CO₂ and steam produces a gas blend with basically a 2/1 proportion of H₂ to CO. This formed gas is also called ‘met gas’ to underline its distinction from broadly utilized syngas blends of different H₂/CO proportions. The formation of syngas with this ratio has potential applications in Fischer-Tropsch operations for the preparation of long hydrocarbon chains [73–75], as well as in the production of methanol [76–78].

Furthermore, bi-reforming [79–94] of CH₄ has captivated massive interest from both environmental and industrial perspectives. CO₂ and CH₄ are the most abundant carbon-containing, ozone-depleting substances from an environmental perspective, which can be used successfully in this reaction and can undergo conversion to useful chemical products. In reality, the combination of both steam and dry reforming provides a more pragmatic route for enhancing the H₂/CO ratio compared to the introduction of CH₄ [95–97]. Additionally, this method possesses the merit of producing synthesis gas by using methane and carbon dioxide which are coined as greenhouse gases.

Fig. 1 – Evolution of the number of hydrogen vehicles, population, and annual hydrogen demand, Adapted from Ref. [32].

Fig. 2 – Hydrogen demand potential in Japan (Special Lecture conducted at 2012 General Meeting of Hydrogen Energy Systems Society, Japan), adapted from Ref. [33].

Fig. 3 – Supply and demand for hydrogen from various sources, adapted from Ref. [34].
It has been reported [98] that at lower temperatures higher conversion of methane can be achieved in the bi-reforming process. In addition to the operating conditions, catalysts also play a crucial role in bi-reforming reactions. One of the most important advantages of bi-reforming [85,98–104] is that the consumption of major greenhouse gases occurs, thereby creating a significant environmental impact. These gases are water vapour, which accounts for 36–70% of the feed gas, CO2 at 9–26%, CH4 at 4–9% and ozone (O3) for the rest (3–7%) [105]. Hence, there has been a renewed interest in the application of these gases via bi-reforming of methane towards the production of value-added chemicals that are useful for both scientific and industrial communities.

Additionally, bi-reforming technology can be regarded as a method for enhancing the caloric value of biogas, which is composed of CO2, H2 and CH4 through the solar reforming process [106,107]. One of the biggest stumbling blocks for the methane reforming process is related to the sudden catalyst deactivation, which might be due to sintering and coke formation on the active sites [108,109]. CH4 decomposition (Eq. (3)), CO disproportionation (Eq. (4)) and CO reduction (Eq. (6)) are the primary processes that lead to coke formation. The reaction in Equation (3) shows an endothermic reaction that is highly favourable at higher temperatures and lower pressures, whereas Equations (4) and (5) are exothermic in nature and favoured at lower temperatures [110] and higher pressures through the reverse water gas shift reaction (Eq. (6)).

\[
\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2 = \Delta H, -74 \text{ kJ/mol (4)}
\]

\[
2\text{CO} \leftrightarrow \text{C} + \text{CO}_2 = \Delta H, -172 \text{ kJ/mol (5)}
\]

\[
\text{CO} + \text{H}_2 \leftrightarrow \text{C} + \text{H}_2\text{O} = \Delta H, -131 \text{ KJ/mol (6)}
\]

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 = \Delta H, -41 \text{ kJ/mol (7)}
\]

\[
3\text{CH}_4 + \text{CO}_2 + 2\text{H}_2\text{O} \leftrightarrow 4\text{CO} + 8\text{H}_2 = \Delta H, +220 \text{ kJ/mol (8)}
\]

Since catalysts deactivation is caused by formation of coke from the above reactions (4), (5) and 6, hence, it is desirable to establish promising catalysts that demonstrate greater selectivity, excellent stability and activity during the production of syngas. Several investigations [49,50,111], have been reported for assessing the most suitable catalyst for syngas production employing different technologies. Common catalysts that have been used in reforming reactions include catalysts such as copper, nickel supported by transition metals and other supported noble metal catalysts such as ruthenium, platinum, rhenium. Several noteworthy reviews reporting on various innovations recorded in catalyst development for DRM reactions have mainly focussed on catalysts configurations [112], the influence of process parameters [50], noble metal catalysts [49], coke deposition and management [113], development of oxygen carriers in chemical looping [113], Ni and Ni-based catalysts [51], low temperature dry reforming [114], and advances in synthesis of catalysts with mesoporous SBA-15 support [115]. Fidalgo et al. [36], conducted a review on carbon black catalysts and activated carbon which have the unique characteristic of operating without being deactivated by carbon deposition. The catalysts role on methane decomposition and carbon dioxide reforming of CH4 was assessed, and the characteristics of carbon deposits during CO2 reforming of CH4 were listed. The influence of nanocatalysts [38] on the oxidative coupling, steam reforming and CO2 reforming of CH4 has been previously reported, which suggested that methane conversion over a nanocatalyst occurred significantly than the ordinary catalyst and there existed no interdependence between the average particle size of nanoparticles and the conversion of methane.

Pakhare et al. [49], reviewed DRM for catalysts based on metals such as palladium, platinum, rhenium and ruthenium, which involved the role of these elements on the mechanism, deactivation, kinetic behaviour of these catalysts. Abdullah et al. [51], conducted a comprehensive review on the potential of nickel based catalysts employed during syngas production using dry reforming process. Their result suggested that strong metal support interactions were dependent on the catalyst supports and these factors were responsible for highest coke resistance, high thermal resistance and greater stability. The authors also examined the synthesis of catalyst supports from cellulosic materials and stressed the enhanced catalytic activity of the cellulose in the DRM reaction due to its superior mechanical strength and distinct structure.

However, to the author's knowledge there is a lack of comprehensive literature on the synthesis, characterisation and the role of catalysts and their promoters in the generation of synthesis gas during bi-reforming of methane (BRM). Therefore, the present review encompasses in details the role of various catalysts: Ni-based, Co-based, Ru-based, mesoporous and La-based, on BRM process. Additionally, the review describes the recent progress relating to the most relevant topics on catalysts used in bi-reforming technology.

### Catalysts used in Bi-Reforming reactions

#### Nickel-based catalysts

Though Ni-based catalysts [116] are inexpensive, they display exhibit superior performance in comparison to precious metal catalysts. Nevertheless, sintering and formation of carbon affects the sudden deactivation of catalysts. Since bi-reforming employs low S/C ratios for adjusting the H2/CO ratio, hence catalysts involving Ni undergo deactivation by carbon deposition [76]. Two main methods have been documented to diminish the deactivation of catalyst due to formation of coke. One method described the effect of promoters such as lanthanum [117], cerium, magnesium and calcium [118,119], on the characteristics of the catalysts during the reforming process and other was aimed at controlling the particle size at the nano-level in the active metals.

It has been established that during bi-reforming [120–122] and DRM, deactivation of Ni supported catalysts occur due to coke formation. Hence, it is highly imperative for the development of most active and stable catalysts in bi-reforming. Several authors [120,121,123], have developed nickel catalyst
of high activity and stability supported by Ce–ZrO₂, ZrO₂, and MgO during the DRM process. Several literature studies on the effect of nickel catalysts and their promoters during bi-reforming of methane have been documented in the present review. For example, Roh et al. [121] employed numerous supported Ni catalysts during bi-reforming reactions for production of syngas having H₂/CO = 2. The supported Ni catalysts were prepared by incipient wetness method with Ni(NO₃)₂. The Ni catalysts were supported by small nanoparticles of ZrO₂ or MgO which were highly active and stable for BRM. Fig. 4 illustrates scanning electron microscopic (SEM) images of catalysts used in the reaction and the coke formation observed when subjected to 800°C. The authors observed that the degree of carbon formation and shape varied with different catalysts. Ni catalyst with MgO–Al₂O₃ as support generated filamentous coke but of insignificant intensity (Fig. 4a). However, Ni catalyst with MgO as support generated a lot of coke from the filaments (Fig. 4b) during occurrence of BRM reaction while Ni/ZrO₂ exhibited a worm-like coke feature (Fig. 4c). Similar shape of coke (Fig. 4d) was observed for Ni/CeO₂ catalyst. Nevertheless, Ni/α-Al₂O₃ generated rod shaped-like coke (Fig. 4e).

The authors [121] also made a comparative study between the Ni/MgO–Al₂O₃ catalyst and the commercial Ni catalyst supported with MgAl₂O₄ (Fig. 5) at various temperatures. The methane conversion was 83% and the conversion of carbon dioxide was 71% in presence Ni catalyst supported by MgO–Al₂O₃ at 700°C, while CO₂ and CH₄ conversions with Ni/MgAl₂O₄ were both found to be 20% lower during BRM of methane. Commercial Ni/MgAl₂O₄ was used as a reference.

![Fig. 4 - Scanning electron microscopy images of various catalysts: (a) Nickel catalyst supported by MgO–Al₂O₃, (b) Nickel catalyst supported by MgO, (c) Nickel catalyst supported by Zirconium oxide (d) Ni catalyst supported by Cerium oxide and (e) Ni/α-Al₂O₃, adapted from Ref. [121].](image-url)
Also, coke formation was more severe with the commercial Ni/MgAl₂O₄ catalyst than with Ni/MgO-Al₂O₃, which was attributed to the efficient dispersion of Ni [124] supported MgO-Al₂O₃. The high activity and stability of Ni/MgO-Al₂O₃ catalyst was attributed to the beneficial role of MgO which resulted from basic property, fine dispersion of nano-sized Ni and strong interaction of Ni to the support.

From Fig. 6 it was clearly observed that the CH₄ conversion was highest for Ni catalyst supported by MgO-Al₂O₃ and approximately 90% methane underwent conversion which continued for 2 h. However, rapid catalyst deactivation occurred in the case of Ni-γ-alumina catalyst with changes in time attributed to carbon formation. Moreover, Ni/MgO catalyst exhibited around 60% CH₄ conversion and Ni/ZrO₂ demonstrated around 70% CH₄ conversion. Both the catalysts were found to be highly stable during the reforming process. Nevertheless, the conversion of methane for Ni catalyst supported by CeO₂ was initially 57% which decreased to 50% followed by its saturation. Results revealed that Ni/MgO-Al₂O₃ possessing lowest nickel oxide crystallite size exhibited highest stability along with higher CH₄ conversion with time on stream.

