

Review Article

Influence of Catalytic Supports on Methane Steam Reforming: A Short Review

Sani Nasiru Alhaji, Haruna Anas, Salisu Aliyu*

Department of Chemistry, Federal University, Gusau, Nigeria

Email address:

nasirualhajisani@yahoo.com (Sani Nasiru Alhaji)

*Corresponding author

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Abstract: Steam Methane Reforming (SMR) is by far one of the key industrial processes that can help in achieving green and sustainable energy. As a major source of hydrogen (the so called future and green fuel), valuable oxygenated chemicals and key reaction for solid oxide fuel cells, the process solely depends on the presence of a metal supported catalyst to carry out the conversion of the feeds. The methane steam reforming (MSR) reaction is one of the major hydrogen sources in the industry. It is a significant means of transforming natural gas into valuable liquid fuels and oxygenated chemicals catalytically. Several techniques such as the inclusion of promoters, the development of improved catalytic supports, and structural modification, among other things have been developed in the past decade with the target of improving the catalytic activity, coking resistance and thermal stability of SMR catalysts. Meanwhile, a number of innovative processes for more efficient and energy-saving SMR process have been investigated. In this case, an examination of the influence of catalyst supports on the catalytic SMR is presented to gain a useful understanding of the impacts of supports on the SMR. This review is design to give a brief summary on methane steam reforming reaction, its thermodynamics and kinetics and finally the influence of support materials on the activity of noble and non-noble active metals used in SMR.

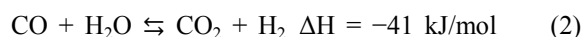
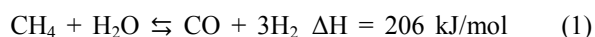
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1. Introduction

Fossil fuels still accounts for more than 80% of the current global energy demand [1]. As a consequence, the global warming effect and the climate changes are still on the raise. Apparently, renewable energy source like solar and wind possessed all the potentials of competing with coal if harnessed properly in the future. For instance, a lot of researches are ongoing to improve the capacity of the energy storage devices to help to store the excess energy produce by renewable sources at their peak of the production [2]. This will indeed, help in overcoming the unreliable nature of the wind and the solar energy and further contribute to the average energy produce by these sources. Another solution worth considering is biomass valorization or valorizing the global warming agents (CH_4 and CO_2 most notably) into valuable chemicals catalytically.

Natural gas is known to be converted into hydrogen fuel and other oxygenated chemicals [3]. Unlike fossil fuels, hydrogen fuel (H_2) is very clean and sustainable with net zero effect to the environment. Furthermore, compared to any other known fuel, H_2 is abundantly available in the universe and has the largest energy content per unit weight. It is seen as the energy carrier of the future and has the potential of reducing the over dependence on fossil fuel and can help in the mitigation of greenhouse gas emissions significantly [4]. H_2 is always present in nature, tied up in organic compounds and water. It is produced from a variety of materials, including coal, natural gas, liquefied petroleum gas (LPG), propane, methane (CH_4), light diesel, dry biomass, biomass-derived liquid fuels (such as methanol, $\text{C}_2\text{H}_5\text{OH}$, and biodiesel), gasoline etc [5]. The global movement of fuels from solid to liquid to gas, as well as the "decarbonization" trend that has accompanied it, suggests that the transition to H_2 energy is unavoidable [6, 4].

Methane being one of the green-house gases has been considered as a suitable candidate among all accessible hydrogen sources due to its low-cost, availability and efficacy for hydrogen via methane reforming processes [7]. Despite being an endothermic reaction, catalytic methane steam reforming (SMR) is the most often employed among alternative methods such as autothermal reforming, oxidative steam reforming, partial oxidation, and coal gasification, because of its hydrogen's excellent energy, efficiency and low cost [7]. In addition to H_2 , carbon monoxide (CO) and a small amount of carbon dioxide (CO_2) were recovered from SMR, which was originally created to produce syngas (H_2 and CO) a valuable feedstock for Fischer Tropsch or methanol synthesis. The co-product CO from SMR could react with steam to produce one extra H_2 and CO_2 as the final products when combined with a water-gas shift (WGS) reaction. SMR can be thought of as a catalytic process that speeds up the breakdown of methane into H_2 gas and carbon species [8].



