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Modified nickel-based catalysts for improved steam reforming of biomass tar: A critical review

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Abstract

The gasification of biomass produces a syngas that can be used for electricity generation and fuels/chemicals production. However, tar is generated along with the syngas as a by-product which causes issues in the syngas usage such as blockages, plugging and corrosion. Catalytic steam reforming is a suitable option to convert tar into more syngas in the presence of nickel-based catalysts, as the preferred catalyst, mainly due to their activity and low cost. There has been considerable research reported in the literature on modified nickel-based catalysts for steam tar reforming. These modifications have been carried out in order to improve the performance of the Ni-based catalysts for tar reforming, mainly in terms of catalyst stability and activity. Such improvements are achieved by manipulating the catalysts properties. This paper therefore presents a critical assessment of these modifications on Ni-based catalysts available in the literature for improved tar reforming. The modifications considered in this review were categorised as: the addition of secondary metal (Fe, Co, Cu, Cr), the addition of noble metals (Pt, Pd, Rh, Au, Rh, Ir), addition of rare earth metals as promoters (Ce, La), alkali and alkaline earth metals (Sr, Ba, Ca, Mg,Ba) and modification of support. The paper aims at understanding the properties responsible for the improved performance of the modified Ni-based catalysts in comparison with unmodified Ni-based catalysts. The review paper will serve as a guide for further improvement of the Ni-based catalysts for biomass tar reforming.

Keywords: Biomass; Gasification; Tar; Reforming; Modified nickel-catalyst

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1. Introduction

Increasing world population and advancement in technology has led to a continuous increase in the world's energy demand. In the year 2017, a total of 17.9 terawatts (TW) of energy was consumed by over seven billion people worldwide [1], and it is projected that by 2050, an energy demand of 30 TW will be needed by nine billion people [2]**.** However, currently, more than 80% of world energy supply is obtained from non-renewable, fossil-based fuels (Figure 1) [3]. The continuing dependence on fossil fuels as the major global source of energy is a threat to energy security for many countries, together with the associated environmental issues such as global warming and climate change. These factors are driving the search worldwide for an alternative, renewable and clean source of energy. Energy from biomass is considered as a viable source that satisfies those requirements due to being inexpensive, with ready availability [4] and with overall carbon neutrality. Thus, biomass is regarded as a promising short to medium term source of energy [5].

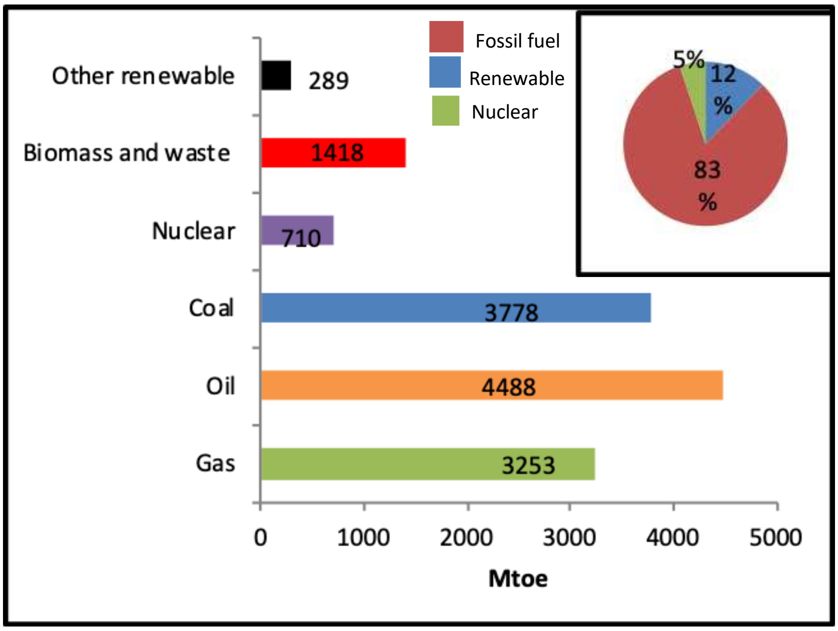


Figure 1: World energy consumption in 2018 [3]

Conversion of biomass to energy can be achieved by either thermochemical (combustion, pyrolysis, and gasification) or biological methods [6,7]. Thermochemical methods have the potential to accept a wide range of biomass as feedstock, including wastes such as lignocellulosic agricultural residues. The wide range of feedstock acceptability, together with the concept of conversion of waste to energy makes it an attractive method when compared to biological methods that are somewhat selective in the required choice of biomass. Among the thermochemical methods, gasification is favoured due to its higher energy efficiency and wider range of applications of the product syngas (Figure 2). For example, the syngas from biomass gasification can be used for heating, electricity generation, and chemicals production such as hydrogen and liquid fuels through the Fischer-Tropsch process.