Catalytic nickel membrane
Ryi et al. [125] conducted tests over a catalytic nickel membrane during bi-reforming of methane for a shorter residence time of 120 ms for various CO₂/H₂O ratios in the range of 0–1.0, along with (H₂O + CO₂)/CH₄ ratio of around 3.0 in the reactant feed for temperatures ranging from 923 to 1023 K.

The purpose of this study was to examine the performance of bi-reforming of methane over a catalytic nickel membrane for the GTL (gas to liquid) process. GTL process possess two advantages. One is that carbon formation is reduced due to the oxidation of carbon precursor species and a desirable H₂/CO can be achieved by adjusting CH₄/H₂O/CO₂ ratio in the feed stream. Porous wall of catalytic nickel membrane was chosen for reforming studies since hydrogen passed through the catalytic nickel membrane was faster than the other gases because of viscous and Knudsen flow. Generally, the catalyst that contained relatively small size pore was more affected by internal diffusion than the one which has large sized pores.

The results revealed that the change in the feed ratio of CO₂/H₂O strongly affected the conversion of methane and furthermore an increase in the feed ratio of CO₂/H₂O at a temperature of 923 K (Fig. 7) decreased the methane conversion. The authors noted a very high conversion of methane in the range of 92.7–96% above 973 K, when the CO₂/H₂O feed ratios were in the range of 0–1.0 during bi-reforming of methane. The authors ascertained that with change in the CO₂/H₂O ratio during the reforming reaction, a change in H₂/CO also occurred. Hence H₂/CO molar ratio obtained at 973 k were 8.1, 5.7, 3.7 & 2 when the molar ratio of CO₂/H₂O were 0, 0.11, 0.33 and 1.0. However, increase in temperature to 1023 K changed the H₂/CO molar ratio to 7.5, 5.3, 3.4 and 1.8 respectively for similar values of H₂O/CO₂. Additionally, the CO₂ registered an increase with increasing temperature attributed to CO₂ reforming of methane occurring at higher temperatures, which remained almost constant at ≥ 973 K attributed to the limitations of CH₄ as the reacting species [125].

![Fig. 5](image1.png)

**Fig. 5** – Scanning electron microscopy images of (a) used Ni catalyst supported by MgO–Al₂O₃ and (b) commercial Ni catalyst supported with MgAl₂O₄, adapted from Ref. [121].

![Fig. 6](image2.png)

**Fig. 6** – Conversion of methane with change in time over various nickel catalysts (H₂O/CO₂/CH₄ ratio is 0.8/0.4/1.0; Temperature: 800 °C), adapted from Ref. [121].
Ni/Al₂O₃ based catalyst

Al-Nakoua and El-Naas [126] experimented with different molar proportions of H₂O/CH₄ and CO₂/CH₄ in a detachable reactor covered by catalyst B Nickel (33%)–Chromium (5.6%)–Barium (11%)/La₂O₃ (19%) and catalyst A which represents Ni (49%)/Al₂O₃ (51%). The author observed that rapid carbon deposition was observed at 700 °C, 1 atm during dry reforming of methane. However, when CO₂ reforming was performed in conjunction with steam reforming reaction in thinner channels deposited with a thinner layer of catalyst, a reduction in carbon deposition was noticed on the surface. The authors determined the equilibrium compositions of the CH₄ and CO₂ reactants, which are shown in Figs. 9 and 10 at pressures of 1, 2, 3, 4, 5, 10, and 20 bar respectively. Fig. 8 shows that CH₄ conversion was highest (85–90%) at pressures ranging from 1 to 3 bar and at temperatures in the range of 810–900 °C. Similarly, CO₂ conversion (Fig. 9) was found to be above 80% in the pressure range of 1–3 bar and temperatures varying from 840 to 900 °C. SEM studies (Fig. 10) revealed that
cracks formed in catalyst A possessed a length of 250 μm and width of about 10 μm, whereas for catalyst B the cracks were formed with a width of 20 μm and was spread up to a certain length where the cracks were interconnected. Furthermore, the results [126] established that there was a significant improvement in the catalyst stability when the H2/CO was around 2.2 during bi-reforming of methane. These conditions were appropriate for Fischer-Tropsch applications and synthesis of methanol. Additionally, the authors observed a five-fold increase in the resistance of coke formation displayed by Ni/Al2O3 catalyst A upon addition of Cr, Ba, and La2O3 during a continuous reaction time of 140 h. The SEM results were also supported by EDX analysis.

The results of catalyst activity test on Ni/Al2O3 in the ratio of 1:1 for Catalyst A is represented in Fig. 11. The catalyst film exhibited 50% conversion of CH4 and 15–10% conversion of CO2 when the reaction was continuously operated for 24 h at 630°C. Furthermore, with increase in inlet pressure from 1 to 23 psig, carbon deposition was noticed. The flow rate of CO2 was 0.2 mol/h and the flow rate of CH4 was 0.8 mol/h and the steam: carbon ratio was 0.51. However, Ni−Cr−Ba/La2O3−Al2O3 (Catalyst B) displayed CH4 conversion in the range of 50–75% and conversion of CO2 increased from 20% to 60%.

The authors found a reduction in the conversion percentage (Fig. 12) of methane and carbon dioxide when the reactor pressure of steam was increased up to 42 psig during continuous operation from 25 to 90 h. However, the conversion percentage of methane and carbon dioxide underwent an increase with further increase in temperature. Since catalyst deactivation has been caused by carbon deposition, hence suppression of coke formation was important. This was only achieved by optimization of the H2O/CH4 and CO2/CH4 and feed ratios.

Formation of coke is usually attributed to the following reactions 9 and 10:

\[
2\text{CO} \leftrightarrow \text{C} + \text{CO}_2 \tag{9}
\]

\[
\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2 \tag{10}
\]

Major amount of coke formed in the temperature range of 850 to 900°C [127] resulted from disproportionation reaction involving carbon monoxide (reaction 9) and pyrolysis of methane (reaction 10).

Son et al. [128], observed that Ni/γ-Al2O3 catalyst was rendered stable by pre-treatment with steam at a temperature operated at 850°C. Ni/Al2O3 based catalysts are relatively cheap because precious metals are not used and these catalysts can operate stably with high activity under excess steam. Ni/γ-Al2O3 catalyst used in this study was prepared by incipient wetness method. Thermodynamically, the catalyst promoted very high conversion of CH4 (98.3%) and CO2 (82.4%) when subjected to bi-reforming of methane for 200 h and resulting in H2/CO ratio of 2.01. Furthermore, the results revealed that the conventional catalyst system produced 15.4% coke after 200 h while the mass of carbon deposited was around 3.6% for catalysts exposed to steam. This novel steam pre-treatment technique significantly increased the resistance towards carbon formation in the presence of catalysts, thereby improving both long-term stability and activity.

**Fig. 11** – Plot of continuous time on stream vs conversion % and pressure over Ni/Al2O3 at 630 °C catalyst loading in detachable reactor, adapted from Ref. [126].

**Fig. 12** – (A) Plot of continuous time on stream vs conversion % and reactor temperature over Ni−Cr−Ba/La2O3−Al2O3 catalyst for pressure varying from 0 to 42 psig. (B) Plot of continuous time on stream vs conversion % and pressure over Ni−Cr−Ba/La2O3−Al2O3 at 670–850 °C, adapted from Ref. [126].

Transmission electron images of fresh untreated Nickel Aluminium and fresh steam-treated NiAl (WNiAl) catalysts shown in Fig. 13 (a) and (c) revealed that it was difficult for
distinguishing nickel nanoparticles dispersed in the Nickel Aluminium catalyst, owing to their small size. However, the WNickel Aluminium catalyst showed the presence of distinct Ni nanoparticles in the range greater than 10 nm. Severe carbon deposition (Fig. 13b) was noticed for Ni/Al catalysts treated with steam for 200 h. The shape resembled to wire-type resembled carbon and the size of the nanoparticles were enhanced from 4.2 nm to 23.5 nm from Hydrogen chemisorption measurements. Nevertheless, carbon coke with wire typed shape did not appear in the WNickel Aluminium catalyst (Fig. 13d).

Two alumina supported Ni catalysts with pore sizes of 5.4 nm and 9 nm were synthesized and tested in the bi-reforming process [129] for the production of hydrogen rich gases. Structural and functional characterisation of catalysts showed that Ni/Al2O3 with the largest pore size exhibited better characteristics i.e. higher capacity to adsorb CO2, higher surface area, higher proportion of stronger catalytic sites for hydrogen adsorption and lower Ni crystallite sizes. At all the investigated temperatures, for a CH4: CO2: H2O molar ratio of 1:0.48:1.2, a (H2 + CO) mixture with H2:CO ratio around 2.5 was obtained. The optimum conditions for the production of hydrogen rich gases, were CH4: CO2: H2O = 1:0.48:6.1 and 600 °C.

Dan et al. [130] have investigated the role of Ni/Al2O3, Ni/ MgO−Al2O3 and Ni/La2O3−Al2O3 with bimodal pore structure in the bi-reforming process. The authors observed that La2O3 and MgO promoted catalysts presented better functional and structural properties. Among all the catalysts, Ni/La2O3−Al2O3 was found to be the catalyst with best stability and activity. The presence of both lanthanum and magnesium oxides contributed to excellent dispersion and stabilization of Ni nanoparticles on the catalyst surface. The catalytic activity for the bi-reforming process increased in the order Ni/Al2O3< Ni/La2O3−Al2O3 < Ni/MgO−Al2O3.