Different catalysts based on noble (Rh, Ru, Pt, Pd) and non-noble (most notably Ni) metals have been reported for steam reforming of methane [9]. Coke formation on the catalyst surface, sintering of active metal particles, thermal deactivation over time, excess metal loading for some catalyst and failure to perform in cyclic settings without regeneration are some of the drawbacks associated with typical SMR catalysts. Long-term use reduces the porosity and exposes the

catalysts to reactive gases, causing catalysts deactivation, resulting in higher operating pressures and temperatures [10, 11]. Nonetheless, significant activity can be achieved by coupling the metals with proper support materials which can diminish the coke formation [12].

In this short review, the influence of catalyst supports in methane steam reforming is being presented. The review tries to give an overview of steam reforming process, its thermodynamics and kinetics. Finally, the review tries to summarize the influences of different catalyst supports on the catalytic activity.

2. An Overview of Steam Methane Reforming

Natural gas or the methane gas is a highly flammable gaseous mixture of hydrocarbon with wide application as fuel for electricity generation, feedstock for plastics etc. The typical natural gas composition (Vol%) is: CH_4 : 95%, C_2^+ : 3.5%, N_2 : 1%, CO_2 : 0.5% and small amounts of sulfur and noble gas compounds. Hence the dominant chemical compound from natural gas wells after treatment processes is methane. Natural gas (methane) reforming is a well-established process that can either endothermic or exothermic in nature depending on the target involve. Currently, the process produces almost 48-50% of the world's hydrogen, in addition to many useful end products, Figure 1 below summarizes some of the key indirect routes involve for the production of useful chemicals from natural gas.

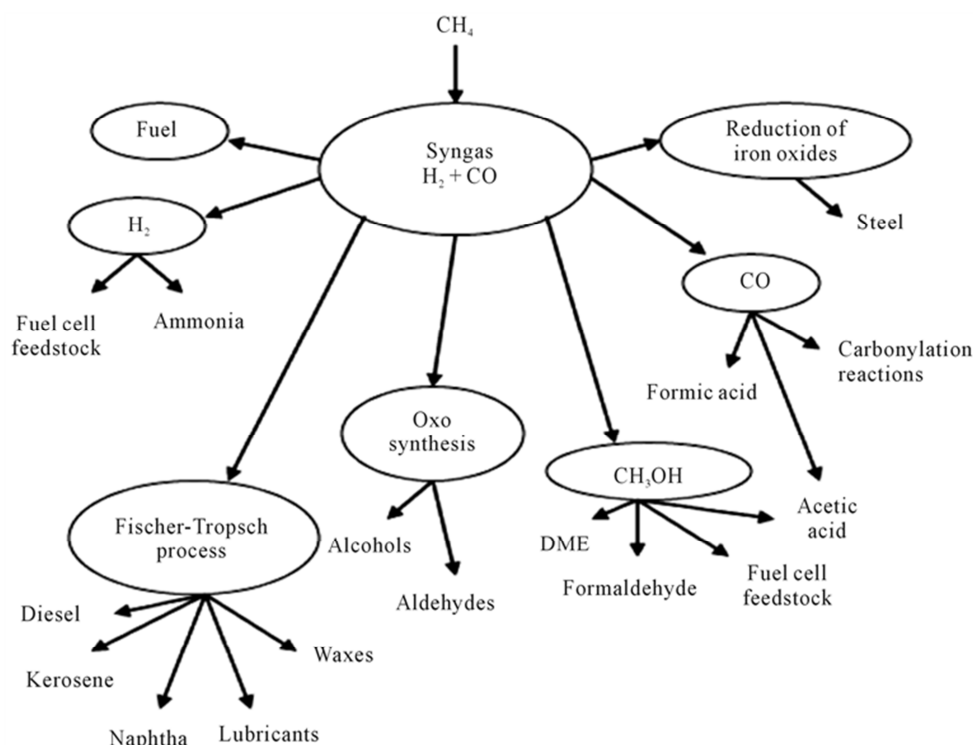
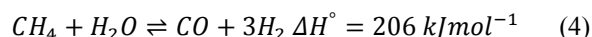
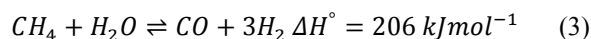


Figure 1. Methane reforming to syngas and other indirect secondary chemicals [3].

