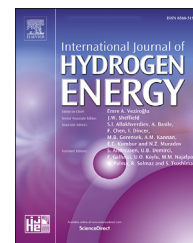


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Review Article

A review on bi/polymetallic catalysts for steam methane reforming



Siqi Wang, Seyed A. Nabavi, Peter T. Clough*

Energy and Sustainability Theme, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK

HIGHLIGHTS

- Recent research on bi/polymetallic catalysts for (SE)SMR is reviewed.
- The catalysts are evaluated based on activity, stability, and physical properties.
- Metal loading and material structure greatly influence catalytic performance.
- Future research includes evaluation of sulphur- and sintering-resistant abilities.

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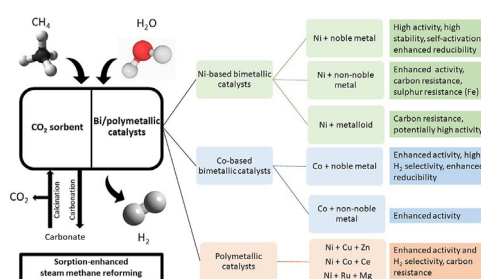
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GRAPHICAL ABSTRACT



ABSTRACT

Blue hydrogen production by steam methane reforming (SMR) with carbon capture is by far the most commercialised production method, and with the addition of a simultaneous in-situ CO₂ adsorption process, sorption-enhanced steam methane reforming (SESMR) can further decrease the cost of H₂ production. Ni-based catalysts have been extensively used for SMR because of their excellent activity and relatively low price, but carbon deposition, sulphation, and sintering can lead to catalyst deactivation. One effective solution is to introduce additional metal element(s) to improve the overall performance. This review summarizes recent developments on bi/polymetallic catalysts for SMR, including promoted nickel-based catalysts and other transition metal-based bi/polymetallic materials. The review mainly focuses on experimental studies, but also includes results from simulations to evaluate the synergistic effects of selected metals from an

Abbreviations: at.%, Atomic percentage; CCUS, Carbon capture utilization and storage; CL-SMR, Chemical looping steam methane reforming; DFT, Density Functional Theory; SESMR, Sorption-enhanced steam methane reforming; SMR, Steam methane reforming; WGS, Water-gas shift reaction; wt.%, Weight percentage; YSZ, Yttria-stabilized zirconia.

* Corresponding author.

E-mail address: P.T.Clough@cranfield.ac.uk (P.T. Clough).<https://doi.org/10.1016/j.ijhydene.2023.01.034>

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Sorption-enhanced steam methane reforming
Hydrogen production
Syngas

atomic point of view. An outlook is provided for the future development of bi/poly-metallic SMR catalysts.

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Contents

Introduction	15880
Nickel-based bimetallic catalysts	15881
Nickel-based catalysts promoted by noble metals	15881
Nickel-based catalysts promoted by non-noble metals	15883
Nickel-based catalysts promoted by metalloids	15884
Cobalt-based and other transition metal-based bimetallic catalysts	15885
Polymetallic catalysts	15886
Conclusions and outlook	15889
CRedit author statement	15889
Funding	15889
Data access statement	15889
Declaration of competing interest	15889
References	15889

Introduction

In recent years, hydrogen has gained increasing attention as an alternative to fossil fuels, enabling net zero targets to be realized. As stated in the 2021 UK Hydrogen Strategy [1], the UK is aiming for a total of 10 GW of low-carbon hydrogen production capacity by 2030 to decarbonize vital industries and provide clean energy across the heat, power, and transport sectors. This requires considerable effort in scaling up and optimizing carbon capture and storage systems as well as new hydrogen production processes, such as sorption-enhanced reforming.

Hydrogen can be produced from a variety of renewable and non-renewable sources, and can be divided into three categories depending on its production pathway.

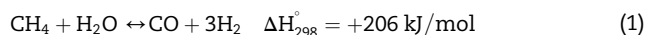
- Black/Grey/Brown hydrogen: from fossil fuel-based production (coal, natural gas, and lignite, respectively) with CO₂ released to the atmosphere.
- Blue hydrogen: from fossil fuel-based production with carbon capture, utilization, and storage (CCUS).
- Green hydrogen: from renewable sources, commonly electrolysis-based production.

Different hydrogen production pathways using renewable sources have been investigated, including water electrolysis [2], thermochemical (pyrolysis and gasification), or biological conversion (fermentation and photolysis) of biomass [3]. However, various techno-economic studies have demonstrated that compared to these processes, fossil fuel reforming with CCUS remains the most cost-competitive option with the highest hydrogen production efficiency [4–6]. Steam reforming, partial oxidation, and autothermal reforming are three

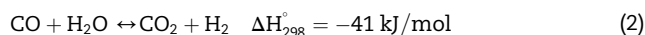
main fossil fuel reforming technologies for hydrogen production, among which the steam reforming of methane (SMR) is by far the most deployed method. Although SMR is a mature technology, one of the most significant problems is its high CO₂ emission. It is estimated that without CCUS, hydrogen from SMR has an emission factor of 222–325 gCO_{2eq} per kWh of H₂ (10 tCO₂/tH₂) [4,7].

Apart from the traditional approach of employing a downstream amine scrubbing process, an alternative option to mitigate carbon emissions is adding a simultaneous carbon capture step to the conventional SMR process. A novel hydrogen production technology, known as sorption-enhanced steam methane reforming (SESMR), combines the conventional SMR process with a simultaneous in-situ absorption of CO₂ using a solid sorbent (usually CaO). The main reactions involved in the SESMR process are as follows [8].

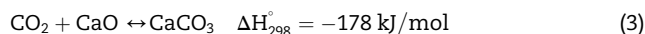
Steam reforming of methane



Water-gas shift (WGS) reaction



CO₂ sorption and sorbent regeneration



Overall equation for SESMR



In comparison to the traditional SMR process, SESMR enables the removal of CO₂ from the reaction zone, which shifts the equilibrium towards the product side, enhancing the production of hydrogen. The high-purity CO₂ stream released

from the sorbent regeneration step can also be easily separated from the sorbent, and transported or stored for further use. The sorption enhanced steam reforming process has been applied to other feedstocks as well, including phenol [9], glycerol [10], ethanol [11], and biomass [12]. In general, the CO₂ sorbent is combined with active catalytic metal(s) to form a bi-functional material, using alumina, perovskite or mayenite as the structural support. Since both SMR and SESMR require the use of catalysts to proceed, and the types of catalysts used for both processes are in general identical, they will be reviewed holistically in this paper.