Ni–Ce based catalysts
Lanthanide group metals (La, Ce) have been reported [131–133], to be efficient promoters for Ni-based catalysts. Recently, literature reports have suggested [120,121], that
during the bi-reforming of methane smaller nanoparticles of Ce–ZrO$_2$, ZrO$_2$ and MgO supported by Ni catalysts were found to be highly stable and active. Koo et al. [134], used a stable and extremely active magnesium oxide promoted Nickel/Al$_2$O$_3$ catalyst to investigate catalytic activity and coke formation during bi-reforming for potential applications in gas to liquid (GTL) processes. In their study, the incipient wetness technique was employed to synthesise Ni/Al$_2$O$_3$ catalysts with different concentrations of MgO. The authors used H$_2$-chemisorption, CO$_2$-temperature programmed desorption (TPD), BET analysis, and X-ray diffraction (XRD) to examine the characteristics of the prepared catalysts. Furthermore, the authors established that by changing the feed ratio of H$_2$O/CO$_2$, a H$_2$/CO ratio of 2 was obtained during the bi-reforming reaction. Additionally, catalysts containing 20 wt % magnesium oxide (MgO) showed high coke resistance and excellent catalytic performance during the bi-reforming reaction. MgO addition to the catalyst formed a stable MgAl$_2$O$_4$ spinel phase at high temperatures and was quite effective in eliminating formation of coke by enhancing the adsorption of CO$_2$ because of higher base strength on the surface of the catalyst. SEM images of reduced Ni/MgO/Al$_2$O$_3$ catalysts with changing concentrations of MgO content are illustrated in Fig. 14.

In particular, Cerium oxide has been widely recognized as an efficient promoter for Ni-based catalysts. This is because the redox properties of Ce$^{4+}$/Ce$^{3+}$ results in easier gasification of the settled coke on the surface of the catalyst and also helps in storage and delivering of active oxygen thereby enhancing the dispersion of Ni. In another study [132], Ce-promoted Ni/MgAl$_2$O$_4$ catalysts synthesized by co-impregnation showed higher metal dispersion than Ni/MgAl$_2$O$_4$ catalyst alone and demonstrated outstanding reducibility properties at lower temperatures of around 550$^\circ$C, as established by XPS. The authors found that the catalytic activities of Ni–Ce/MgAl$_2$O$_4$ catalyst were the highest and it generated enormous coke resistance during the bi-reforming reaction performed at lower temperatures with Ce/ Ni ratio of 0.25. These were due to stronger metal-support interactions and powerful dynamic oxygen movement through close contact with Ni–Ce. Furthermore, when no Ce was present, the NiO crystallite size in the Ni/MgAl$_2$O$_4$ catalyst was observed to be enormous at a value of 11.0 nm and indicated a lower metal scattering of 3.49%. The authors used Brunauer–Emmett–Teller, (BET) adsorption H$_2$-chemisorption, CO$_2$-TPD and TPR to ascertain the crystallite size of NiO, basicity and reduction temperature of the catalysts. Results revealed that the nickel oxide (NiO) crystallite size, reduction degree and dispersion of the metal were significantly affected by cerium addition to the Ni/MgAl$_2$O$_4$ catalyst.

The authors [132] also employed Raman spectroscopy in the range of 1200–1800 cm$^{-1}$ to investigate coke formation in the presence of Nickel Cerium/MgAl2O4 catalysts with varying Cerium/Nickel ratios. The spectra in Fig. 15 revealed two peaks in the vicinity of 1600 cm$^{-1}$ and 1350 cm$^{-1}$ which corresponds to G band and D band. The role of the G band is to provide useful information related to the electronic characteristics of filamentous carbon [135] while the D band arose from imperfect and polycrystalline graphite. Additionally, Ce-promoted Ni/MgAl2O4 showed a decrease in peak intensity with a Cerium/Nickel ratio of 0.25 due to minimal coke formation on the surface of the catalyst in comparison to Ni/MgAl2O4 catalyst without addition of cerium. These results were also in accordance with results obtained from TGA studies: quantification of coke deposition by TGA established a rise in graphitic and amorphous carbon with an increase in Ce/Ni ratio to 1, which was further confirmed by the increase in D band peak intensity (Fig. 15) for amorphous carbon. The advantages of using a Ce-promoted Ni/MgAl2O4 catalyst in...
the bi-reforming reaction relate to its inherent ability to eliminate formation of amorphous coke in comparison to the Ni/MgAl2O4 catalyst.

Recently, there has been renewed interest in developing Ce1-x-Zr2O3 catalytic systems [136]. It has been established that addition of zirconium oxide (ZrO2) to cerium oxide results in significant improvement in the oxygen storage capacity of cerium oxide, its thermal stability, metal dispersion and its redox properties. These improvements were attributed to the preferential replacement of Ce4+ with Zr4+ ion existing in the structure of the lattice surrounding cerium oxide (CeO2). [136–138]. The Ce1-x-Zr2O2 catalytic unit has also been regarded as an outstanding material for support in Ni-based catalyst systems [139–141]. CeO2–ZrO2 has been reported to be an effective promoter for the Ni/Al2O3 catalytic system and helps in significant suppression of coke formation with a high catalytic stability [142] Bae et al. [143], investigated the catalytic activity of Ni/MgAl2O4 catalyst in presence of cerium oxide-zirconium oxide (CeO2–ZrO2) during combined steam and CO2 reforming of methane. The synthesis of the catalysts were performed by employing an impregnation technique followed by co-precipitation process of CeO2–ZrO2 components.

Furthermore, the basic supports such as MgO or ex-hydratocitic MgAl2O4 employed in this study possessed beneficial effects such as minimising coke formation due to the reduced acidic site density [144,145]. The Cerium oxide-zirconium oxide (CeO2–ZrO2) component demonstrated a key role in the conversion of CO2 by increasing CO2 activation when contacted with crystallites of nickel. The catalysts synthesized by co-precipitation technique showed higher catalytic characteristics in comparison to catalysts synthesized by successive impregnation of Ni on support of MgAl2O4 with cerium zirconium oxide (CeO2–ZrO2).

Addition of lanthanum to Ni/Al2O3 catalysts inhibited the agglomeration of Ni particles due to the enhancement of strong metal to support interaction (SMSI). SMSI of catalysts was reported to enhance thermal stability [145–147]. Park et al. [148], synthesized 10 wt % Nickel–xLanthanum/MgAl2O4 catalysts where x ranges from 0 to 5% by co-impregnation technique during the bi-reforming of coke oven gas (COG). They conducted aging treatment with a H2: H2O: N2 ratio of 1:10:1.25 with temperature around 900°C run for 50 h. The results revealed an increase in the Ni crystallite size for all the investigated catalysts subjected to ageing. Furthermore, the lanthanum promoted catalysts exhibited greater nickel dispersion than Ni/MgAl2O4 catalyst due to their enhanced interactions between the metal and support. Results from catalytic tests performed at 900°C and at a pressure of 5 atm of atmospheric pressure for 40 h with a CH4: H2O: CO2: H2:CO: N2 ratio of 1:1.2:0.4:2.0:3.0:3.0 also revealed that aged Ni–2.5La/MgAl2O4 catalyst showed maximum sinter stability and activity due to its enhanced nickel dispersion and surface area.

Furthermore, the role of Ce/Zr ratio on the catalytic activity of Ni–Ce0.8Zr0.2O2 catalyst and coke formation was demonstrated by Roh et al. [131], during the bi-reforming reaction. The authors used co-precipitation method to synthesise Ni–Ce–Zr2O3 catalysts having different ratios of CeO2/ZrO2 for syngas production having potential applications in gas to liquid (GTL) processes. 15% Ni–Ce0.8Zr0.2O2 demonstrated excellent stability and highest activity during BRM which was attributed to the dispersion of nickel oxide having higher oxygen storage capacity and intimate contact with the support. Recently, it has been reported [131] that Cerium content along with nickel-cerium loading technique has a significant effect on the transfer of O2 occurring between nickel (Ni) and cerium (Ce). Studies have also shown an improvement in coke resistance of 12 wt % Nickel/α-Al2O3 catalyst in the bi-reforming reaction. [133,149]. However, the characteristics of supports play a marked effect on coke formation [132]. For example, α-Al2O3 support caused carbon deposition due to its acidity [150]; active nickel metal and Al2O3 supports underwent interaction to form inactive NiAl2O4, resulting in deactivation of the catalyst [134]. Additionally, Baek et al. [151], observed higher coke resistance and enhanced catalytic stability of Ni–Ce/ MgAl2O4 (MgO/Al2O3 = 3/7) in comparison to Ni–Ce/α-Al2O3 in bi-reforming process.

Gao et al. [152] develop an ideal Ni–Ce/ZSM-5 catalyst by the impregnation method for the bi-reforming process. The authors noted that by adjusting the parameters properly, highest conversion i.e. 99% and 94% of CH4 and CO2 to syngas was achieved in presence of Ni–Ce/ZSM-5 catalyst. Furthermore, the catalyst did not show any deactivation and maintained high activity for 40 h. SEM, XRD and H2-TPR analysis further established the structure as well as composition of the catalysts and provided better understanding of the catalytic performance.

Chen et al. [153] synthesized highly dispersed mNi/xL/Si catalysts by one-pot sol-gel process and applied to the bi-reforming process for syngas production. Results revealed that the addition of lanthanum improved the stability, catalytic activity as well as the coke resistance of these catalysts. The17.5Ni/3.0La/Si catalyst prepared using ethylene glycol and poly (ethylene glycol) displayed the best catalytic activity, coke resistance and stability. Additionally, the H2/CO ratios in the product gas were tuned by varying the C/S ratios in the feed.

Ni–MgO based catalysts Jabbour et al. [154], employed a one-pot method followed by evaporation-induced self-assembly (EISA) to synthesise two types of catalyst namely Ni50%M5%M5%, where M represents Ca or Mg and NiM% where X corresponds to 5–10 wt % along with packing of mesoporous Al2O3.