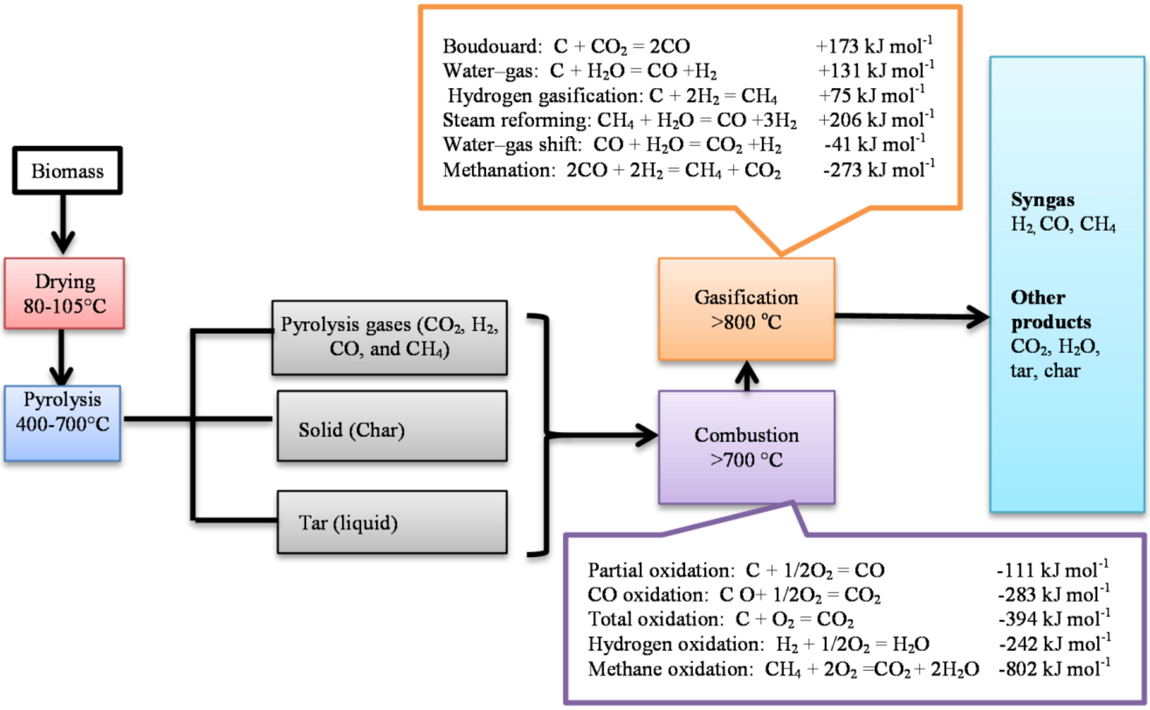


Figure 2: Processes involved in biomass gasification

However, one of the major problems of biomass gasification is the generation of tar along with the syngas. Tar is a viscous, complex mixture of high molecular weight organic material that causes serious operational issues such as plugging, fouling, and corrosion in downstream fuel lines, filters, engine nozzles and turbines, which prevents direct utilization without removal or conversion. Condensed tars can undergo polymerization to form more complex compounds[8] and can also interact with particulates causing difficulty in particle removal. The overall effects of tar are frequent shut down of plant for maintenance and low gasification efficiency. Syngas with high tar content is regarded as low-quality, thereby affecting the application potential of the syngas. The syngas quality requirement for tar is <100 mg/Nm^3 for IC engines, <5 mg/Nm^3 for gas turbine power applications [9], while <1 mg/Nm^3 is required for fuel cell applications [7]. In addition, tar is known to contain high concentrations of polycyclic aromatic hydrocarbons (PAHs) identified by the US Environmental Protection Agency (EPA) as substances with high carcinogenic potential [10].

The production of tar is unavoidable in biomass gasification, as a result, several methods have been developed for tar removal or conversion [11]. They are categorized into two types [9]:

primary and secondary methods, as shown in Figure 3. The primary method is an in-situ method which eliminates tar during the gasification process or within the gasifier. Whereas, secondary tar removal (ex-situ) is a post-gasification tar reduction method which removes tar with a process outside the gasifier or gasification process and requires additional equipment. Primary methods influence the quality of the product gas and can be achieved through a proper gasifier design, selecting the best operating parameters, and the desired chemical method (thermal/catalytic cracking and catalytic reforming).