The main reaction steps of SMR are listed in Table 1, including the dissociative adsorption of the reactants, dehydrogenation and bond reformation steps. It is generally agreed that the activation of the first C–H bond of the CH₄ decomposition step (step 1) is the rate-determining step of SMR [13–15]; but at lower temperatures ($T < 500\text{ }^{\circ}\text{C}$), the CO formation step (step 7) becomes dominant [14]. The energy barrier for C–H bond activation over Ni surface is relatively low, and at the same time, the adsorption of C*, H* and O* is not so strong that the species cannot react off the surface easily. Nickel is also widely employed commercially due to its low price and high availability. However, Ni-based catalysts are prone to sintering and coke formation [16,17], hydrogen reduction of nickel-based catalysts before the reforming process is also necessary for activating the material. It is, therefore, of interest to investigate the anti-sintering ability, coke resistance, as well as the reducibility and self-activation ability of SMR catalysts.

Apart from nickel, noble metals (Rh, Ru, Pd, Pt, and Ir) are also promising candidates for SMR because of their excellent catalytic ability and resistance to carbon formation. Currently, there is no definitive conclusion as to how the noble metals are ordered regarding their catalytic activity for SMR, however, several experimental [18,19] and numerical [20,21] studies reported that the catalytic activity of noble metals follows the order of Rh ~ Ru > Ir > Pt ~ Pd. Despite their advantages, noble metal-based catalysts are limited by their high prices.

One way to maintain the excellent performances of noble metals while maintaining a reasonable price is by combining two or more types of metals, using cheap transition metals (usually nickel or cobalt) as the base and noble metals as promoters. Bi/polymetallic catalysts have gained increasing attention in recent years, and the synergistic effect between commonly used metal elements has been investigated experimentally and numerically. Numerical studies focus on

the reaction pathway, activation energies of certain reaction steps (in particular the C–H bond cleavage of the CH₄ decomposition step), as well as the adsorption energies of atomic or molecular species on the catalyst's surface, which are indicators of the material's catalytic activity and stability. Some materials were also tested experimentally, usually in lab-scale reactors, and evaluated based on their methane conversion ability, hydrogen yield, etc. To the best of the author's knowledge, there has been no literature that systematically summarizes the bi/polymetallic catalysts that have been employed in (SE)SMR. The aim of this review is therefore to provide an overview of the bi/polymetallic catalysts that have been tested for (SE)SMR, to summarize their advantages and limitations, and to identify the gap in current (SE)SMR catalyst development for future studies.

Nickel-based bimetallic catalysts

Nickel-based catalysts promoted by noble metals

Amongst the eight noble metals, platinum group metals (including Rh, Ru, Ir, Pt, and Pd) have the highest SMR activity and are most commonly used as a promoter for Ni-based catalysts. Their catalytic performance arises from the partially filled *d*-subshells – electrons can be easily added to or removed from these orbitals, resulting in an optimal interaction between the metal surface and the gas-phase adsorbate. A lower degree of *d*-band filling leads to the too-strong adsorption of both reactants and reaction products on the metal surface, which easily blocks the active catalytic surface. On the other hand, with a higher degree of filling, the metal surface does not interact strongly enough with the reactants, which is the case for both Ag and Au. This results in a relatively low catalytic activity but a more stable and clean metal surface, which is why Ag and Au are usually added for their coke-resistant property. There is currently no literature available regarding the use of Os as an SMR catalyst, possibly due to its tendency to form a volatile and toxic oxide – OsO₄ [18].

Ru–Ni catalysts have been tested under lab-scale experimental SMR conditions by Jeong et al. [22] to study the effect of doping Ru over Ni/Al₂O₃ and Ni/MgAl₂O₄. They concluded that adding a small amount of Ru (0.5 wt.%) greatly suppressed coke formation on the catalyst surface and facilitated NiO reduction. The coke-resisting ability of Ru was studied on an atomic scale using Density Functional Theory (DFT) study [23]. It was demonstrated that when the noble metal was added, the activation energy of the CHO*-producing step (step 5 shown in Fig. 1) was significantly lower than that of the C* and H*-producing step (step 4), meaning CO production was favoured over carbon deposition.

Results also showed that Ru-promoted Ni catalysts were able to self-activate at a temperature of 700 °C without any pre-reduction using hydrogen, which is beneficial from an economic and process operation point of view [24,25]. Ni-based catalysts doped with small (0.5 wt.%) or even trace amounts (0.05 wt.%) of Ru showed good self-activation properties without pre-reduction, and achieved a higher CH₄ conversion rate compared to monometallic Ru or Ni catalyst. Ru decreased the reduction temperature of Ni by inducing

Table 1 – Main reaction pathway of SMR.

Reaction step	No.
$\text{CH}_4(\text{g}) + 2^* \leftrightarrow \text{CH}_3^* + \text{H}^*$	1
$\text{H}_2\text{O} + 2^* \leftrightarrow \text{OH}^* + \text{H}^*$	2
$\text{OH}^* + 1^* \leftrightarrow \text{O}^* + \text{H}^*$	3
$\text{CH}_3^* + 1^* \leftrightarrow \text{CH}_2^* + \text{H}^*$	4
$\text{CH}_2^* + 1^* \leftrightarrow \text{CH}^* + \text{H}^*$	5
$\text{CH}^* + 1^* \leftrightarrow \text{C}^* + \text{H}^*$	6
$\text{C}^* + \text{O}^* \leftrightarrow \text{CO}^* + 1^*$	7
$2\text{H}^* \leftrightarrow \text{H}_2(\text{g}) + 2^*$	8
$\text{CO}^* \leftrightarrow \text{CO}(\text{g}) + 1^*$	9

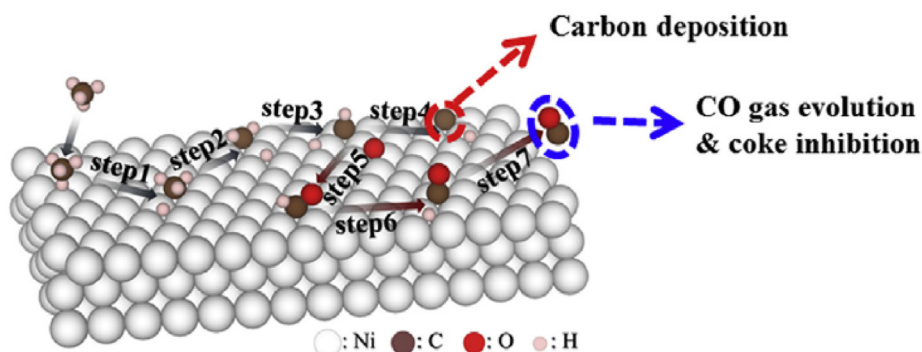


Fig. 1 – Reaction mechanism on Ni(111) and Ni–Rh/Ni–Ru (111) systems. Reprinted from Ref. [23] with permission from Elsevier.

hydrogen spill over on the Ni surface, a process in which H_2 molecules disassociate on the noble metal surface to H species and diffuse into Ni via the catalyst support.