Low cost and widely available Mg2+ and Ca2+ containing salts were used as the additives based on their potential to yield basic properties (in their oxide form) and their positive impact on bi-reforming process [155]. Temperature programmed reduction (TPR) of calcined Ni-loaded samples displayed a strong reduction peak at higher temperatures ranging from 550 to 800°C (Fig. 16b–f), which was ascribed to the reduction of oxidised nickel (Ni) undergoing stronger interaction with the support present in the mixed spinel phase [156]. The author observed that there was no peak signifying weakly-bounded Ni species below a reduction temperature of around 500°C, which was similar to the finding for non-porous impregnated alumina samples [82,157]. The authors in their studies noted that after the reduction process, the catalysts demonstrated higher dispersion of Ni within the arranged oxide cavity, possessed elevated activities and also
showed long-lasting stability in bi-reforming of CH₄ performed at 800°C. They also observed that a relationship existed between carbon deposition and reactivity level in the presence of Mg free catalysts.

SEM (Fig. 17A, B) and TEM (Fig. 17C, D) images for spent Ni₁₀%Al₂O₃ clearly identified long carbon filaments on the exterior area of the alumina containing grains, with some grains which were found to be more protected than others. These images also showed some Ni nanoparticles containing coke were situated either at the boundary between the support and the filament embedded into it. These images also resembled carbon nanotubes nucleation with a ‘closed end’ consisting a nanoparticle at either their closure or located inside the tip [158–160]. For both Ni₅%Mg₅%Al₂O₃ and Ni₅%Ca₅%Al₂O₃, a peak was observed at very high temperatures of above 800°C, as shown in Fig. 18A (e and f); this was a possible indication of free metallic Ni existing under stronger interactions or may have been related to the reduction of Mg- or Ca-derived species. Furthermore, a linear correlation was established between H₂ uptake and Ni content, which confirmed that all Ni used in the synthesis was completely reclaimed in the solid after preparation. The authors also reported that, due to the
endothermic nature of the bi-reforming reaction, the conversion of both CH4 and CO2 decreased at lower temperatures, and CO2 conversion was more significant below 700°C.

Results also revealed that there was a beneficial effect when 5 wt% magnesium or calcium was used for the conversion of both CH4 and CO2 represented by d and e (Fig. 18A, B), compared to catalyst containing 5 wt% Nickel and without additive. The enhancement in the reactivity in presence of 5 wt (wt%) magnesium or calcium was higher than with Ni7.5% Al2O3 despite the lower Ni content reported in previous literature [161–163]. Jabbour et al. [154], established that in addition to high activity levels, doping of the Ni catalysts with Mg or Ca additive resulted in excellent catalytic stability for high temperature bi-reforming operations. The authors found that mesoporous catalysts synthesized by one-pot method served as an ideal candidate for catalysing met gas production from biomass-related natural resources. The beneficial effect of nickel confinement in the pores was twofold, one in protecting the metal nanoparticles against sintering phenomenon and second against coking due to steric constraints.

Kang et al. [164], synthesized core shell structured Ni catalysts Ni/MgO–Al2O3 and Ni/Al2O3 and via technique coined multi-bubble sono-luminescence and conducted tests using these catalysts for the bi-reforming process. The authors observed that Ni catalysts constituting of 10% Ni loaded on Aluminium oxide or MgO–Al2O3 exhibited exemplary performance during the steam reforming of methane, achieving 97% conversion of CH4 at a temperature of 750°C. Additionally, methane conversion was 96% at 850°C during dry reforming of CH4 and demonstrated greater thermal stability for the initial duration of 50–150 h. The results also established that supported Ni catalysts demonstrate excellent performance in both mixed and auto-thermal reforming of CH4, where satisfactory thermal stability was noted for the first 50 h. An interesting observation was that no significant carbon formation was obtained on surface of the investigated catalysts after the reforming reaction. Very recently, Koo et al. [118], synthesized nickel catalysts in the nanoscale by employing a mixture of magnesium oxide–aluminium oxides (MgO–Al2O3) obtained from a structure resembling hydrotalcite. Their results revealed an enhancement in the coke resistance with various mixed ratios of Mg/Al for the generation of syngas during bi-reforming for applications in GTL processes.

Mesoporous SBA-15 has aroused enormous interest among researchers in steam reforming [165,166], and CH4 dry reforming [68,167], process due to its high surface area, high silanol group density, uniformity of pores and enhancement in active metal dispersion with smaller crystallite size [168]. A group of Nickel/SBA-15 catalysts with Ni content ranging from 5 to 15 wt % were synthesized by Huang et al. [169], along with 10% Ni/MgO/SBA-15 catalysts with MgO content ranging from 1 to 7 wt (wt%) during combined steam and dry reforming reaction in a continuous micro-reactor. XRD, H2-TPR and CO2-TPD techniques were used to investigate the structure of catalysts. The authors observed that selectivity of carbon monoxide (CO) for these reactions was almost 100% and they also noticed that with the change in the molar ratio of H2O/CO2, there can be effective control of the H2/CO ratio. After reaction at 850°C for more than 120 h with 10 wt % of Ni/SBA-15 catalyst, the conversion of methane underwent a decrease from 98% to 85% while the conversion of CO2 reduced from 86% to 53%, respectively. Additionally, the catalyst containing 3% MgO/SBA-15 loaded with Ni demonstrated excellent catalytic activity after a reaction for 620 h and the CO2 conversion over this catalyst underwent a decrease from 92% to 77%, while no change in CH4 conversion was observed. Furthermore, certain changes in the MgO promoter enhanced the NiO species dispersion and resulted in an increase in the adsorption affinity of CO2, thereby inhibiting coke deposition and retarding the deactivation phenomenon.

Mg–Al mixed oxides derived from hydrotalcite-like materials are reported [118,154], to exhibit higher activity and stability in bi-reforming process due to its basic property, enhanced steam and CO2 adsorption, strong Ni to support interaction and fine dispersion. These catalysts were synthesized using various preparation methods such as impregnation of pre-calcined carriers or simultaneous co-precipitation of the mostly nitrate-based solution of all the constituents. Roohollahi et al. [170], synthesized numerous Ni-based catalysts supported on mesoporous MgO–Al2O3 resembling a
Mg–Al hydrotalcite structure with Mg/Al ratio of 1. Mg–Al hydrotalcite-like components, represented by the formula [Mg$^{2+}$]$_{1-x}$[Al$^{3+}$]$_x$[(OH)$_2$]$^{x-}$[CO$_3^{2-}$]$_{1/2}$·mH$_2$O, have been regarded as the best candidates for precursors employed in the synthesis of mesoporous MgO–Al$_2$O$_3$ carriers possessing high surface area [171]. The synthesis of hydrotalcite-like components was performed at an optimized pH of 10, which were then calcined at various calcination temperatures from 500 to 800 °C to obtain a homogenous texture. Results from the bi-reforming reaction conducted on the catalysts at 800 °C demonstrated high activity/selectivity during all of the reforming processes tested. When CO$_2$ reforming was performed in conjunction with steam reforming process a drastic reduction in carbon deposition from 25.96% to 1.08% was observed for a feed composition of CH$_4$:CO$_2$:H$_2$O = 1.0:0.55:0.55 [174]. Furthermore, the authors noted that complete conversion of CH$_4$ to synthesis gas. Choudhary et al. [174], have reported the role of NiO–CaO catalysts during SRM, DRM and combined steam and CO$_2$ reforming of methane to produce CO and H$_2$ at varying temperatures ranging from 700 to 850 °C and gas hour space velocities (5000 to 70,000 cm$^3$ g$^{-1}$ h$^{-1}$). They characterised the catalysts using various techniques including XRD, XPS and TPR. Their results revealed that the catalysts demonstrated high activity/selectivity during all of the reformation processes tested. When CO$_2$ reforming was performed in conjunction with steam reforming process a drastic reduction in carbon deposition from 25.96% to 1.08% was observed for a feed composition of CH$_4$:CO$_2$:H$_2$O = 1.0:0.55:0.55 [174]. Furthermore, the authors noted that the feed composition was maintained for CH$_4$:H$_2$O = 1:1 during the steam reforming reaction, the reaction characteristics were outside the coke formation control. Nevertheless, for the dry reforming reaction with a reactant feed composition of CH$_4$:CO$_2$ in the ratio of 1:1, the coke formation was obtained from a gas mixture formed at equilibrium.

The authors [174] also noticed that by changing the carbon dioxide/steam (CO$_2$/H$_2$O) ratio in the reactant feed, a significant improvement in the selectivity, activity and productivity in the oxidative conversion of methane to synthesis gas. Choudhary et al. [174], have reported the role of NiO–CaO catalysts during SRM, DRM and combined steam and CO$_2$ reforming of methane to produce CO and H$_2$ at varying temperatures ranging from 700 to 850 °C and gas hour space velocities (5000 to 70,000 cm$^3$ g$^{-1}$ h$^{-1}$). They characterised the catalysts using various techniques including XRD, XPS and TPR. Their results revealed that the catalysts demonstrated high activity/selectivity during all of the reformation processes tested. When CO$_2$ reforming was performed in conjunction with steam reforming process a drastic reduction in carbon deposition from 25.96% to 1.08% was observed for a feed composition of CH$_4$:CO$_2$:H$_2$O = 1.0:0.55:0.55 [174]. Furthermore, the authors noted that when the feed composition was maintained for CH$_4$:H$_2$O = 1:1 during the steam reforming reaction, the reaction characteristics were outside the coke formation control. Nevertheless, for the dry reforming reaction with a reactant feed composition of CH$_4$:CO$_2$ in the ratio of 1:1, the coke formation was obtained from a gas mixture formed at equilibrium.

The authors [174] also noticed that complete conversion of methane to syngas with 100% selectivity consisting of both CO and H$_2$ and during bi-reforming reaction at 800 °C with GHSV ranging from 20,000 to 30,000 cm$^3$ g$^{-1}$ h$^{-1}$. The authors observed that by changing the carbon dioxide/steam (CO$_2$/H$_2$O) ratio in the reactant feed, a significant improvement in the bi-reforming process occurred and also a desirable H$_2$/CO ratio from 1.5 to 2.5 was seen. TPR studies were performed to measure changes in the concentration of H$_2$ owing to reduction of nickel oxide in the catalyst. The TPR curves (Fig. 19) revealed maximum value in the range 400 and 450 °C, in accordance with the maximum peak temperature observed around 418 °C attributed to reduction of bulk nickel oxide.