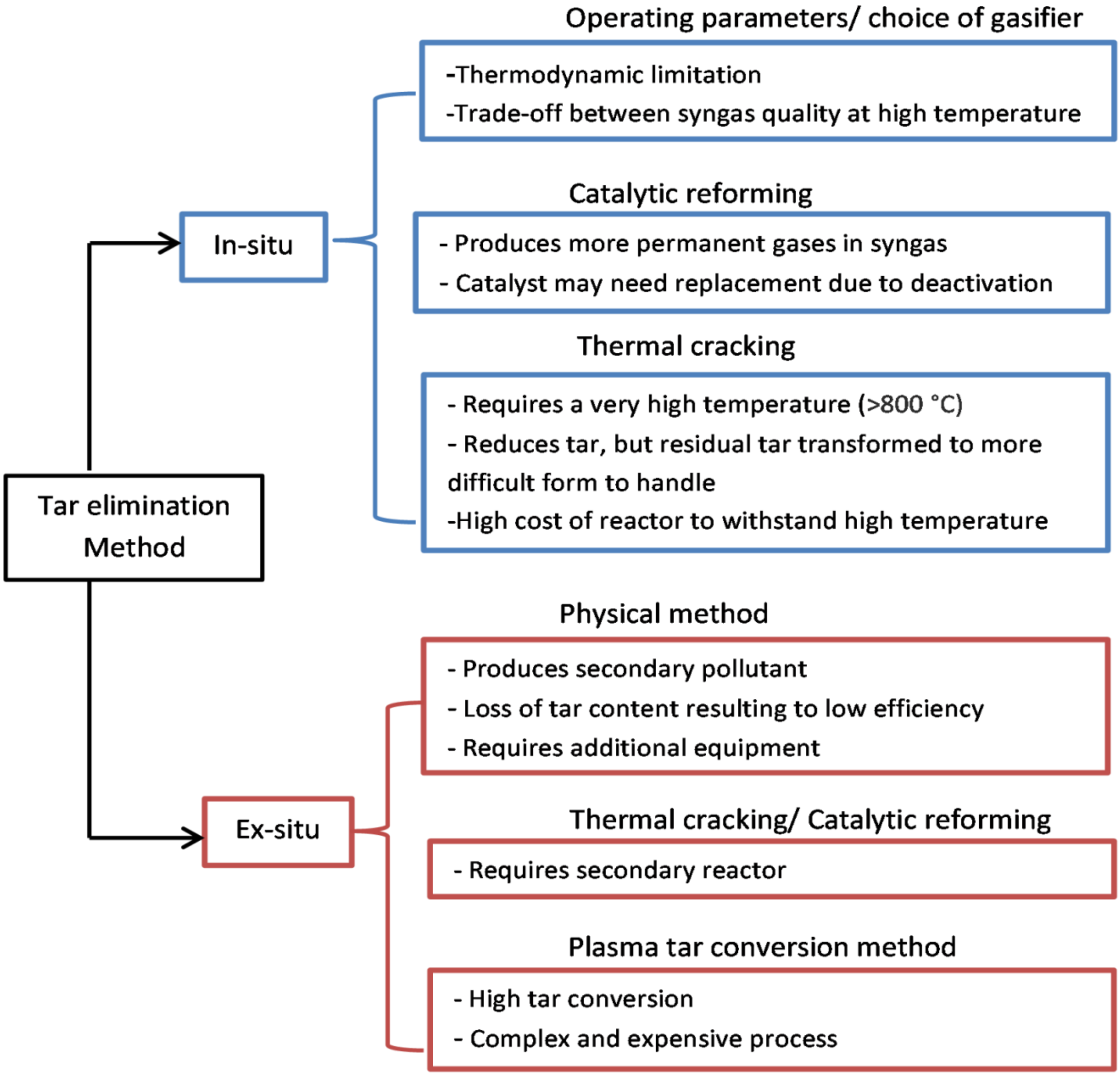


Figure 3: Tar elimination/conversion methods

Secondary methods include the removal of tar through physical methods such as using scrubbers, filters, wet electrostatic precipitators, or through a post chemical method (catalytic cracking and catalytic reforming) in another separate reactor or process. Chemical methods either in-situ or downstream (ex-situ) remove tar by converting it to more useful smaller molecular components (mainly, H_2, CH_4, and CO). Whereas, physical methods only remove the tar and the energetic content of the tar is lost. Therefore, chemical methods offer much greater potential for removal as well as conversion of the tar. Among the chemical methods, catalytic steam reforming of tar is promising because a syngas rich in H_2 can be further produced and besides it require a lower temperature than thermal cracking.