Similar to Ru, the addition of Rh was also found to facilitate Ni reduction and produce a synergistic effect [26,27]. The bimetallic catalyst (with 0.2 wt.% Rh) showed higher activity compared to the linear combination of monometallic Rh or Ni catalyst. This was attributed to the enhanced textural properties of the bimetallic catalysts – the exposed metallic surface area and metal dispersion of the bimetallic catalysts, measured by CO chemisorption, were greatly promoted by the addition of Rh, and the increase was more significant with a higher Rh loading. The same synergistic effect was observed by Morales-Cano et al. as well [28], who studied the promoting effect of Ru, Rh, and Ir on Ni/ α - Al_2O_3 catalyst. The catalysts were also aged for 240 h at 800 °C with an S/C ratio of 6 to induce the sintering of Ni particles. The activity of the aged Ni–Rh and Ni–Ir was found to be significantly higher than the aged monometallic catalysts, proving their ability to resist Ni sintering. This ability was attributed to the migration and diffusion of Ni into the Face Centred Cubic structure of Rh and Ir during the aging process, which enabled the formation of Ni–Rh and Ni–Ir alloys, and retained the high surface area of the materials.

The optimal loading of noble metals in Ni-based catalysts was also investigated. Katheria et al. [29] tested a series of Ni/ $MgAl_2O_4$ catalysts with Rh concentration varying from 0.1 to 1 wt.%. Results showed that 0.1 wt.% of Rh was sufficient to increase CH_4 conversion by 20%, whereas a further increase in Rh concentration did not have a significant effect. A higher metal loading does not necessarily mean a better catalytic ability due to the less evenly distribution of active metal in the support. This observation was also verified by testing a series of Ni/ $MgAl_2O_4$ catalysts with Pt loading varying from 0.01 to 1 wt.% [30,31]. Both studies reported that a Pt loading of 0.1 wt.% resulted in the highest catalytic activity. Further increase in Pt loading led to a decrease in both catalytic activity and stability. Results from the physical characterization of the materials showed that the highest surface area and maximum dispersion of active metal were achieved with 0.1 wt.% Pt loading, whereas higher Pt concentration, resulted in agglomeration on the material surface.

Chaichi et al. [32] synthesized a novel supportless Ni–Pd–carbon nanotube material and compared its performance with Ni and Ni–Pd catalysts under SMR conditions. The addition of Pd facilitated the reduction of metallic oxides, whereas both Pd and carbon nanotube increased the specific surface area. The resultant CH_4 conversion of the Ni–Pd–carbon nanotube material was 22% higher than the monometallic Ni/ MgO catalyst. Reducibility enhancement by Pd was also reported by Batebi et al. [33] in a test of Ni–Pd/ Al_2O_3 for combined steam and CO_2 reforming of methane. By adding Pd, the reduction degree was increased from 69% to 83%, leading to higher CH_4 conversion and H_2 yield while reducing coke deposition. Bimetallic Ni–Pd materials have also been tested for the oxidative SMR process [34–38]. Results from these studies demonstrated that the addition of Pd promoted the reduction of Ni, Pd–Ni alloy was also found to form preferentially on the material surface, contributing to its high activity and coke resistance.

Li and Miyata conducted a series of tests to study the doping effect of Ru [39,40], Rh [41,42], Pt [42–44], and Pd [42] on Ni/ $Mg(Al)O$ catalysts in a daily start-up and shut-down operation of SMR under steam purging. As was presented previously, the addition of all four types of promoters improved the reducibility of the catalyst by decreasing Ni reduction temperature and increasing the amount of hydrogen uptake on Ni. Ru, Rh and Pt were also capable of suppressing the deactivation of the catalyst due to Ni oxidation, which was attributed to the self-regeneration of Ni^0 from Ni^{2+} assisted by hydrogen spill over on the noble metal surface and the reversible reduction-oxidation between Ni^0 and Ni^{2+} in the $Mg(Ni, Al)O$ periclase. Self-activation without any reduction treatment of Rh-, Pt-, and Pd–Ni bimetallic catalysts was also observed during the daily start-up and shut-down operation. Compared to the complete deactivation of the pure Ni catalyst after the first steam purging, the CH_4 conversion of the bimetallic catalysts was kept at the value of thermodynamic equilibrium even after 4 cycles of steam purging. The self-activation and self-regeneration properties of these bimetallic materials proved Ru, Rh, Pt, and Pd to be useful additives to the conventional Ni-based catalysts.

Although the reactivity of monometallic Ag and Au is relatively low, they have also been tested as promoters for Ni-based SMR catalysts due to their excellent stability. DFT-based

studies [45,46] showed that the Ag-doped Ni surface is less prone to carbon deposition – the threefold Ag–Ni–Ni adsorption site is unstable for carbon atoms. Carbon atoms initially positioned at these sites will therefore move to the adjacent Ni–Ni–Ni site, which has lower adsorption energy. These negative interactions between the carbon atom and the Ag–Ni alloy surface indicate that Ag can be added as a coke-resistant promoter, which was also validated against experimental findings [47–49]. Both research teams studied the promoting effect of Ag (0.03–1 wt.%) on Ni/ γ -Al₂O₃ and concluded that even the minimum Ag loading of 0.3 wt.% could reduce carbon deposition significantly. However, this also compromised the catalytic activity of the material, which decreased by 25% compared to monometallic Ni catalysts. This is due to the fact that Ag atoms are energetically favoured to replace Ni atoms on the step edges, which are the most active sites for methane decomposition, compared to the terrace sites [50]. Similar properties were found in Au-doped Ni catalysts. Both computational [51–53] and experimental [54,55] studies suggested that the overall catalytic activity of Au–Ni was affected by the higher energy barrier for C–H bond cleavage in the rate-determining CH₄ dissociation step; whereas the stability of the material was enhanced due to the suppression of carbon formation.

Ag and Au have also been employed as promoters to Ni electrodes for solid oxide fuel cells under internal SMR conditions. Ag [56] or Au [57] with a loading of 1–5 wt.% doped on Ni/yttria-stabilized zirconia (YSZ), as well as Au with a loading of 1–4 at.% doped on Ni/CeO₂-Gd₂O₃ [58] anode were tested at temperatures ranging from 650 to 800 °C. Both exhibited satisfying performance with enhanced tolerance to carbon formation. However, the performance of Ag-doped materials is largely influenced by the reaction temperature. At temperatures higher than 750 °C, the Ag–Ni/YSZ cell degraded rapidly due to the low melting point of Ag [56]. At temperatures lower than 600 °C, the catalytic activity of the Ag–Ni/Al₂O₃ catalyst decreased significantly, whereas the Au-doped catalyst still exhibited higher activity than monometallic Ni/Al₂O₃ [59,60]. Sapountzi et al. [61] reported that an Au amount of 2.3 wt.% promoted the reducibility of Ni catalyst, and the Ni–Au alloy formed on the catalyst surface was able to inhibit the formation of sulphuric compounds, including nickel sulphide.