NiO–SiO$_2$ based catalysts
Chen et al. [153] synthesized mNi/xLa/Si catalysts with efficient dispersion characteristics and comprising of various weight contents of nickel and lanthanum by using sol-gel method, and tested these catalysts for bi-reforming of CH$_4$ to generate syngas. The authors noticed an increase in the stability, catalytic characteristics and an enhancement in the

![Fig. 19 – TPR studies using Ni/CAO catalyst of various proportions, adapted from Ref. [174].](image1)

![Fig. 20 – Schematic diagram representing the interaction of CH$_4$ with steam and CO$_2$ on Ni-supported SiO$_2$–MgO catalyst, adapted from Ref. [175].](image2)
resistance of carbon deposited during bi-reforming in presence of mNi/xLa/Si catalysts upon addition of lanthanum. The 17.5Ni/3.0La/Si catalyst prepared using ethylene glycol and poly (ethylene glycol) demonstrated excellent coke resistance and catalytic activity. Additionally, modification of the carbon/sulphur (C/S ratios) in the reactant caused tuning of the H2/CO ratios in the gas generated as products. Furthermore, when the bi-reforming reaction was performed in presence of 17.5Ni/3.0La/Si catalyst produced a H2/CO ratio of about 2 for the C/S ratio of 0.5.

Ni-phylllosilicate (PS) intermediates were used to synthesise Nickel–SiO2–MgO materials for its application in bi-reforming of methane., and the role of reaction temperature as well as steam on the reforming process were also investigated. The results revealed that catalytic performance was excellent and resulted in 80% conversion of CH4 and 60% CO2 conversion respectively, at 750°C for 140 h in presence of a Ni–30 wt % SiO2–55 wt % MgO catalyst. Furthermore, carbon deposition was found to be stable when the H2/CO ratio was maintained at 2. The catalytic behaviour of the investigated catalyst was ascribed to its structural stability, acidic strength and enhanced basicity for the reforming reaction conducted at high temperatures. The presence of nickel-magnesium comprising phyllosilicates in the reduced catalysts were established by TEM and XRD technique. Furthermore, a TPR profile of around 750°C substantiated the presence of strong interlinkage between nickel and Silicon dioxide–Magnesium support species. A representative schematic diagram of this is illustrated in Fig. 20.

Jabbour et al. [82], used an one pot method (Fig. 21) for synthesis of mesoporous nickel–alumina catalyst containing 5 wt % Nickel and possessing an ordered structure. From their observations, the ordered Ni–alumina sample exhibited excellent stability in comparison to non-porous and impregnated catalyst during the bi-reforming process at 800°C over 40 h. The conversion percentage of methane was consistent with the thermodynamically expected variants. The authors also noted that nickel catalyst loaded with SBA-15 demonstrated enhanced catalytic activity than Ni/celites, however both these catalysts underwent rapid deactivation on stream which was attributed to the partial re-oxidation of the Ni active phase under the investigated conditions (see Fig. 22).

SBA-15 support has been employed for suppressing carbon formation in steam reforming reactions [165,167], and has aroused significant interest due to its high surface area, high silanol group density, pore uniformity. An incipient wetness method was employed by Singh et al. [176], to synthesise SBA-15–packed Ni catalyst by impregnating nickel nitrate onto the SBA-15 support. They found that the surface area decreased from 669.5 m² g⁻¹ to 538.6 m² g⁻¹ with the change in catalyst support from SBA-15 to 10 wt % Nickel/SBA-15 catalyst was confirmed by BET surface area analysis. Analysis by H2-TPR demonstrated the complete reduction of NiO nanoparticles beyond 576.85°C where the temperature of reduction from nickel oxide to metallic nickel was completely dependent on metal-support interactions which was correlated to the location, confinement effect and crystallite size of nickel oxide. CO2 and H2O had a significant role in controlling formation of carbon during bi-reforming of methane due to their unique capability in converting the partially dehydrogenated CxH1-x to a mixture of CO and H2. The authors observed that carbon dioxide conversion and methane conversion was 58.9%, and 61.6% respectively. Furthermore, the resulting H2/CO ratio was found to be 2.14 during the combined CO2 and steam reforming of CH4 under stoichiometric conditions. A steep increase in the H2 and CO yield was noticed while increasing

![Fig. 21 – Schematic diagram of synthesis of impregnated and one-pot Ni–Al2O3, adapted from Ref. [82].](image-url)
the CO$_2$/\((\text{CH}_4 + \text{H}_2\text{O})\) ratio, and a considerable decrease in the ratio of both hydrogen and carbon monoxide ratio ranging from 2.14 to 1.83 was observed with a decrease in the H$_2$O/\((\text{CH}_4 + \text{CO}_2)\) ratio. Furthermore, Ni/SBA-15 exhibited higher resistance towards both coking and sintering which was related to the efficient distribution of nickel particles and steric effects caused by SBA-15.

The synthesis, catalytic activity and characterisation studies on Ni/SBA-15 catalysts during BRM has been reported [177]. The authors observed that 25 wt % Nickel/SBA-15 SGM catalyst showed the maximum conversion of CH$_4$ (23%, 548 C), which was followed Ni/SBA-15 HTM (CH$_4$ \approx 20% at 548 C) and 10% CH$_4$ conversion was achieved in presence of 25 wt % Ni/SBA-15 CG catalyst. CO$_2$ and CH$_4$ conversion were found to be 82% and 23% at 548 C, respectively. These differences in the catalytic activity were related to the degree of availability of active metal for the reaction. Due to excellent catalyst activity of these catalysts, these catalysts were employed for the formation of membrane reactor with hollow fibres and catalytic hollow fibres.

The authors employed commercially available SBA-15 for comparison. SEM micrographs (Fig. 23) revealed a needle shaped particle having a grain size of around 0.6 \mu m (A1 and A2). The SBA-15 particles synthesized by the sol-gel method did not display a homogeneous shape and consisted of a hard shell covering smaller particles whose grain size was approximately around 0.1 \mu m.

Mesoporous siliceous SBA-15 material has been used as support for preparing active metal catalysts in several reforming processes [66,178]. The mesoporous SBA-15 support possessed uniform mesopores with thick framework walls, high thermal stability and wide specific surface area [179], [180]. Additionally, the ordered hexagonal mesostructure of SBA-15 support provided a confinement effect to anchor the nano-particles inside its channels and also prevented deposition of carbonaceous species metal sintering [115]. Siang et al. [180], used the incipient wetness impregnation technique to synthesise stable and active boron (B) aided catalyst for bi-reforming of methane. Results revealed that B$_2$O$_3$ and nickel.

Fig. 22 – SE micrographs of different sizes of SBA-15 silica: (A1 and A2) market grade SBA-15, (B1 and B2) SBA-15 synthesized by sol-gel method, (C1 and C2) SBA-15 synthesized by the hydrothermal method, adapted from Ref. [177].
Oxide particles were scattered on the outer area of SBA-15 support possessing higher surface area. Additionally, the authors observed an enhancement in catalytic activity that underwent a linear increase with temperature due to the endothermic behaviour of the catalysed process. They obtained H₂/CO molar ratio of 2.7 and 67.3% of CH₄ conversion at 799.8°C which was highly significant for downstream Fischer-Tropsch (FT) applications. Furthermore, XPS measurements revealed that B facilitated the adsorption of CO₂ through the electron transfer to the Ni cluster at the neighbourhood, thereby improving its catalytic activity. More importantly, analysis by XRD and Raman showed that boron doped catalyst was completely free from graphitic and amorphous carbon deposition. This was due to the incorporation of B into the octahedral sites occupied by NiO, resulting in inhibition of carbonaceous deposits.

Encapsulation of Ni particles in a suitable support material has been reported [181] to enhance the sintering resistance and coke resistance of Ni catalysts. The introduction of promoters namely rare-earth metals, metal oxides, alkaline earth and alkali metals is also one of the effective strategy to prevent the sintering of active sites/supports and enhance the coke-resistant ability of catalysts [182]. Chen et al. [153], synthesized highly dispersed mNi/xLa-Si catalysts by employing one pot sol-gel process by varying the weight percentages of nickel and lanthanum. These catalysts were subsequently applied to generate syngas during bi-reforming of CH₄. The authors observed that La addition enhanced the stability, coke resistance and catalytic activity of mNi/x Lanthanum–Silicon catalysts. The 17.5Ni/3.0LaSi catalyst prepared by employing poly (ethylene glycol) and ethylene glycol displayed the coke resistance, maximum selectivity and catalytic activity. One notable observation was that a H₂/CO ratio of about 2 was obtained when the carbon to sulphur ratio was maintained at 0.5, for the 17.5Ni/3.0LaSi catalyst, suitable for potential applications in Fischer-Tropsch synthesis.

Ni–Sn catalysts

Literature reports [183] have established that CeO₂–Al₂O₃ combinations are potential supports for reforming reactions. Furthermore, the redox properties of CeO₂ resulted in a significant improvement in the oxidation of deposits thereby enhancing the lifetime of the catalysts [184,185]. Furthermore, second metal addition promoted the formation of an active phase along with modification of the support. Bimetallic systems [186] have been known to display superior catalytic activity and increased the resistance of carbon formation in comparison to their own counterparts. The bimetallic combination of Ni–Sn has proved to be of considerable interest in reforming reactions. Additionally, the dispersion of nickel over the catalyst surface has been shown to be enhanced in the presence of Sn [187]. Straud et al. [188], synthesized a set of multicomponent advanced catalysts composed of Sn, CeO₂ and Ni/Al₂O₃. A schematic diagram representing the production of syngas in the presence of the investigated catalysts are shown in Fig. 23. The authors observed that addition of minute amounts of the investigated dopants improved the performance of methane reforming using CO₂. From their results it was noticed that a multicomponent Sn 0.02 Nickel/Cerium-Al catalyst showed excellent catalytic characteristic and remained active over a long period of 92 h. The catalyst also demonstrated an exceptional level of stability and conversion during BRM. Comparison of dry reforming and BRM reactions over the Sn0.02Ni/Ce—Al catalyst at 700°C revealed that H₂/CO ratio remained above 1.6 for 24 h. This suggested that the catalyst could generate high quality synthesis gas by introduction of water into the reforming mixture.