Catalytic tar removal can be used in either primary (in-situ) or secondary (ex-situ) gasification systems and, various types of catalyst have been used to convert tar from biomass gasification, these catalysts are generally grouped into; (i) Natural based; olivine [12,13], dolomite [12,14,15], CaO[16–18], zeolite[19], char [20,21], ilmenite [22] (ii) Alkali-based; K and Ca [23], [24] (iii) metal-based; Fe [25–27], Co [28–30], Zn[31], Pt [32,33], Ru [32], Ce [23] and Rh [34].

Nickel-based catalysts have been the most used and accepted choice of catalyst for tar reduction, since they are also the most commonly used catalysts for commercial scale natural gas reforming for the production of hydrogen. The reasons for their preferred choice are mainly based on the combined factors of low cost and enhanced catalytic activity. For example, it has been reported that among the transition metals, nickel has been reported to have better catalytic activity for catalytic steam reforming of heavier hydrocarbons [35,36] and light hydrocarbons [7]. Furthermore, nickel catalyses the reverse ammonia reaction, which increases H_2 concentration in the final syngas composition [37]. However, the main drawback of Ni-based catalysts is their proneness to deactivation, which shortens their life cycle. Deactivation is mainly caused by carbon deposition and sintering [31,38,39]. Carbon deposition on the catalyst may encapsulate the active metal particles and prevent the reactants reaching the metal, sintering involves metal particle agglomeration which reduces the available active metal surface and thereby reduces catalyst activity.

The issue of catalyst carbon deposition is less of a problem with noble metal catalysts. Carbon can quickly diffuse into or form on the Ni catalyst surface, however, with noble metals (Ru, Rh, Pd, Ir, and Pt), these phenomena are absent, making them superior materials for tar conversion and with high catalytic stability. For example, at a temperature of 823 K, Miyazawa et al. [40]found that the order of catalytic activity for tar conversion of metals supported on CeO_2-SiO_2 to be: Rh > Pt > Pd > Ni = Ru. In later work it was also reported that Rh exhibited both higher catalytic activity and stability compared with nickel, USY zeolite, and dolomite as catalysts for tar reduction during wood gasification [38]. However, key factors such as limited availability and high cost have hindered the commercial application of those noble metals, and they are mostly used now as promoters added to the nickel-based catalyst [41].

In a bid to extend the lifespan of Ni-based catalysts for tar conversion in biomass gasification, many researchers have tried to modify the catalyst by (i) alloying the active nickel metal with other metals (ii) modification of the nickel support with other material (iii) addition of promoters. These modifications are usually carried out through optimal catalyst design, which modifies the catalyst properties and subsequently improves catalyst performance for tar conversion. These properties can be in the form of strengthening the interaction between the active metal and support, increase in metal dispersion, increase in surface area/pore volume, decrease in crystalline sizes, provision of better mechanical strength, resistance to coke formation and/or alteration of the acidity/basicity properties of the catalyst. However, despite the wealth of research literature on the topic, there are very few reviews focused on modified nickel-based catalysts for tar reforming.

This review paper, therefore, focuses on some of the modifications that have been applied to nickel-based catalysts used for improved tar conversion. The paper aims to provide insight into those modifications reported in the literature and serves as a future direction towards continuous improvement of those nickel-based catalysts for better catalytic performance in the area of steam tar reforming. Previous literature review articles on biomass tar removal have focused on: general elimination methods for impurities in biomass gasification [42], catalytic and non-catalytic absorption methods [43], various types of catalysts [44,45]**,** supported metal based catalysts [46], nickel-based catalysts [10,47,48] and char [49]. The methodology employed in this review paper is based on comparing the activity and stability of the modified nickel-based catalysts to that of unmodified nickel-based catalysts.