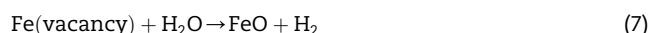
Liu et al. [62] reported that Ni–Ir alloy supported on MgAl₂O₄ was a durable catalyst for steam and CO₂ bi-reforming of methane under pressurized conditions. The bimetallic catalyst was composed of small metallic clusters (with a mean size of ~2 nm) and the cluster size was retained for a duration of 434 h, in contrast to the significant increase in cluster size of the monometallic Ni/MgAl₂O₄ catalyst, showing the anti-sintering ability of Ir. The coke resistance of the bimetallic material was attributed to the combined effect of small ensemble sizes, increased surface oxophilicity, and higher activation barrier for CH₄ dissociation. The number of active sites was evaluated by H₂ chemisorption, it was found that an Ir loading of 0.1 wt.% was able to quadruple the quantity of active sites of Ni/MgAl₂O₄, and the promoting effect increased with a higher Ir loading. The bimetallic Ir₁₀Ni₉₀/MgAl₂O₄ catalyst achieved CH₄ and CO₂ conversion of 95% and 98%, respectively, at 1 bar; and was able to maintain a relatively high CH₄ and CO₂ conversion of ~60% when pressurized to 20 bar.

Nickel-based catalysts promoted by non-noble metals

Despite multiple advantages, the use of noble metals is still constrained for economic reasons. Therefore, many researchers have turned to the application of non-noble metals as potential promoters of Ni-based catalysts.

Ni–Fe-based catalysts/oxygen carriers have been tested for chemical looping steam methane reforming (CL-SMR). Hu et al. [63] used Ni–Fe modified calcite as an oxygen carrier and concluded that a Fe/Ni ratio of 0.67 was optimal for the reaction, while higher Fe concentration led to sintering. The novel material exhibited good catalytic performance with the highest CH₄ conversion of 98.9%, and high stability during the long-term reaction process. Garai et al. [64] tested Ni-ferrite supported on ZrO₂ and CeO₂, which showed high H₂ and CO selectivity, as well as high CH₄ conversion (93%, 98%, and 99%, respectively). No carbon deposition was observed on the used material, due to the ability of iron oxides (FeO_x) to remove carbon via a surface redox cycle to produce Fe and CO₂ [65]. Djaidja et al. [66] reported that although the addition of Fe slightly decreased the CH₄ conversion of the (Ni–Mg)₂Al catalyst from 93% to 91%, both H₂ and CO yield were improved and carbon formation was significantly suppressed.

In addition, the Fe-promoted Ni catalyst was also proved to be sulphur-resistant. Tsodikov's team [67,68] tested Ni–Fe/ γ -Al₂O₃ catalysts prepared by epitaxial coating and a novel core-shell type catalyst containing Ni and Fe (Fig. 2) under SMR conditions in the presence of up to 30 ppm H₂S. The materials showed good catalytic activity, unlike conventional Ni-based catalysts, which lose activity rapidly when the gas-vapour mixture contains H₂S. This property was attributed to the core-shell structure, in which the core containing Ni–Fe nanoparticles provided the catalytic ability while the γ -Fe₂O₃ shell provided vacancies for H₂S to decompose to elemental sulphur following the reactions below:



Cobalt is also considered a promising SMR catalyst additive because of its good activity for the WGS reaction, which assists in shifting the equilibrium towards higher H₂ production. However, one problem related to the usage of Co is its tendency to oxidize when the temperature and steam partial pressure are in the range used for SMR [69]. Alloying it with Ni is a potential solution to this problem while preserving the advantages of both elements. A series of Ni–Co/ZrO₂ bimetallic catalysts with different Co loadings were tested and compared to monometallic Ni and Co catalysts by Harshini et al. [70]. Their results suggested that a Ni/Co ratio of 1:1 was optimal for limiting both oxidation of Co and carbon formation caused by Ni. The material also exhibited long-term stability with a constant CH₄ conversion of 81.8% within 50 h with no surface carbon formation. You et al. [71] tested a series of Ni–Co/ γ -Al₂O₃ catalysts and found that at a temperature of 800 °C Co-modified catalysts exhibited the same reforming activity as unmodified ones with enhanced coke resistance. The performance of the bimetallic catalyst was not as good as

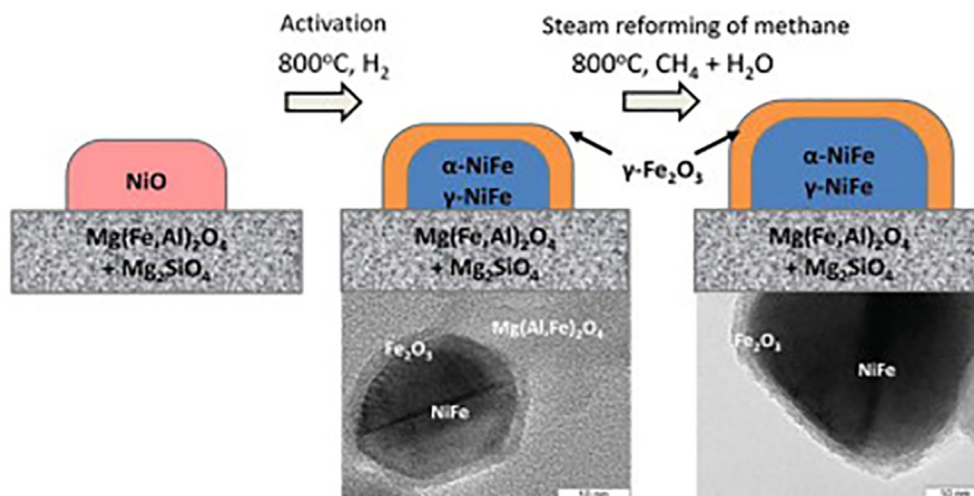


Fig. 2 – Core-shell configuration with the Ni–Fe alloy core surrounded by a superparamagnetic γ -Fe₂O₃ shell. Reprinted from Ref. [67] with permission from Elsevier.

Ni at low temperatures, possibly due to the formation of Ni–Co alloy, which increased the crystallite and particle size of the material, while decreasing metal dispersion and surface area, and blocking low-coordinate active Ni sites where the rate-determining CH₄ dissociation step takes place.

Ni–Cu bimetallic catalysts have been used for the conventional SMR process [60] as well as low-temperature SMR [73–75]. Results showed that by adding Cu as the promoter, a larger Ni crystallite size, surface area, and a better metal dispersion was obtained [74], and the overall carbon resistance of the material was enhanced [66,72]. TGA results before and after a long-term SMR test (20 h) showed that carbon formation on Ni–Cu/Al₂O₃ was greatly suppressed (8.9%) compared to commercial Ni/Al₂O₃ (28.3%). The addition of Cu has also been proven to enhance the activity of the WGS reaction [76], which explains the increase in CH₄ conversion when using Cu–Ni as the catalyst. However, it should be noted that an upper limit exists in terms of the promoting effect of Cu. A Cu/Ni ratio equal to or higher than 5 in the material will result in reduced catalytic activity, as reported by Huang et al. [73].