Therefore, the addition of water established the suitability of the Sn0.02Ni/Ce—Al catalyst for bi-reforming of CH₄. Furthermore, the results also revealed that presence of ceria created high storage capacities for oxygen and changed both the acidic and basic characteristics of support thereby enhancing the catalyst performance. The multicomponent...
catalyst Sn0.02Ni/Ce−Al proved to be active over period of 92 h and fared well over a range of space velocities and temperatures.

The remarkable level of stability and excellent conversions seen in the bi-reforming process has proved the versatility of Sn0.02Ni/Ce−Al catalyst which can be upgraded to variety of CO2 containing feed stocks.

**Effect of mineralisers on ZrO2−supported Ni catalysts**

Literature reports [189,190] have established the role of ZrO2 as an excellent support for reforming reactions because of its higher oxygen mobilisation, excellent thermal stability as well as its unique basic and acidic properties. The reinforced interaction between nickel and zirconium oxide makes zirconium oxide an effective support for a nickel based catalyst.

Agli et al. [191], reported that basic mineralisers affect the nucleation, rearrangement and crystallisation of gel made of zirconia during the synthesis of zirconium oxide. Hence, Zhao et al. [190], used the hydrothermal method [192,193] with various mineralisers along with L-arginine ligand-using wetness impregnation technique [194] to synthesise Ni/ZrO2 supports for bi-reforming of methane. Results from their studies revealed that the catalysts performance depended on texture of the zirconium oxide support and its morphology was also highly affected by the mineraliser amount. In this study, the authors synthesized Zirconium oxide support with a mole ratio sodium acetate/Zr4+ as 0.5 denoted by (SAc0.5). ZrO2−supported Ni catalyst was synthesized by employing sodium acetate where the mole ratio was $N_{SAC/Zr} = 0$ and also showed increased catalytic activity in comparison to catalyst i.e zirconium oxide synthesized using (SC) where the ratio was $N_{SC/Zr} = 0.5$. The authors established from the results that sodium acetate would serve as a suitable mineraliser for making an excellent ZrO2 support and also in terms of its stability and activity. Furthermore, the authors [190] observed that, in general, the addition of different amounts of mineralisers to ZrO2 supports had a significant effect on textural properties, which in turn affected the behaviour of the Ni-supported catalysts on zirconium oxide and also influenced the catalytic activity of the Nickel/Zirconium oxide catalysts during bi-reforming of methane.

The TEM micrographs in Fig. 24 show that all the investigated zirconium oxide supports resembled cobblestone like structure, with dimension of mesopores. Interestingly, reduction in pore volume and pore diameter along with expansion in the surface area was observed when the $S_{AC}/Zr$ molar ratio rose from 0.5 to 2.0. This provided the Ni/ZrO2 catalyst with a bigger crystallite size but also caused lower dispersion compared to Ni/ZrO2 (SAc0.5). From these studies, the authors noted lowering in the sintering resistance of nickel in Ni/ZrO2 (SAC2.0) catalyst than Ni/ZrO2 (SAc0.5), which was attributed to its imperfect interaction between nickel and zirconium oxide as established by H2-Temperature programmed reduction. Fig. 25 displays the catalytic characteristics of the prepared Ni/ZrO2 catalysts with varying amount of mineralizers present in the support.

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**Fig. 24** – Transmission electron microscopy images of Zirconium oxide supported with various types of mineralisers. (a) Zirconium oxide (Non), (b) Zirconium oxide (SAc0.5), (c) Zirconium oxide (SAc2.0) and (d) ZrO2 (SC0.5), adapted from Ref. [190].
The figure above revealed the initial activity in the order of Ni/ZrO$_2$ (SAC 0.5) > Ni/ZrO$_2$ (Non) > Ni/ZrO$_2$ (SAC 2.0) respectively. Nevertheless, the Ni/ZrO$_2$ catalyst without any acetate in the figure showed least stability among all the catalysts.

**Co-based catalysts**

Itkulova et al. [195], used Group VIII metals (0.25–1 wt %) along with alumina as a support to synthesise 5% bimetallic Co-based catalysts. The bimetallic Co constituted catalysts were
synthesized by impregnation of Al₂O₃ with solutions comprising of both cobalt and platinum compounds followed by a thermal treatment. The authors investigated the stability of these catalysts by varying the temperature (300–800°C), composition of feed mixture and space velocity (SV) (500–3000 h⁻¹) during bi-reforming as well as DRM. The authors observed that methane conversion was almost 100% at 750°C and 770°C for 5 wt % Co–Pt (9:1)/Al₂O₃ catalyst during both DRM and BRM. However, the results in Fig. 26 reveal a decrease in CO₂ conversion during the reforming process (Fig. 26 b) performed over the entire temperature range compared with DRM due to the suppression of CO₂–CH₄ reaction by the competing CH₄–H₂O interaction. The authors also observed a surge in the H₂/CO ratio from 0.84 to 1.0 when 20 vol % steam was added to the feed with equal amounts of CH₄ and CO₂.

The effect of Pt on BRM for various feed compositions was also investigated [195]. Results in Fig. 27 revealed an enhancement in the catalytic activity with increased platinum loading varying from 0.25 to 1 wt %. It was also noted that higher temperatures were necessary for the total conversion of CH₄ when there was a decrease in platinum content in the catalyst. It was established that addition of 10–30% steam had a marked effect on the conversion of CH₄, which further decreased the temperature required for conversion of methane and an increase in the ratio of H₂/CO.

Syngas produced during bi-reforming of methane over 5% Co–Pt/Al₂O₃ catalyst showed a desirable H₂/CO ratio >1. Pt

![Fig. 27 – Bar graphs signifying the role of 5 wt% Co–Pt/Al₂O₃ catalysts in bi-reforming conversion at 700°C (P = 0.1 MPa, S.V. = 1000 h⁻¹, H₂O = 20 vol %), adapted from Ref. [195].](image1)

Fig. 28 – (a) CH₄ and (b) CO₂ conversions in the CO₂ reforming of CH₄ only in the absence of water T = 799.85 C; P = 1 atm; CH₄:CO₂ = 2:1 on (a) Pt–ZrO₂ and (b) Pt–Ce–ZrO₂, adapted from Ref. [208].
was responsible for the formation and stabilization of highly dispersed and reduced bimetallic nanoparticles. Itkulova et al. [196] have investigated the role of 5% Co–Pt catalysts modified with 0.25–0.5 mass% Pt supported on alumina and modified with zirconia (ZrO₂) with amounts ranging from 5 to 10 mass% of Zr in the bi reforming process in the temperature range of 300–755 °C, and CO₂/CH₄ in 1:1 ratio. The results revealed that introduction of 20 vol% of steam into the CO₂–CH₄ feed was highly beneficial to the performance of the bi-reforming process. The improved performance of the 5%Co–Pt/Al₂O₃–ZrO₂ catalysts was attributed to the synergistic effect caused by the combination of two reactions i.e. dry and steam reforming of methane.

Pt–based catalysts

The major issue affecting commercialisation of the reforming process is coke formation, which causes deactivation of catalysts. The most effective way for decreasing coke formation is by coupling CO₂ with steam. It has been established that the support plays a significant role in suppressing formation of coke on Group VIII metals during the CO₂ reforming of CH₄ [197–200]. Several researchers [201,202], have demonstrated that the addition of promoter such as cerium led to a marked improvement in the activity of catalyst, stability and also decreased the sintering of ZrO₂ during calcination performed at high temperature. Literature reports [203–207], have also established that Pt–ZrO₂ catalysts demonstrate high stability and activity under extreme deactivated environment.

The activity for CO₂ reforming of methane has been investigated by Noronha et al. [208], on Pt–ZrO₂ (Fig. 28 a) and Pt–Ce–ZrO₂ (Fig. 28b) catalysts under CH₄:CO₂ molar proportion of 2:1. The authors noticed that the conversions of CH₄ and CO₂ decreased slightly in the presence of Pt–ZrO₂ catalysts (see Fig. 29).

Interestingly, after the removal of water the conversion of carbon dioxide and methane remained roughly constant, and at the same level as after interaction with water (Fig. 28a). A more drastic reduction in H₂/CO from 0.82 to 0.45 was also noticed after 22 h. However, the authors observed that DRM of CH₄ in presence of H₂O occurred differently with Pt–Ce–ZrO₂ Pt–ZrO₂ catalysts. Furthermore, CH₄ and CO₂ conversion underwent a decrease upon addition of water during the ongoing reaction on the Pt–ZrO₂ (Fig. 28 a) catalysts, with the decrease in conversion of CO₂ being significant. This was attributed to the reaction between excess H₂ and higher amount of CO₂ through water-gas shift reaction [209] in the reverse mode. The reduced stability observed in the Pt–ZrO₂ catalyst was related to the diminishing of oxygen vacancies on the support and oxidation behaviour. Furthermore, Temperature Programmed Oxidation analysis established that water addition enhanced the amount of mass of carbon deposited on the surface. Nevertheless, Pt–Ce–ZrO₂ exhibited excellent stability in presence of H₂O and its stability was due to higher number of vacancies caused by O₂ on the support. Both the Pt catalysts with and without Ce were relatively stable during CO₂ reforming of methane performed at 105 psig.