Steam reforming is one of the seven reforming process that

found wide application in the industries. Neumann and Jacob

initially described this catalytic reaction between methane and steam in 1924, and it sparked a lot of curiosity at the time. However, the first industrial application of SRM was implemented in 1930 [13, 14]. Steam methane reforming is a catalytic process that produces hydrogen gas (H_2) and carbon (II) oxide (CO) by reacting natural gas or methane-containing streams, such as biogas or landfill gas, with steam in the presence of a catalyst [3].



In the process, natural gas and steam are fed to the steam reformer after pretreatment or desulfurization at a typical operating condition of 800-900°C, 1.5 to 3.0 MPa, in the presence of a metal based. Supported nickel-based catalysts in the range of 15-25wt%, are the most common non-noble based catalyst used in MSR. Noble metal-based catalysts such as Ir and Ru support catalysts are also reported for MSR [15].

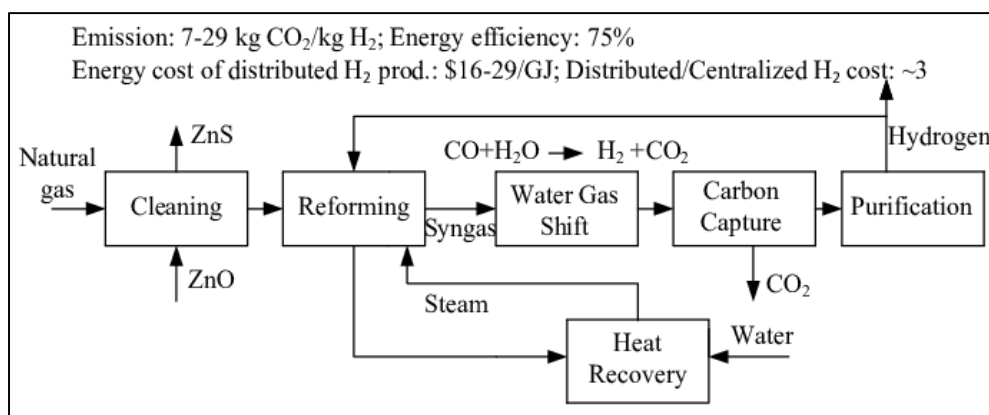
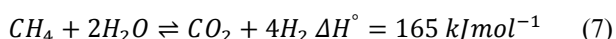
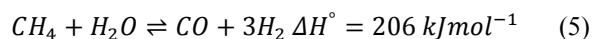


Figure 2. Steam reforming of natural gas to hydrogen [18].

The direct product from the reforming process is the reformer's synthesis gas which is high in H_2 and CO content in the ratio of 3:1. In many cases the produced syngas goes through a heat recovery stage then fed into a water-gas shift reactor (side reaction) to produce more H_2 gas and CO_2 [16]. The water gas shift reaction is often a good strategy for boosting the H_2 production. In addition, CO content is also reduced in this process. This is normally achieved by employing the high temperature shift (HTS) and the low temperature shift (LTS) processes [17]. The hydrogen produced by these processes is afterwards purify through the pressure swing absorption techniques, and finally compressed under 60 bar pressure [14]. The Figure 2 below summarizes the different processes involved in methane steam reforming.

3. Thermodynamics

Several chemical reactions are involved in methane steam reforming process. The strongly endothermic reactions (as shown in equation 1 and 3), as well as the moderately exothermic water-gas shift reaction.



It is noteworthy that CO_2 is produced not only by the water gas shift reaction as shown in equation (6), but also by the reforming reaction directly (7). Despite the fact that steam-methane reforming is frequently thought to be a

combination of reactions (5) and (6) solely, this means that reaction (7) is not simply the 'overall reaction [19].'

Reforming is favored by low pressure because of its endothermic nature. Low temperature, on the other hand, favors the exothermic water gas shift reaction, which remains unaffected by pressure fluctuations. The same equilibrium constants can be used to compute the enthalpy change (ΔH) and Gibbs free energy (ΔG°). To achieve sufficient reaction activity, the SMR reaction requires a temperature above 700°C. As the temperature rises, the enthalpy (ΔH) increases, and the free energy of the system (ΔG°) decreases, and hence thermal deactivation of a catalyst may occur. On the other hand, the low reaction temperature causes coke deposition over time [13]. At the same time, the size of the employed support is critical for minimizing reaction bed area. Hence, the reaction must be carried out under high pressure. Raising the reaction pressure is expected to reduce the methane conversion due to the higher net number of product molecule.