The promoting effect of Zirconium was investigated by Lertwittayanon et al. [77] using Ni/ α -Al₂O₃ catalysts containing CaZrO₃ nanoparticles. CaZrO₃ loading between 10 and 15 wt.% showed the best catalytic performance with a CH₄ conversion of 67%. Results also showed that unlike conventional SMR catalysts requiring an S/C ratio of approximately 3, an S/C ratio of 1/3 or 1 was most appropriate for the CaZrO₃-modified catalyst. This is because a high S/C ratio causes an excessive amount of steam to adsorb on the CaZrO₃ surface, which competes with the adsorption of CH₄.

Boudjeloud et al. [78] tested a series of La-promoted Ni/ α -Al₂O₃ catalysts. The highest CH₄ conversion (97%) and H₂ yield (94%) were obtained with a Ni/La ratio of 7:3. The improved activity compared to monometallic Ni was credited to the decrease in Ni particle size and enhanced metal dispersion, which prevented the agglomeration and sintering of the bimetallic material. The addition of La also facilitated the reduction of Ni, however, its effect on coke resistance was not significant [27].

The effect of doping Molybdenum was studied by Maluf and Assaf [79] using Mo–Ni/Al₂O₃ catalysts with different Mo concentrations. The addition of Mo decreased the surface area of the catalyst, possibly due to the blockage of active Ni sites by MoO_x. However, the specific activity of each active site was increased, which was attributed to the transfer of electrons from MoO_x to Ni particles resulting in an increase in electron density in Ni. Molybdenum carbide has also been employed in the methane reforming process and is known to have good catalytic activity and stability at high pressures [80]. However, its stability quickly drops at atmospheric pressure due to the surface oxidation of Mo₂C to MoO_x by CO₂. This problem can be mitigated by combining Mo₂C with nickel. Despite being a major reason for the deactivation of traditional Ni catalysts, carbon deposited on the bimetallic Ni–Mo₂C surface promotes the carburization of NiMoO_x back to its carbide form [81,82]. Ni–Mo₂C catalysts have been tested for dry methane reforming [81–83], steam reforming of methanol [84], as well as steam–CO₂ bi-reforming of methane [85], and have shown more promising results than unpromoted Mo₂C catalyst or Ni–Mo catalyst in their reduced form.

The promoting effect of the rare earth element, rhenium, was reported by Xu et al. [86]. They concluded that by coating a Ni–Re bimetallic layer on the surface of a high cell density Ni monolith catalyst, the reducibility and catalytic performance of the material were enhanced. The low hydrogen adsorption energy of Re atoms also facilitates the adsorption of hydrogen atoms on Re and adjacent Ni atoms, which suppressed the oxidation of Ni and led to enhanced catalyst stability.

Nickel-based catalysts promoted by metalloids

Silicon is one of the most studied metalloids as it is often employed as the catalyst support for the SMR process, usually in its oxide or carbide form, because of its thermal stability and potentially high surface area. Silica is generally considered an inert material, as it has weak metal-support interaction with the active metal (Ni in most cases) due to its low reducibility [87]. The lack of metal-support interaction in Ni/SiO₂ is also a

source of filamentous whisker carbon formation [88]. To improve the interaction between Ni and the silica support matrix, Majewski et al. [89] synthesized a core-shell typed Ni/SiO₂ catalyst using the Stöber-deposition-precipitation method, and tested it under different SMR conditions. Results showed that the core-shell structure increased the coke resistance of the catalyst, as deposited carbon was only detected at a low s/c ratio (1:1) and temperature (550 °C). Other characteristics of the support material, including crystallite size and metal dispersion, are affected by the acidity/basicity of the support and are also known to influence the rate of carbon growth on the catalyst surface. The acidity of the silica support facilitates the decomposition of methane, but at the same time promotes cracking and polymerization leading to catalyst deactivation because of carbon formation [88]. To achieve a better acid-basic balance, basic metal oxides, including ceria [90,91] and magnesia [92,93] are often added to Ni/SiO₂ to tune the surface acidity of the support, and it was found that a homogeneous distribution of the basic sites on the acidic silica framework improved the long-term stability of the catalyst.

Elements with a similar electronic structure of carbon include tetra- and penta-valent *p* such as Sn, Sb, As, Ge, Pb, Ag, etc. The addition of these metals was predicted to have a coke-resisting effect, because, similar to the formation of nickel carbide (interaction between 2*p* electrons of carbon and 3*d* electrons of Ni), the reaction between these metals with Ni could potentially reduce the chance of Ni–C interaction. A few of the above candidates were tested by D.L. Trimm [94], and their coke-resistant ability followed the order of As > Ag > Sb > Sn > Pb.

The addition of Sn was also investigated by Nikolla et al. [95–97] experimentally and numerically. The bimetallic Ni–Sn catalysts showed lower CH₄ conversion during the first 30 min of the reaction, however, its long-term stability was greatly enhanced. The carbon resistance of the Ni–Sn/YSZ catalyst was explained by DFT calculated reaction energy barriers, which showed that the Ni–Sn alloy surface preferentially oxidizes C* rather than forming C–C bonds. The presence of Sn also lowers the binding of C* to low-

coordinated sites, which is the position for carbon nucleation. The decrease in the catalytic activity of Ni–Sn alloy is possibly due to the blockage of low-coordinate Ni sites by Sn, as these sites are the most active for the rate-determining C–H bond activation step.

Similar to Sn, boron-promoted Ni catalyst has also demonstrated good stability due to the reduction in carbon nucleation centres. A boron loading of 1 wt.% was sufficient to enhance the overall stability of the material without compromising its catalytic activity [98]. Apart from this, Lighthart et al. [27] also reported the structural-promoting ability of boron for obtaining small Ni particles. However, one limitation of the bimetallic material is that the addition of boron strongly impeded the reduction of Ni.

Apart from the experimental work mentioned above, the SMR activity of metalloid-promoted nickel catalysts was also studied using numerical methods. In the work by Xu et al. [21], the catalytic activity of a series of bimetallic alloys was predicted based on a microkinetic model, and DFT-calculated atomic adsorption energies on the bimetallic M₁M₂ (211) surface. By setting the conditions as 793 °C, 12.2 bar, and with gas composition as 50% to equilibrium, alloys including Ni₃M (M = Sn, Sb, Ge, and As) and Co₃Ge were predicted to have the highest activity (Fig. 3). Although these elements showed promising results, experimental validation of the *in-silico* study has not been found. Further study can be carried out on these metalloids (Sb, As, Ge)-based catalysts in search of an optimal balance between activity and stability.