Porous Ni–based catalysts

BRM is considered to be an endothermic process which involves optimization of the temperature within the bed containing the catalyst and also a large amount of heat transfer into the reaction system occurs with the aid of external source. This suggests that catalysts used in these processes should have greater thermal conductivity, which can be

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**Fig. 29** — (●) CH₄ and (○) CO₂ conversions during CO₂ reforming of methane using water T = 1073 K; pressure = 1 atm; 15 mL/min H₂O,CH₄:CO₂ = 2:1; on (a) Pt–ZrO₂ and (b) Pt–Ce–ZrO₂. (Δ)CH₄ conversion in the steam reforming of methane on Pt–ZrO₂ catalyst, adapted from Ref. [208].
attained by employing metallic supports [210]. Several authors have reported the role of numerous catalysts that operate on these supports [211,212].

A promising under layer for Ni catalysts is MgO due to its high thermal stability, ability to decrease carbonisation and ability to easily form solid solutions with NiO, also aids in promoting the dispersion of reduced nickel crystallites [213]. There have been numerous studies on supported Ni catalyst with a MgO underlayer: supports on metal foams [213], porous Ni plate [212] and Al₂O₃-SiO₂ [214].

Danilova et al. [215], reported the synthesis of thick porous Ni ribbon (pNirb) with a MgO underlayer supported by Ni catalyst on the top. The under layer constituting magnesium oxide was synthesized by packing of the support with Mg(NO₃)₂ solution, then subjected to drying followed by calcination performed at 550 °C in presence of air designated as Support 1 and the calcination performed in flowing H₂ was known as Support 2. The catalyst was reduced under the atmosphere of flowing H₂ at 750 °C was termed catalyst I and the catalyst reduced at 900 °C was termed catalyst II. Use of these supported catalysts resulted in 49% and 56% conversion of CH₄ with support 1 and support 2, respectively. The greater activity of support 2 in comparison to support 1 was attributed to efficient dispersion of Ni crystallites that was produced from solid solution reduced in presence of reaction medium. The authors further remarked that catalyst II (2.7% Ni/(p Nirb +8.6% MgO) and 4.0% Ni/(pNirb +10.4% MgO) exhibited excellent stability for CH₄ conversion over a period of 18 h compared with catalyst I (4.6% Ni/(pNirb +6.0% MgO) and 4.6% Ni/ (pNirb + 6.0% MgO) under the following conditions: GHSV = 62.5 L h⁻¹, CH₄/CO₂/H₂/N₂ = 35/23/39/3).

Fig. 30 – Field Electron-Scanning electron images of pure (a) ZnLaAlO₄ support, (b) 3%Ru/ZnLaAlO₄, (c) 3%Pt/ZnLaAlO₄, (d) 10%Ni/ZnLaAlO₄ and (e) 10%Ni/c-Al₂O₃ nanocatalysts, adapted from Ref. [218].
Recently, nanocatalysts have attracted much attention [38]. Nanocatalysts show better selectivity, outstanding stability and higher activity, due to their special crystal structure, higher amount of surface atoms in comparison to their micro-sized counterparts and larger specific surface area [216]. Many works [217] have shown that catalyst preparation with larger surface area affected significantly the physical and chemical properties, which can only be achieved by a nanocatalyst.

Khani et al. [218], synthesized novel M/ZnLaAlO4 nanocatalysts where M consists of 3%Ru, 10% Ni and 3% Pt using wet impregnation technique and characterised these by using TPR, FT-IR, TEM, XRD, FE-SEM, Thermogravimetric analysis and Differential Thermal Analysis. The authors evaluated the catalytic characteristics of the these catalysts in the SRM, DRM and BRM of methane at temperatures varying from 600 to 800 °C at different gas hourly space velocities values of 10,500, 7000, 3500 h⁻¹. TGA revealed that the nanocatalysts namely 3% Pt/ZnLaAlO4 and 3% Ru/ZnLaAlO4 did not exhibit any coke formation during SRM, which was also supported by FE-SEM (Fig. 30).

The authors noted that an increase in temperature during the bi-reforming (BRM) of methane increased the CH₄ conversion, however decreased conversion of CO₂ (Fig. 31). Furthermore, Fig. 30 shows that 3% Ruthenium/ZincLaAlO₄ demonstrated the lowest activity while 10% Ni/γ-Al₂O₃ showed marked activity for CO₂ conversion. Additionally, among the four tested catalysts (Figs. 30), 3% Ru/ZnLaAlO₄ displayed the highest catalytic CH₄ conversion. The authors observed a reduction in H₂/CO ratio with the rise in temperature from 600 to 700 °C for the investigated catalysts used in the bi-reforming process. The authors observed 3% Ru/ZnLaAlO₄ a H₂/CO of 2.0, while 3% Pt/ZnLaAlO₄ had a H₂/CO of 1.3.

Fig. 31 – CH₄ and CO₂ percentage of conversion, Hydrogen yield and H₂ and CO ratio in the bi-reforming reaction having GHSV = 10,500 h⁻¹ using various nanocatalysts, adapted from Ref. [218].

Fig. 32 – Bi-reforming of methane: Effect of H₂O (A) Mole-fraction of CH₄ (B) Mole fraction of CO₂ as a measure of temperature over Ru/ZrO₂-La₂O₃ as the catalyst, adapted from Ref. [221].
2.1 at a temperature of 800 °C, while for 10% Ni/γ-Al2O3 catalyst a lowest value of 1.6 was obtained. 3% Ru/ZnLaAlO4 was considered as the potential catalyst for potential applications based on its resistance to formation of carbon and catalytic efficiency in BRM, dry reforming and SRM. TPR profiles of the nano-catalysts showed lowest reduction temperatures at the onset for 3%Pt/ZnLaAlO4, 10% Ni/ZnLaAlO4, 3%Ru/ZnLaAlO4 at 264°C, 333°C and 230°C respectively.

Potdar et al. [219], noted that the nanocatalyst Ni–Ce–ZrO2 synthesized by employing co-precipitation technique exhibited excellent coke resistance and highly stable catalytic activity attributed to the greater mobility of oxygen in the carbon dioxide reforming of methane and higher surface area. Roh et al. [212], demonstrated that higher stability and activity of Ni/MgO–Al2O3 catalyst with nano dimensions was due to the beneficial effects of magnesium oxide (MgO) namely stronger interaction between nickel and support, basicity, enhanced steam adsorption and also the crystallite size of nanosized NiO. Sadykov et al. [220], investigated the role of catalysts made of nanocomposites in the bi-reforming reaction. Nanocomposite catalysts consisting of nickel particles implanted into an oxide matrix of Yttrium or Scandium-stabilised Zr (YSZ, ScSZ) mixed with doped Ce–Zr oxides or Lanthanum–Manganese–Chromium–Oxygen (La-Pr-Mn-Cr-O) perovskite along with promoters namely Pd, Ru and Pt were synthesized via different routes [101].

**Ruthenium based catalysts**

Soria et al. [221], investigated the role of H2O along with Ru/ZrO2–La2O3 catalyst placed in a fixed-bed Palladium reactor with membrane during bi-reforming of methane. The authors observed that addition of H2O along with CO2 during the reforming reaction significantly affected the catalyst activity. Fig. 32 shows that the presence of small concentrations of H2O (1–2 vol %) did not affect the conversion of CH4 appreciably, but an increase in steam to 5 vol % did result in increased CH4 conversion. Furthermore, the CO2 conversion gradually decreased with increasing concentration of H2O from 1 to 5 vol %, and the CO2 conversion exhibited lower values below 330, 375 and 450°C for water content ranging from 1 to 5 vol %. Furthermore, at a designated temperature, the composition of syngas (H2/CO ratio) was altered with the change in the concentration of H2O feed.

The authors [221] also investigated the stability of the Ru/ZrO2–La2O3 catalyst during both bi-reforming and carbon dioxide reforming of methane at 500°C. It was observed that without steam presence in the reaction feed, the Ru/ZrO2–La2O3 catalyst was very stable and 15% of deactivation was noticed. Fig. 33 shows that the addition of water had a marked effect on the stability, which increased in a significant manner with the increase in steam amount. The deactivation values were 5%, 11%, 8% for addition of 5, 1, 2 vol % H2O, respectively.

Research has indicated that steam addition to the CO2 during the bi-reforming reaction and formed strontium carbonate (SrCO3), which possessed the unique ability of inhibiting carbon sources by producing La2O2CO3. The addition of Sr particles covered the support sites thereby resulting in large-sized Ni particles by decreasing the interlinkage between the support and active metals. The authors [223] recommended using a small amount of Sr in the perovskite-based catalyst for obtaining greater resistance to carbon deposition. Furthermore, larger Ni particles were formed, with diameters of 30.8, 29.9, 27.6 nm for concentrations of 10%, 50%, 30% SrO containing La2O3–NiO4 catalysts in comparison to a La2O3–NiO3 particle size of 13.5 nm.

Kim et al. [224], investigated the bi-reforming reaction of methane employing mixed oxides of La, Sr and Ni packed on β-SiC catalysts loaded with Al2O3 for assessing the conversion
of carbon dioxide at a certain concentration of Al₂O₃ used as a modifier. The authors found that though all the investigated tested catalysts provided close activation energies values, the increase in dispersion of aluminium oxide on silicon carbide with 10 wt % Al₂O₃ as modifier was in agreement with the higher distribution of perovskite containing La₂NiO₄ crystallites. Additionally, larger amounts of adsorption of carbon dioxide on the efficiently distributed basic Sr and La oxides were also responsible for enhanced carbon dioxide conversion. CO₂ and CH₄ conversion also correlated well to the IA₁/INi ratios obtained from XPS analyses.

**Ni foam as the catalytic support**

Park et al. [225], have described the use of various foam catalyst embedded with metals to enhance the heat transfer of reaction during BRM process. The authors characterised heat transfers based on the Nusselt number and also used a pellet shaped catalyst to improve the heat transfer of the foam catalyst. The results revealed that the Nusselt number of foam catalyst packed with metals was larger than the pellet catalyst used conventionally. Additionally, uniform temperature distribution was noticed in the reformer throughout the catalyst bed along with the foam catalyst.