Increasing the amount of steam used will improve CH_4 conversion, but at the consequence of more energy to produce the steam. The commonly used steam to carbon ratio [i.e. $P(H_2O)/P(CH_4)$, or $S/C \geq 3$] is about 3. This S/C ratio is well known to improve the CH_4 production and mitigate the coke formation through CH_4 decomposition.

The catalysts, particularly the active metal and the nature of the support, have a role in the steam reforming reaction mechanism. Early research on the kinetics of methane steam reforming was predicated on the premise that methane adsorption occurred [9]. In the case of methane, there is widespread agreement that the reaction is first order, but there is less agreement on the kinetic characteristics. This is due in

part to the use of various catalysts and experimental settings, but it is also related to a failure to address diffusion and heat transfer constraints.

4. Catalyst Supports

A catalyst support is a material to which a catalyst is attached or supported. It is usually metal oxide or a solid with a large surface area. The large surface area increases the accessibility of the reactants to the active metal and enhances the dispersion. The activity of heterogeneous catalysts is primarily by the active metal atoms present on the material's accessible support surface. Distributing the catalysts over the surface of the support is a popular method for increasing surface area and the activity of a given catalyst [20].

Refractory oxides such as CeO_2 , YSZ, TiO_2 , ZrO_2 , $\text{CeO}_2\text{-ZrO}_2$, SiO_2 , Al_2O_3 and TiO_2 are common oxide support materials. Additionally, carbon and graphene are also widely employed especially in processes where large surface area is very important. Zeolites are also known for their wide application in oil refining and petrochemical processing. Recently, an increasing number of ordered mesoporous materials and metal organic frameworks have been exploited, as model supports [21, 22]. Hence, depending on the intended application, a catalytic support can attain different morphology and chemical composition. Different research is still on going towards improving the specific properties of these support materials [23, 24].

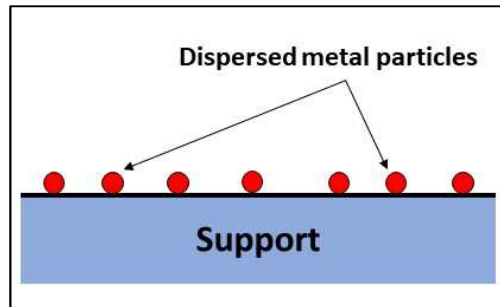
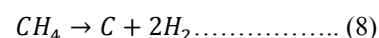


Figure 3. Typical illustration of metallic supported catalyst.

The importance of the support in the steam-reforming process cannot be overstated. It determines not only how well dispersed the catalytically active metal particles can be (which improves the activity), but also the overall reactivity of the system. Additionally, the support material improves the catalysts resistance to sintering, and coke formation. There are some reports showing that the support materials can solemnly catalyze or participate in the catalytic reaction [15]. However, in most cases it is the synergy between the metal and the support material that determine the performance of the catalysts. Different support material, offer different activity. For instance, it has been shown that Ir/CeO_2 is more active than Ir/RuO_2 using the same metal loading in methane reforming [15]. In summary, the catalyst's support is an essential component that of catalysts that improves the overall performance of a reaction [25].

5. Influence of Catalyst Supports in Methane Reforming

From the name “support”, it is literally used to provide a aid for the catalytically active metal species, in order to obtain a stable dispersion and high active surface area [26]. The catalytic activity and thus the reactivity of the metal are affected by the type of the chemical bonding between the support and the metal atoms. Acidity in the support, for example, is known to aid in the decomposition of methane (8), but it also promotes cracking and polymerization, resulting in the production of carbon (coke formation) which in turn deactivate the catalysts over time. In general, a methane steam reforming catalysts with a strong connection between the metal and the support is more resistant to sintering and coking, resulting in a good catalytic stability [27].



The porosity of the support, its surface area and the active metal size are also worth considering in the design of a given catalyst. If the porosity of a given support is high, it will result to an extended contact time between reactants and catalyst. Maintaining a large active surface area is also critical because the support can influence metal particle migration and coalescence in a variety of ways. The final particle size of the metal is determined by the support's porous structure, morphology, and phase transitions [26].