2. Deactivation of nickel-based catalysts

The emergence of tar steam reforming Ni-based catalysts is due to the need to convert tar into combustible syngas components. In addition, the catalysts function could also extend to favouring the production of some desired components (especially H_2) or lowering the reaction temperature [50]. The main components of a heterogeneous catalyst is a catalytic active phase, a promoter with the purpose to either increase catalytic activity or stability and a support that provides surface area for dispersion of the active phase [51]. A good catalyst employed in biomass gasification must possess the following criteria [52]: (i) effectiveness in tar conversion (ii) provide a desired component ratio for the intended end-use application (iii) be resistant enough to deactivation (iv) should be easily regenerated, and (v) should be mechanically strong and inexpensive. In summary, a suitable catalyst should have the technical ability in terms of activity and economic viability in the form of initial cost and long-time stability.

Active metals are normally supported on metal oxides to provide mechanical strength and good surface area for dispersion of the metal. In addition, supports can interact with reactants to enhance adsorption [53]. Due to its mechanical strength, Al_2O_3 is the most commonly used support for Ni-based catalysts for tar reduction. For biomass gasification, nickel supported on Al_2O_3 catalysts have been reported to have higher activity compared with nickel supported on MgO, TiO_2, CeO_2 and ZrO_2 [33], ZrO_2, MgO, TiO_2, SiO_2 [54]. In addition, nickel has also been supported on other materials, for example, dolomite [55,56], char [37,57,58], olivine [59], ceramic foam [60], mayenite[61], HZSM-5 [62] and MCM-41[63].

Catalyst deactivation is the loss of catalyst activity or selectivity over operational time due to the chemical and physical changes undergone by the catalyst during use. Figure 4 illustrates catalyst deactivation of a Ni catalyst used for steam reforming of biomass pyrolysis volatiles over time as shown by transmission electron microscopy (TEM). The TEM images show the formation of carbon deposits on a Ni-based catalyst. These changes are caused as a result of the catalyst interaction with the reaction environment and the influence of the operating conditions. These processes are inevitable but can be prevented or slowed down to extend the catalyst life. The causes of catalyst deactivation are categorised into: coking (carbon deposition), sintering/ phase transformation, mechanical deactivation (attrition and erosion) and catalyst poisoning [64].