![Photographic image of the synthesized metallic foam catalyst: (a) uncoated Ni foam, (b) γ-Al₂O₃/Ni foam, (c) calcined Ni/γ-Al₂O₃/Ni foam, (d) H₂ reduced Ni/Al₂O₃/Ni foam, adapted from Ref. [225].](image)

![Methane, carbon dioxide conversion using the uncoated Al₂O₃ bead, uncoated Ni foam, Al₂O₃/Ni foam and Ni/Al₂O₃/Ni foam, adapted from Ref. [225].](image)
Images of the various metallic foam catalysts are shown in Fig. 34.

Fig. 35 shows that the uncoated Al\textsubscript{2}O\textsubscript{3} and bare Ni foam were reactive without Ni catalyst loading. Additionally, the bare Ni foam displayed greater methane conversion than the uncoated aluminium oxide. The results established that the Ni foam exhibited a significant role in improving heating characteristics of the catalyst bed and mass transfer inside the reactor. However, after wash coating of a layer of Al\textsubscript{2}O\textsubscript{3} on the nickel foam, the conversion of carbon dioxide and methane increased to 34% and 69.1% and, respectively.

The syngas flow rate along with molar ratio of hydrogen/ carbon monoxide in presence of Nickel/Al\textsubscript{2}O\textsubscript{3}/Nickel foam, uncoated Nickel foam, uncoated Al\textsubscript{2}O\textsubscript{3} bead and Al\textsubscript{2}O\textsubscript{3}/Ni foam are shown in Fig. 36. The syngas flow rate exhibited a similar behaviour both for carbon dioxide and methane conversions. Nevertheless, the H\textsubscript{2}/CO molar ratio was different and furthermore molar ratio of H\textsubscript{2}/CO of uncoated Ni and uncoated Al\textsubscript{2}O\textsubscript{3} bead was less than 2.0. The metallic foam catalyst is potentially useful for GTL-FPSO applications based on the enhanced mechanical properties of the catalyst and compactness of the reformer. Additionally, higher selectivity levels and activity are associated with nickel inside the coating layer, which serves as active sites for methane, water and carbon dioxide.

**Carbide-based catalysts**

Brush et al. [181] reported the ability of Ni/Mo\textsubscript{2}C to catalyse the bi-reforming of methane. The authors noted that by altering the ratio of carbon dioxide: water, the resulting Hydrogen: Carbon monoxide (H\textsubscript{2}:CO) ratio could be changed from 0.91 to 3.0, which covers a wide range of H\textsubscript{2}:CO ratios common to various hydrocarbon syntheses. Most importantly, the catalytic activity changed from very high (50% conversion) to very low (10% conversion) within a time interval of 10 min. Additionally, for various inlet feed compositions similar performance was exhibited by the catalyst. However, enhanced activity was followed by greater deactivation shortly after the exposure to stream.

Claridge et al. [226], synthesized Mb and W carbide materials of larger surface area to assess the performance of carbide catalysts formed from non-metals for various CH\textsubscript{4} reforming reactions including bi-reforming. Their study revealed that carbides activity was similar to those of iridium and ruthenium catalysts used in reforming of methane.
Nevertheless, conversion values were in agreement with the values obtained during thermodynamic equilibrium. HRTEM images revealed the absence of deposited macroscopic on the catalysts during the reforming process.

Conclusions and future outlook

The present review article demonstrates a comprehensive review of various catalysts, including Ni, Co, Rh and Pt-based catalysts, used for BRM. It also describes the role of various promoters and supports on the conversion efficiencies of CH4, CO2 and H2/CO ratio. Ni catalysts supported by smaller nanoparticles of Ce−ZrO2 ZrO2, MgO were observed to be extremely stable and active for BRM processes. The degree of coke formation was dependent on each investigated catalyst. Coke formation was found to be more severe in commercial Ni/MgAl2O4 catalyst than Ni/MgO−Al2O3 catalyst, which was attributed to higher dispersion of Nickel over MgO−Al2O3.

Bi-reforming of methane over a catalytic nickel membrane for the GTL (gas to liquid) process produced a very high conversion of methane in the range of 92.7–96% above 973 K, when the CO2/H2O feed ratios were in the range of 0–1.0. GTL process possessed two advantages. One was that carbon formation was reduced due to the oxidation of carbon precursor species and a desirable H2/CO was achieved by adjusting CH4/H2O/CO2 ratio in the feed stream. Cerium containing Ni/MgAl2O4 catalysts synthesized by both co-preparation and impregnation technique exhibited higher metal dispersion than Ni/MgAl2O4 alone and showed marked reducibility at lower temperatures around temperature 550 °C as confirmed by XPS since the redox properties of Ce4+/Ce3+ resulted in easier gasification of the settled coke on the surface of the catalyst and also helped in storage and delivering of active oxygen thereby enhancing the dispersion of Ni. The catalyst Ni/γ−Al2O3 promoted very higher conversion of carbon dioxide (82.4%) and methane (98.3%) when subjected to bi-reforming of methane for 200 h since the Ni/Al2O3 catalyst exhibited characteristics such as high metal dispersion, high catalytic activity large specific surface area, and stronger metal support interaction respectively. Presence of MgO in 20 wt % MgO/Ni catalyst was quite effective in preventing coke formation due to the formation stable MgAl2O4 spinel phase at higher temperatures. The presence of CeO2 in Ce1−x−Zr1−x−ray−Al2O3 catalystic systems caused a marked improvement in redox properties, thermal stability, and promotion of metal dispersion and also enhanced the oxygen storage ability of CeO2. A drastic reduction in carbon deposition from 25.96% to 1.08% was observed for a feed composition of CH4: CO2: H2O = 1.0:0.55:0.55 when CO2 reforming was performed in conjunction with steam reforming process in presence of NiO−CaO catalyst due to its high selectivity, activity and productivity in the oxidative conversion of methane to synthesis gas. Nickel/Santa Barabara Amorphous −15 (SBA-15) exhibited enormous resistance both towards sintering and coking. 10% Nickel/3% MgO/Santa Barabara Amorphous 15 catalyst demonstrated higher catalytic performance after reaction for 620 h since the mesoporous SBA-15 support possessed uniform mesopores with thick framework walls, high thermal stability and wide specific surface area. Bimetallic systems such as Sn 0.02 Nickel/Cerium−Al catalyst displayed superior catalytic activity, increased the resistance of carbon formation and remained active over a long period of 92 h in comparison to their own counterparts. The remarkable level of stability and excellent conversions seen in the bi-reforming process has proved the versatility of Sn0.02Ni/Al catalyst which could be upgraded to variety of CO2 containing feed stocks. Ni-based catalysts supported on mesoporous MgO−Al2O3 resembling a Mg−Al hydrotalcite structure with Mg/Al ratio of 1 demonstrated excellent conversion efficiencies for CH4 (93.7%) and CO2 (75.2%) and higher resistance to coke formation due to its basic property, enhanced steam as well as CO2 adsorption, strong Ni to support interaction of these catalysts. The excellent catalytic performance of Ni 30 wt % SiO2 55 wt % MgO catalyst was ascribed to its acidic strength, enhanced basicity and structural stability under high temperatures. NdCOO3 perovskite-type mixed-oxide catalysts proved to be highly efficient for carbon-free bi-reforming process. Pt−Ce−ZrO2 catalyst exhibited excellent stability in presence of H2O and its stability was attributed to the greater number of O2 vacancies present in the support. Lanthanum promoted catalysts exhibited greater nickel dispersion than Ni/MgAl2O4 catalyst due to their enhanced interactions between the metal and support. Ni−2.5La/MgAl2O4 catalyst showed maximum sinter stability and activity due to its enhanced nickel dispersion and surface area.

It is highly essential to develop Ni-based catalysts containing bi-metallic and tri-metallic configuration since Ni displayed stronger stability and enhanced activity. However, the biggest constraint in this approach is the coke formation. Bi-reforming process is endothermic and would require higher activation energy to achieve the synthesis. Future studies should be undertaken to design an appropriate bi-metallic and tri-metallic catalyst that can be suitable at lower temperatures. Furthermore, the approach towards catalyst formation has a significant influence on the catalyst’s capability. Therefore, selecting a suitable catalyst and its synthesis technique can provide improved SMSI, superior activity, enhanced Ni dispersion on the catalytic support and stability against coke formation.

Among the evaluated inlet feed compositions, conducting bi-reforming process under a stoichiometric feed composition (CH 4: CO 2: H 2 O = 3:1:2) is considered the ideal one for selective production of syngas within the operating temperature of 750–800 °C range. One of the major drawback associated with nano-based catalysts is that the up scaling of catalyst preparation from laboratory batches to continuous industrial production. Henceforth, development of reproducible and economical synthetic strategies is imperative for linking all advantages of nano-based catalysts to large-scale metgas generation facilities.

Nomenclature

| Acronym | Description                        |
|---------|------------------------------------|
| XPS     | X-ray photo electron Spectroscopy  |
| XRD     | X-ray diffraction                  |
| FT      | Fischer-Tropsch Synthesis          |

References
pNirb Thick porous Nickel carbon
H2-TPR Hydrogen Temperature Programmed Reduction
CO2–TPD Carbon dioxide Temperature Programmed Desorption
TEM Transmission electron Microscopy
DRM Dry reforming of methane
GHG Greenhouse gas emissions
SRM Steam reforming of methane
POM Partial oxidation of Methane
BRM Bi-reforming of methane
CRM Carbon dioxide reforming of methane
SEM Scanning Electron Microscopy
TPR Temperature Programmed Reduction
GHSV Gas Hourly Space Velocity
SBA-15 Santa Barbara Amorphous-15
EISA Evaporation Induced Self-assembly
WHSV Weight hourly space velocity
FTIR Fourier Transfer Infrared Spectroscopy
TGA Thermogravimetric analysis
DTA Differential Thermal Analysis
Ceria Cerium (IV) Oxide
Zirconia Zirconium dioxide
SGM Sol-Gel method
CG Commercial method
HTM Hydrothermal Method
GTL-FPSO Floating Production, Storage and Offloading

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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