Cobalt-based and other transition metal-based bimetallic catalysts

Apart from nickel, some other transition metals, such as Co, Cu, and Fe, have been used as catalysts for reforming processes (dry and steam reforming of hydrocarbons, glycerol, or bio-derived material). Shen et al. [99] tested a series of monometallic Co/CeO₂ and bimetallic Co-M/CeO₂ catalysts (M = Ni, Al, and Cu) under conventional SMR conditions to

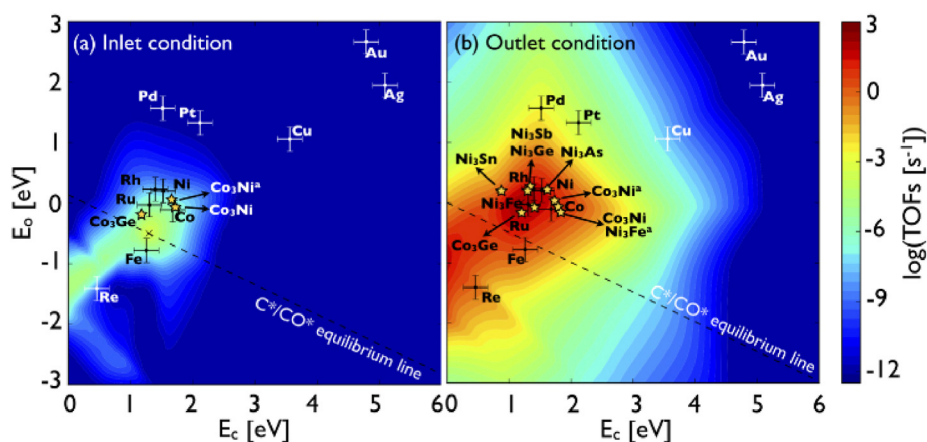


Fig. 3 – Turnover frequencies for CO production under industrial (a) inlet conditions: T = 638 K, P = 14.3 bar, with a gas composition of 14.5% CH₄, 83.1% H₂O, 0.1% CO, 0.4% N₂ and 1.9% H₂; and (b) outlet conditions: T = 1066 K, P = 12.2 bar, with a gas composition of 2.4% CH₄, 65.8% H₂O, 6.5% CO, 0.3% N₂ and 2.5% H₂. Reprinted from Ref. [21] with the permission from IOP Publishing.

study the effect of Co loading and different promoters. As mentioned previously, higher active metal loading does not necessarily mean better performance because of the uneven distribution of active compounds in the support. A Co loading of 12% was found to be optimal in terms of CH₄ conversion and H₂ yield. The addition of both Ni and Al increased CH₄ conversion, whereas Cu slightly reduced the overall catalytic activity, possibly due to the sintering of Cu. The combination of Ni–Co was chosen over Al–Co because it exhibited higher CH₄ conversion (76.1%), H₂ selectivity (58.5%), and H₂ yield (44.5%).

The cobalt-based catalyst prepared from hydrotalcite precursors using the anion-exchange method was tested by Lucredio and Assaf [100] with low H₂O/CH₄ feed ratios of 2 and 0.5 to test the stability of the material under extreme conditions. For an H₂O/CH₄ ratio of 2, CH₄ conversion was maintained at 80% during 6 h of reaction; the carbon amount on the used catalyst was found to be only 2.7 wt.% after 30 h of reaction. The catalyst began to show a deactivation tendency due to the deposition of excess carbon when H₂O/CH₄ ratio is further decreased to 0.5, and CH₄ conversion decreased from ~60% to 40% during 6 h of reaction.

Although Co is less prone to coke formation compared to Ni, the interaction between Co and the metal oxide support is strong, leading to the formation of cobalt oxides with limited reducibility [101]. As presented in section 2.1, by adding a small amount of noble metal the reducibility of the transition metal-based catalysts can be largely improved because of the hydrogen spill over effect. Profeti et al. [102] explored the effect of noble-metal promoters (0.3 wt.% Pt, Pd, Ru, and Ir) on Co/Al₂O₃ catalysts. Results showed that the addition of the noble metals significantly decreased the reduction temperature of cobalt species, with their promoting effect following the order of Pd > Pt > Ru > Ir. In terms of their catalytic activity, the Co-based bimetallic catalysts did not show satisfying results. Average CH₄ conversion of 50–60% was obtained for Pd-, Pt- and Ir–Co, 30% for Ru–Co, and only 7% for Co/Al₂O₃, which was possibly due to the partial oxidation of cobalt active sites in the presence of water molecules.

Akbari-Emadabadi et al. tested a Ca–Co bi-functional catalyst/sorbent (with a mass ratio of Ca/Co = 9) in the CL-SMR process, and investigated the promoting effect of yttrium [103] and zirconium [104], with a mass ratio of Ca/Y = Ca/Zr = 4.5. Both promoted samples remained stable at 700 °C for up to 16 redox cycles, whereas the unpromoted one was deactivated after 10 cycles. The catalytic performance of the materials is summarized in the table below (Table 2). Both Y and Zr showed promoting effect regarding catalytic activity for SMR and H₂ selectivity, and the usage of Zr was more advantageous in comparison to Y. Based on the results from catalyst

characterization, the addition of Co reduced the overall surface area of the material by more than 30%, whereas the addition of Zr compensated this negative effect to some extent. Results also showed that Zr prevented the formation of Ca₂Co₂O₅ spinel in the structure of the bimetallic material, which lowered the risk of losing active sites of Co. The study proved Y and Zr to be promising textural promoters of the bi-functional catalyst/sorbent materials employed in CL-SMR.

Apart from Co-based bimetallic catalysts, catalysts combining two types of noble metal have also been studied. The research by Roy et al. [105] focused on a novel Pt–Rh (1.2 wt.%) catalyst supported on metal foam. The sample was tested in a multichannel heat exchanger platform reactor to evaluate its potential in solid oxide fuel cell application. The combination of Pt and Rh was proven to enhance the production of hydrogen by SMR, with CH₄ conversion, H₂ yield, and H₂/CO ratio of 97.2%, 3.16 mol per mol of CH₄ input and 6.03, respectively, all of which were higher than commercial monometallic Ni and Ru catalysts. The novel catalyst also showed excellent stability, negligible coke deposition was found after 200 h of SMR reaction at 800 °C. Further research from an economic point of view should be carried out to evaluate the potential of these materials in large-scale applications.

Polymetallic catalysts

Compared to the relatively simple mono and bimetallic system, the application of catalysts containing three or more types of active metals in SMR has not been investigated in detail. Existing literature mainly examined Ni-based material with the addition of two or three commonly used elements, such as Co, Cu, Ru, Pt, etc.

The effect of the simultaneous presence of copper and zinc in Ni/Al₂O₃ catalyst was investigated by Nazari and Alavi [106]. They reported that Cu and Zn affect the Ni-based catalyst in different ways – Cu enables a better resistance to coke formation while Zn improves the catalyst's activity, stability, and H₂ selectivity. The optimal combination of the three metals for SMR was found to be 15%Ni–1%Cu–5%Zn, which achieved a CH₄ conversion of 94% and an H₂ yield of 3.12.