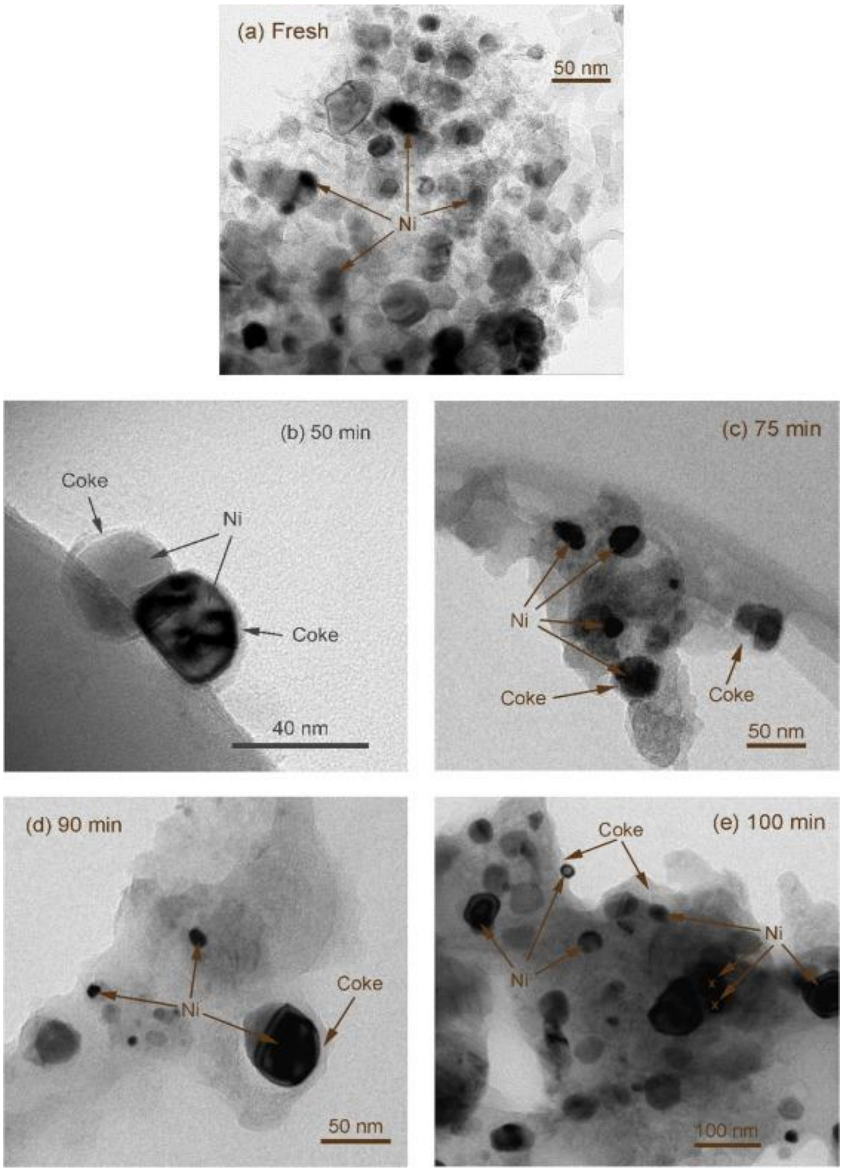


Figure 4: TEM images of fresh commercial Ni catalyst (G90LDP) and the used catalyst at various time of steam reforming of pyrolysis volatiles from biomass, reproduce with permission[65].

2.1. Carbon deposit deactivation

Carbon deposits on a catalyst are the major cause of deactivation for steam reforming Ni-based catalysts. The carbonaceous deposit (coke) covers or blocks the pores of the active nickel metal, and these carbons can be in three forms (shown in Figure 5); (i) polymer (ii) whisker (iii) pyrolytic. The polymeric form of carbon is formed on the nickel surface as a result of slow polymerization of hydrocarbon radicals which encapsulates the active nickel surface, usually favoured at low temperature (<500 °C) [66]. Whisker-like carbon occurs as a result of carbon diffusing into the nickel crystal particle at > 450 °C [67], causing separation of Ni from the support, as a result, the carbon is formed at the Ni–support/promoter interface [68]. Precursors to the whisker form of carbon are due to the Boudouard reaction, decomposition of methane and decomposition of other lighter hydrocarbons (Figure 2). This type of carbon deposit has less effect on catalyst deactivation, however, it may result in catalyst breakdown, which leads to reactor plugging.

The pyrolytic type of carbon is formed due to the decomposition (thermal cracking) of hydrocarbons which encapsulate the nickel particle. They are usually the most problematic type of carbon responsible for catalyst deactivation, and their formation is favoured at high temperature(> 600°C) and by the acidic nature of a catalyst [67]**.**

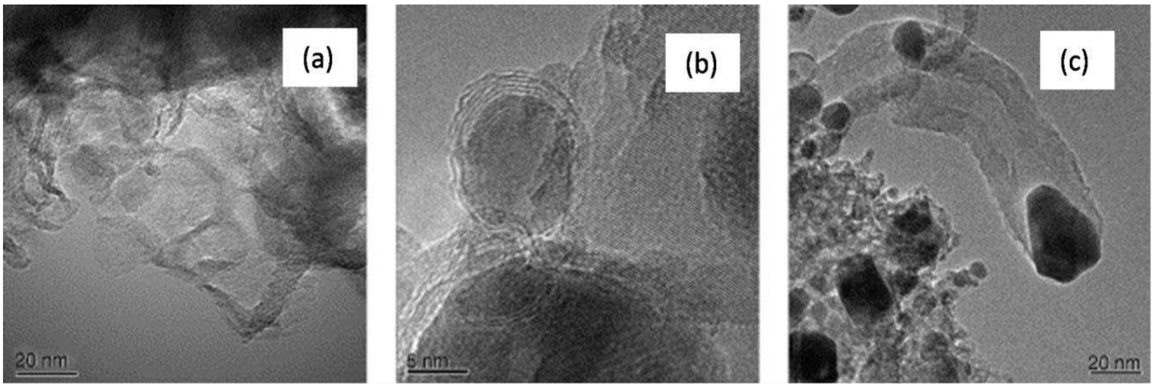


Figure 5: SEM images of carbon deposit on steam reforming catalyst: Ni/$MgAl_2O_4$ (a) pyrolytic carbon, (b) encapsulating carbon resulting from polymeric carbon, and (c)whisker carbon, reproduce with permission[69].