According to the report of Nieva et al., the catalytic activity of Ni-based catalysts is mostly determined by the support, which is crucial in the catalytic process [28]. As mentioned elsewhere in this write up, the supports have an impact on metal dispersion, mitigate sintering and in some cases can even directly engage in the processes by facilitating reactant adsorption. The activity order of Ni-active catalysts on different supports materials for SMR at 600°C was reported to increase in the following order: $\text{Ni/MgAl}_2\text{O}_4 > \text{Ni/ZnAl}_2\text{O}_4 > \text{Ni/Al}_2\text{O}_3 > \text{Ni/SiO}_2$. It is noteworthy, the aforementioned order is based on the support's resistivity to coke deactivation. Hence, Ni/SiO_2 deactivates quickly, owing to surface oxidation and carbon deposition, whereas $\text{Ni/ZnAl}_2\text{O}_4$ has the least amount of carbon deposition and the best sintering resistance.

Furthermore, it was discovered that supports like Al_2O_3 and SiO_2 cause Ni catalysts to gradually oxidize during SMR at 500°C under ambient pressure, but amphoteric support like ZrO_2 , stabilizes the Ni particles and enhances the methane conversion than the aforementioned supports. The authors of this report believed that the reason for this is that the ZrO_2 support gives room for water accumulation, which in turn favors the production of hydroxyl groups that promotes SMR [29].

Because of its great thermal stability, mechanical resilience, and oxygen storage capacity, CeO_2 has been extensively researched as a support and promoter of Ni-based catalysts and other catalytic system used in steam reforming [30, 15]. Dan et al., investigated SMR on an Al_2O_3 -supported Ni catalyst that has been modified using CeO_2 and La_2O_3 [29]. They discovered that morphological traits (i.e., surface dispersion) are

responsible for improved catalytic properties, such as higher methane conversion and lower coke production. Wang *et al.*, used a template technique for SMR to synthesize hierarchically structured NiO/CeO₂ nano-catalysts [31]. The authors claim that the particle size and interaction between NiO and CeO₂ are critical for the activity of the catalyst in SMR process.

Nickel-on-honeycomb catalysts were also studied. The catalyst was made from 30 microns-thick Ni foil in the shape of metallic honeycomb, with no Al₂O₃ or noble metals added. The catalyst demonstrated excellent conversion and H₂ yield with no coke formation on the surface. The catalyst was gradually deactivated due to Ni oxidation, but it was quickly regenerated (reduced), thanks to the presence of H₂. The heat transmission between the catalyst and the surrounding gases was validated by temperature profiles [32].

Addition of other metals may also improve the performance of SMR Ni based catalyst. At low temperature steam reforming, zinc and magnesium are added to the Ni/Al₂O₃-alumina catalyst. With a lower coking ratio, Ni-Zn-Al catalysts had higher activity than Ni-Mg-Al catalysts. However, it was discovered that zinc sublimated during steam reforming, necessitating the activation of the catalyst at 600°C. Nonetheless, there was no reasonable Ni sintering observed, which was attributed to metal support interactions that limit migration [28].

Mierczynski *et al.*, investigated the effect of support composition in oxy-steam reforming of methane, and the physicochemical properties of Ni catalysts [33]. The physicochemical properties of the Ni catalysts synthesized by classical impregnation method revealed that the significant interaction of NiO with the support is responsible for the low activity of Ni catalysts supported on La₂O₃ or binary oxides with a high proportion of lanthanum oxide.

The influence of different dopants (Mg, Ca, and La) were reported in Ni-Ce_{0.8}Zr_{0.2}O₂ based materials. Due to the very high Ni dispersion and strong contact between active material and support observed using La-dopant, the catalyst with La-dopant showed the best catalytic performance. Additionally, the La had the highest basicity of all the samples studied. According to the report [34], combining Ru as an active material with a lanthanum-containing support resulted in an excellent catalyst that provided not only good conversion but also good stability after 30 hrs under testing, with a conversion rate of more than 95% the entire time.

Ni catalysts typically required a high active metal loading than the noble metal catalysts, which were mostly in the range of 1–2 wt%. Amjad *et al.*, investigated the use of Rh, Ru, and Pt in SMR process on various supports such as Al₂O₃ and CeO₂ [35]. The results showed that 1.5 wt% Rh/CeO₂ had the best performance, with high activity at moderate temperatures (about 600°C) and good selectivity for methane. This catalyst produced H₂-rich gas with a low CO concentration, which was essential for H₂ production via methane steam reforming. The catalytic activity of the other noble metals was equally satisfactory. Pt metals supported CeO₂ attained full conversion at 745°C, while Ru/Al₂O₃ reached its full conversion at 699°C.