Jeon et al. [107] investigated the performance of a selection of bi- and trimetallic Ni-based catalysts under steam-deficient conditions. A series of bimetallic catalysts containing 5 wt.% of alkaline earth metal (Mg, Ca, Sr, Ba) or 0.5 wt.% noble metal (Ru, Rh, Pt, Pd), and trimetallic catalysts containing both alkaline earth metal and Ru were synthesized. Results from the tests demonstrated that adding Mg or Ca enhanced the coke resistance of Ni-based catalysts, whereas the effect of Sr and Ba was not significant. Among the noble metals, Ru was the best candidate for suppressing coke deposition. Based on these conclusions, a catalyst with optimized composition – 0.5%Ru–5%Mg–10%Ni/γ-Al₂O₃ – was selected and tested. A CH₄ conversion of 96% was maintained for 250 h, proving its excellent long-term stability.

Bi-functional polymetallic materials combining the catalytic ability of transition metals and CO₂ sorbents are commonly employed for the SESMR process [108]. Chen et al. [109,110] found that a simple physical mixture of Ni/Al₂O₃

Table 2 – Comparison between the catalytic activity of unpromoted and promoted Ca–Co samples.

	CH ₄ conversion (%)	H ₂ yield (%)	H ₂ /CO ratio
Unpromoted Ca–Co	95.0	81.5	5.2
Ca–Co–Y	95.8	82.9	5.3
Ca–Co–Zr	98.3	84.7	10.0

(20 wt.%) and CaO was able to improve H₂ purity to above 95%, compared to 72% without in-situ CO₂ removal. Based on an elemental mapping analysis of the samples, each Ni elemental point was surrounded by several Ca points, which allowed the efficient capture of CO₂ produced during the reaction.

Dewoolkar and Vaidya [111] synthesized hybrid Ni–CaO/Al₂O₃ and Ni-hydrotalcite materials by coprecipitation and incipient wet impregnation, respectively. The materials were tested at T = 500 °C with an S/C ratio of 9 for 20 cycles for stability evaluation. Results showed that CH₄ conversion and H₂ yield of the hybrid materials were higher than those obtained using a physical mixture of catalyst and sorbent, due to the more efficient mass and heat transfer. The hybrid materials also exhibited better stability, Ni–CaO/Al₂O₃ and Ni-hydrotalcite maintained high H₂ purity of 90% for up to 11 and 16 cycles, respectively, compared to the sintering and deactivation of the mixed material after only 2 cycles.

Di Giuliano et al. [112,113] reported the use of mayenite as for bi-functional Ni–CaO material. Results from multicycle sorption/regeneration TGA demonstrated the stable sorption capacity of the material after 20 cycles. This enhanced stability compared to commercial CaO was attributed to the presence of mayenite as an inert binding, preventing CaO from sintering. The same phenomenon was also observed by Dang et al. [9], confirming the role of mayenite as a structural stabilizer. Di Giuliano et al. also concluded that the nickel precursor used for material synthesis may affect the texture and reducibility properties, and nickel nitrate hexahydrate was found to be the most suitable precursor.

Kim et al. used ruthenium as the reforming catalyst, and tested the performance of Ru–CaO/Ca₃Al₂O₆ under SESMR conditions [114]. As Ru is a highly active catalyst for SESMR, the mass fraction of CaO was able to be increased significantly compared to conventional Ni–CaO-based materials. Ca₃Al₂O₆ acted as the structural stabilizer against sintering, and maintained the surface area of Ru–CaO/Ca₃Al₂O₆ at 18 m²/g after 10 cycles of SESMR, compared to 5 and 6 m²/g for Ru/lime and Ru/CaO.

Hafizi et al. [115] modified conventional calcium-based CO₂ sorbent with CeO₂, and tested it for CL-SESMR together with Co₃O₄/SiO₂. The addition of CeO₂ significantly improved the morphology of CaO by increasing its surface area and uniformly distributed pores in the sorbent structure. Combined with the Co-based catalyst, the material was able to produce

high purity H₂ (93–96%) for 8 redox cycles, and maintain the same CO₂ removal efficiency for 3 carbonation/calcination cycles.

Ghungrud et al. [116] reported a novel trimetallic bi-functional material for SESMR, consisting of Ni and Co (with concentrations varying from 0 to 40%) supported on hydrotalcite and promoted by 2.5 wt.% cerium. The hybrid material was evaluated in terms of its H₂ production ability, sorption capacity, and cyclic stability. Results revealed that CH₄ conversion increases with the Co content in the material, which is possibly due to the enhancement of WGS reaction by Co. Under optimal reaction conditions, CH₄ conversion of 95.7% and 90.7% were obtained by two Ce-promoted Ni–Co samples (with Ni/Co ratios of 1/3 and 1, respectively). The maximum sorption capacity was found to be 1.74 and 1.51 mol CO₂/kg, respectively. The material was also tested at optimal conditions for 25 cycles, samples showed good stability by maintaining an H₂ concentration higher than 90%, and remained stable for 21 and 16 cycles. This property was attributed to the effective metal-support interaction and higher active metal dispersion within the promoted material. The author concluded that the hydrotalcite-supported Ce–Ni–Co (2.5, 10, 30 wt.%) trimetallic catalyst/sorbent shows good performance and could be a promising candidate for large-scale SESMR application.

Similarly, Dewoolkar and Vaidya investigated the promoting effect of Ce and Zr on a Ni/hydrotalcite bi-functional material [117]. Results showed that both Ce and Zr were able to increase the surface area and surface basicity, which inhibited coke formation. Both Ce and Zr promoted materials remained stable for 13 and 17 cycles, respectively, whereas the unpromoted material became unstable after 9 cycles. The addition of Ce was found to be particularly beneficial, as the promoted bi-functional material reached a high CH₄ conversion of 96.4% and an adsorption capacity of 1.41 mol CO₂/kg sorbent.

Apart from the type of promoter added to Ni-based catalysts, the structure of the promoted catalyst also influences its overall performance. Cho et al. [118] synthesized a bimetallic catalyst with a novel egg-shell structure by selectively placing Ni and Ru on the shell of alumina. Three types of catalysts were compared, including (a) egg-shell-type bimetallic catalyst (5 wt.% Ni + 0.7 wt.% Ru/Al₂O₃), (b) monometallic 1 wt.% Ru/Al₂O₃ catalyst with the same egg-shell structure, and (c)

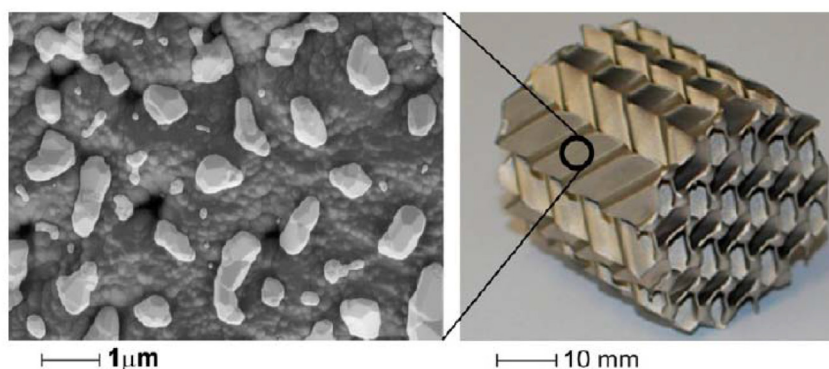


Fig. 4 – Plate-type Pt–Ni/Al₂O₃ catalyst. Reprinted from Ref. [119] with permission from ACS.