During steam reforming, the many different components of tar generate the range of polymeric, whisker and pyrolytic types of carbonaceous coke on the nickel-based catalyst, as shown in Figure 6. Also, it has been shown that the different produced carbons have different thermal decomposition characteristics. As observed by temperature programmed oxidation (TPO) profiles from various studies, three oxidation temperatures represent the heterogeneity of the deposited carbons (Figure 6) [65,70–73]: (i) thermal decomposition mass loss peaks (DTG) at temperatures of <450 °C representing encapsulating carbon coke deposited on the Ni surface, which is easily accessible to oxygen during oxidation; (ii) thermal decomposition peaks (DTG) at temperatures of around 500 °C due to oxidation corresponding to coke in the form of polymer or graphitic coke which is oxidised progressively from the Ni surface; (iii) thermal decomposition peaks (DTG) at temperatures between 500 and 700°C oxidation temperature due to the oxidation of carbon not adsorbed on the nickel surface, but in the form of filamentous (whisker) carbon.

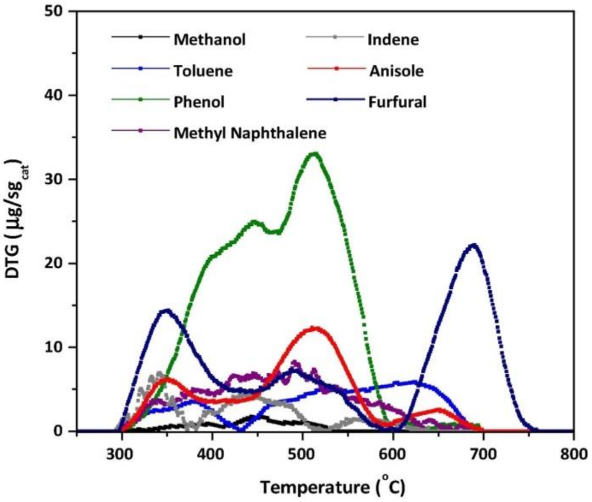


Figure 6: DTG-TPO profiles of used Ni/Al_2O_3 catalyst showing different peaks corresponding to different forms of carbons after steam reforming of different model tar compounds, reproduce with permission[70].

2.2.Sintering and other forms of deactivation

Sintering occurs due to crystallite growth of nickel particles (agglomeration) during steam tar reforming conditions resulting in loss of surface area and loss of metal dispersion, and subsequently loss of catalytic activity（see Fig. 7).High operating temperature and the presence of water favour the occurrence of sintering, for biomass gasification, the temperature is usually around 800 °C, which is higher than the Tammann temperature of Ni. The Tammann temperature is the temperature at which the atoms or molecules of the solid acquire sufficient energy for their bulk mobility and reactivity to become appreciable. The mechanism of sintering has been suggested to be through the metal atoms migration, crystallite migration and/or coalescence [74,75]. Another form of deactivation is catalyst poisoning, which is due to the presence of sulphur contained in the biomass, causing loss of activity caused by strong chemisorption between the metal and the sulphur[69]. The mechanism of sulphur poisoning on Ni catalysts is generally represented as the formation of nickel sulphide and hydrogen from the reaction of the nickel and hydrogen sulphide[76]. Loss of nickel-based catalytic activity by mechanical loss of the nickel is caused by abrasion and collapse of the internal surface area.