Cassinelli *et al.*, investigated the effect of support type on the structure, surface characteristics, and catalytic behavior of Pd catalysts supported Al₂O₃ and mixed La₂O₃-Al₂O₃ oxides synthesized by impregnation and sol-gel methods [36]. It was result revealed that the kind of support has a substantial impact on the catalytic performance of Pd catalysts in SMR. The electronic interaction between Pd and modified Al₂O₃ support surface with La₂O₃ species and production of Pd⁰ [Pd^{δ+}O_xLa] like species, which promote CH₄ activation and carbon oxidation, were linked to the maximum specific reaction rate and TOFs_{CH4} of La-containing Pd catalysts in SRM.

Yokota and colleagues studied the influence of metallic oxide support on the activity of Rh in reforming process [37]. Despite the high dispersion of Rh on α -Al₂O₃, they discovered that 0.5 wt% Rh on SiO₂ is more active than the same loading of Rh on α -Al₂O₃ for the CH₄ reforming at 700°C. This seemingly conflicting conclusion is most likely due to the fact that the synergy (metal-support interaction) of Rh on α -Al₂O₃ is higher and as a result, the Rh/ α -Al₂O₃ system tends to maximize the number of metal-support links, leading to increased metal dispersion. Moreover, the authors further claim that the Rh will then loses its metallic character (i.e., electrons are withdrawn from Rh) which will further increase the metal-support contact. Hence, Rh on α -Al₂O₃ has a cationic character, leading in the creation of less reactive Rh₂O₃-like compounds.

Roy *et al.*, investigated the activity of bi metallic Pd-Rh supported metal foam in SMR and its activity in solid oxide fuel cells [38]. When compared to commercial catalysts such as 13 wt% Ni/Al₂O₃ and 8 wt% Ru/Al₂O₃, the examined catalysts had higher activity, H₂ yield and competitive stability. Additionally, the catalysts exhibit no residues of coke formation at the surface after 200-hours testing. Furthermore, the metal foam was able to reduce the formation of hot spots inside the reactor by using a porous structure that could be prepared in any shape and had a low heat capacity and high heat transport. Another added advantage of the metal foam was that it could be used to lessen pressure loss in a reactor and improve gas mixing.

Ru-based catalysts are also known for their good activity and selectivity in SMR. Even at high temperatures, they were resistant to coking and sintering (800°C). Amjad *et al.*, investigated the catalytic performance of Ru nanoparticles on several supports, including MgO and Nb₂O₅ [39]. In terms of CH₄ conversion, the MgO-based catalyst performed well. For the Ru supported Nb₂O₅, a good synergy between the metal and the support was observed and the activity was excellent, with the majority of them achieving good conversion in the 700–750°C range.

Vita *et al.*, also investigated the activity of Ru supported on ceramic monoliths with varying numbers of channels per square inch and α -Al₂O₃ covering modified with La [40]. Two of the catalysts, one with square channels and the other with hexagonal channels, performed well during the process, attaining quick equilibrium methane conversion. Additionally, the monolith with higher cell density showed somewhat better results.

6. Conclusion and Recommendation

Methane has been considered as an excellent alternative among all accessible hydrogen sources. SMR can be thought of as a catalytic process that speeds up the breakdown of methane into Hydrogen gas and carbon species catalytically. The support of the catalyst and the operation conditions are essential component that cannot be separated from the reaction. The activity of the catalysts depends on the support material used. It is widely believed that the support material enhanced the dispersion of the active metal and efficiently mitigate coke formation, sintering and thermal instability of some the catalytic systems. Hence efficient monitoring of the operational condition; pressures and temperatures, reactant (H_2/CO) ratio and the type of the support material is essential.

Since the interface is considered the highly active location for many catalytic events, the stability problem of some the catalytic system used in SMR is expected to be less by properly understanding the metal support interaction and the interaction between active metal sites and the substrate at some operational conditions. Although some positive advances have been made in this regard; like addition of promoters in both noble and non-metal-based system, there are still numerous hurdles to be overcome. To begin with, accurate synthetic strategies are still in short supply in terms of innovation, and the metal loading for the cost-effective Ni based system is still high.

Furthermore, for industrial requirements, the development of simple, low-cost, and scalable technologies is very desirable. In the future, greater effort should be given to biomass valorization to methane, then to hydrogen and other oxygenated lower chemicals. Finally, proper understanding of the metal support interaction is inevitable for efficient catalyst design.

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Conflicts of Interests

All the authors do not have any possible conflicts of interest.

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