Table 3 – A summary of bi/polymetallic catalysts for SMR (Green/Red: promoter has a positive/negative effect on the overall performance, compared to the monometallic base material. Blank: no data available. *: result based on numerical modelling.).

Base material	Promoter(s)	Catalyst stability				Catalyst performance		Physical/chemical properties	
		Carbon resistance	Sulphur resistance	Sintering resistance	Resistance to metal oxidation	Catalytic activity	H ₂ selectivity	Self-activation	Reducibility
Ni	B	[98]				No significant effect [98]			[27]
	Fe	[63][66]	[67], [68]			Slight decrease [66]	[64][66]		
	Co	[70], [71]			[69]	[71]			
	Cu	[66], [72]				[73]	[73]		[75]
	Ge					*[21]			
	As	[94]				*[21]			
	Zr					For low S/C (1/3) [77]			[77]
	Mo				[80]	[79]			
	Ru	[22], [23]			[39], [40]	[24], [25]		[24], [25]	[22]
	Rh	*[23]		[28]	[41], [42]	[26], [27]	[29]	[41], [42]	[26], [27]
	Pd	[26–31]				[32–38]		[42]	[32–38]
	Ag	[45–49]				[47]			
	Sn	[95]–[97]				[97]			
	Sb	[94]				*[21]			
	Re				[86]	[86]			[86]
	Ir	[62]		[28], [62]		[28], [62]			
	Pt				[42]–[44]	[30], [31]		[42]–[44]	[42]–[44]
	Au	*[51–55]	[61]			*[51–55]			[61]
	La	No significant effect [27]		[78]		[78]			[27]
	Cu + Zn	[106]				[106]	[106]		
	Co + Ce	[116]				[116]	[116]		
	Ru + Mg	[107]				[107]			
Co	Al					[99]	[99]		
	Ni					[99]	Slight decrease [99]		
	Cu	[99]				[99]	[99]		
	Y					[103]	[103]		
	Zr					[104]	[104]		
	Ru					[102]	[102]		[102]
	Pd					[102]	[102]		[102]
	Ir					[102]	[102]		[102]
	Pt					[102]	[102]		[102]
Rh	Pt	[105]				[105]	CO selectivity [105]		

monometallic 1 wt.% Ru/Al₂O₃ synthesized by the conventional wet impregnation method. The comparison between (b) and (c) showed that the novel structure was able to improve methane conversion and maintain it at a higher level when gas hourly space velocity was largely increased. This was because the novel structure enables the active metal, ruthenium, to be mainly deposited on the outer region of the alumina pellets and can therefore be utilized more efficiently. With the addition of nickel, (a) achieved an even higher methane conversion than (b) at higher gas hourly space

velocity. This proved that the novel structure enables the efficient utilization of active noble metals, reducing the metal loading necessary and, therefore, the overall cost.

Obradovic et al. [119,120] proposed a novel plate-type catalyst for SESMR, as demonstrated in Fig. 4. This material was synthesized by depositing Pt and Al₂O₃ on a static mixer element made of Ni alloy. During the SESMR process, it acts simultaneously as the catalyst, the distributor for solid sorbent, as well as the gas-phase radial mixer. The CH₄ conversion obtained by this novel catalyst was 15 times higher than

monometallic Ni under the same conditions. However, its catalytic activity rapidly decreased after 10 h of reaction, temperatures higher than 590 °C also led to activity loss due to carbon accumulation on the material surface. Further investigation on modifying relevant parameters (such as the promoter type, metal loading, and reaction conditions) to increase its stability may be of interest.

Based on the above review, it can be concluded that an increase in catalytic activity is usually achieved either by modifying the textural properties of the material (e.g. increasing surface area and metal dispersion) using a second active metal; or by modifying the energetics of the surface reactions, in particular the rate-determining step (e.g. decreasing activation energy of the first C–H bond in CH₄ dissociation). Although a variety of metal combinations have been studied for their performance in the SMR reaction, there exist many other combinations of elements that have been predicted to be active or have not been evaluated at all regarding their reforming activity.

Conclusions and outlook

SMR is currently the most dominant hydrogen production technology, and extensive research on the catalytic aspect of this process has been carried out. Carbon emissions from SMR can be reduced by adding a CO₂-sorption step. This review provides insights on recent developments in the use of bi/polymetallic catalysts for (SE)SMR. The performance of the bi/polymetallic catalysts presented in this review is briefly summarized in Table 3 and is evaluated based on three main factors: stability (resistance to carbon, sulphur, sintering, and oxidation), catalytic activity and selectivity, as well as their physical/chemical properties (reducibility and self-activation ability).

The most widely used SMR catalyst to date is ceramic-supported nickel because of its relatively good performance and inexpensive price, but problems such as sintering and coke formation still exist. In search of catalysts with better performance, various elements have been added as promoters to conventional Ni-based catalysts. Noble metal-promoted catalysts generally have superior reactivity, coke resistance, and enhanced reducibility, but their applications are often limited by their prices. Researchers have therefore turned to non-noble metals and metalloids. The addition of iron was found to be coke and sulphur-resistant due to the surface redox reaction between Fe⁰ and FeO_x. Both cobalt and copper can enhance the activity of the WGS reaction, thus shifting the reaction towards more hydrogen production. Elements including zirconium, yttrium, and lanthanum were found to be good textural promoters due to their ability to increase the surface area and metal dispersion of the material. Silicon is often used as the catalyst support in its oxide or carbide form, and the addition of ceria or magnesia was able to tune the surface acidity of silica for better long-term stability. The addition of other metalloids (tin, boron) led to enhanced coke-resisting ability, but often at the expense of losing catalytic activity. A DFT-based study has also predicted germanium, arsenic, and antimony to be effective promoters of nickel-

based catalysts, however, further experimental verification is still necessary.

Apart from the type of element selected as the promoter, the loading of each component is also a critical parameter that influences the overall performance of alloy material. A higher active metal loading does not necessarily indicate a higher activity due to the restricted distribution of active metal in the material. The influence of material structure on catalytic activity was also investigated. Although novel core-shell type, plate type, and metal foam-support structures were found to be beneficial to the overall catalytic performance, this largely complicates the synthesis process and limits the wide application of the materials. It is, therefore, necessary to find a balance between improvements to the material properties and a viable and efficient material preparation process.

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Data access statement

All data underlying the results are available as part of the article and no additional source data are required.

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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Wang, Siqu; Nabavi, Seyed Ali

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