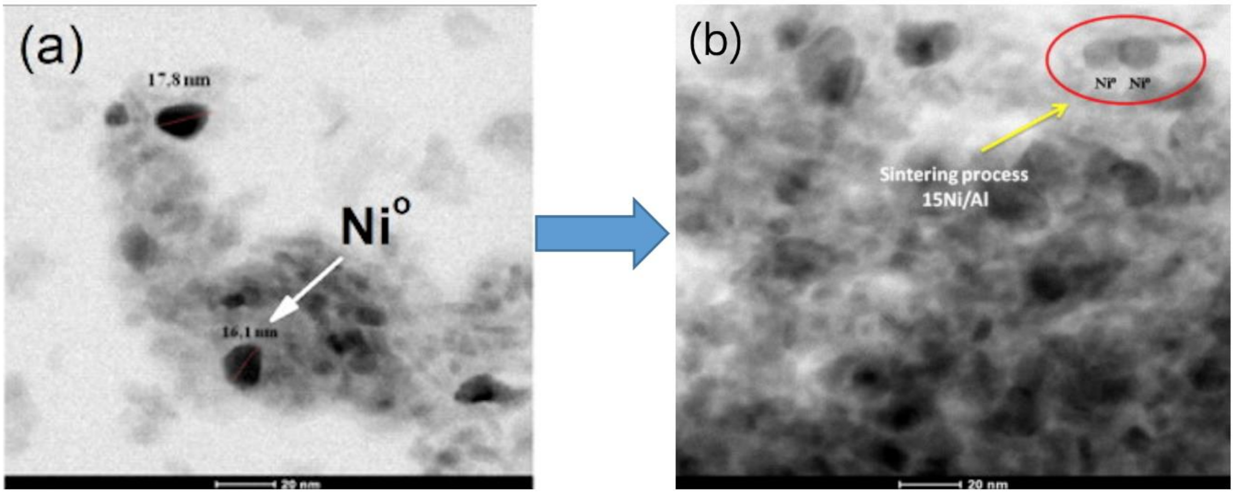
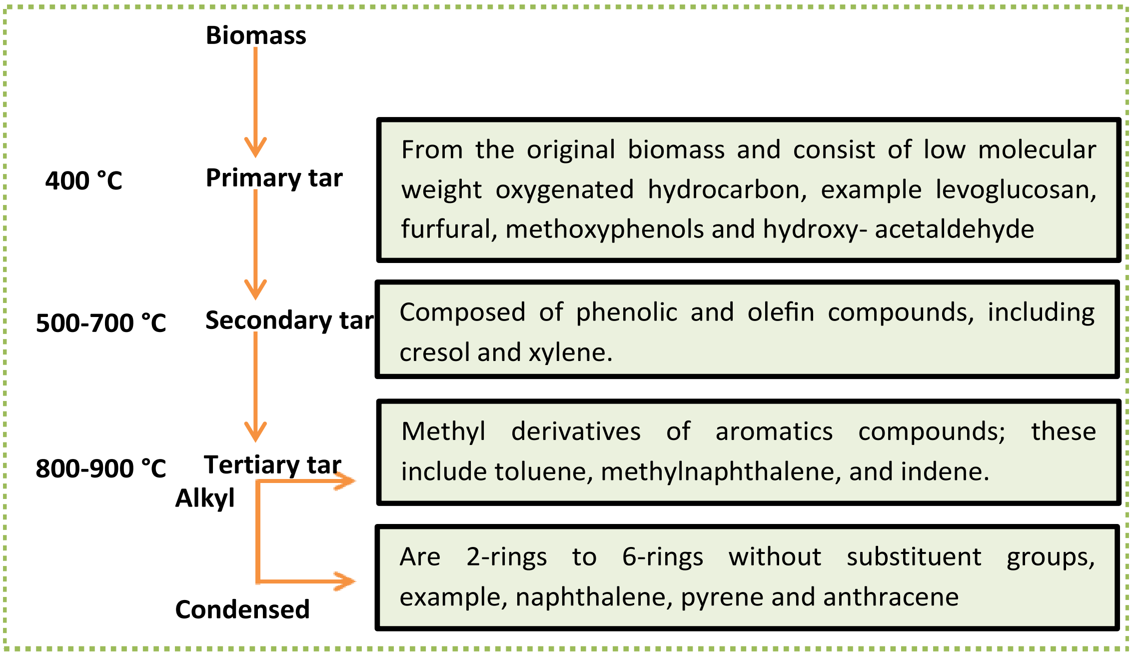


Figure 7: HRTEM images showing sintering process of 15%Ni/Al_2O_3 (a) reduced fresh catalyst (b) catalyst under steam reforming of acetic acid condition, modified from Nogueira et al.[77]

3. Tar

3.1. Transition of tar with temperature.

Tar formations are transitional with temperature, they are transformed from primary tar to phenolic compounds, and then to higher aromatic hydrocarbon, shown in Figure 8. Temperature is one of the key parameters that influences the composition of tar, higher temperature leads to increase in the rate of formation of 3- and 4-ring aromatics, BTEX and naphthalene content [78–80]. While, increasing reaction temperature decreases oxygen-containing (phenol and cresols) and light PAHs. Without a catalyst, 1200°C is needed for the decomposition of tar (Figure 9) in the presence of H_2O and H_2[81]. Higher temperature of 1400°C is even needed to convert soot (carbonaceous residue). Benzene is produced as the key thermal decomposition component while, naphthalene produces soot from all the viable routes. Finally, the produced aromatic structures undergo steam and dry reforming reactions to form CO_x and H_2.



From the original biomass and consist of low molecular weight oxygenated hydrocarbon, example levoglucosan, furfural, methoxyphenols and hydroxy- acetaldehyde

Composed of phenolic and olefin compounds, including cresol and xylene.

Methyl derivatives of aromatics compounds; these include toluene, methylnaphthalene, and indene.

Are 2-rings to 6-rings without substituent groups, example, naphthalene, pyrene and anthracene

Figure 8: Classification of tar components based origin and temperature [82]

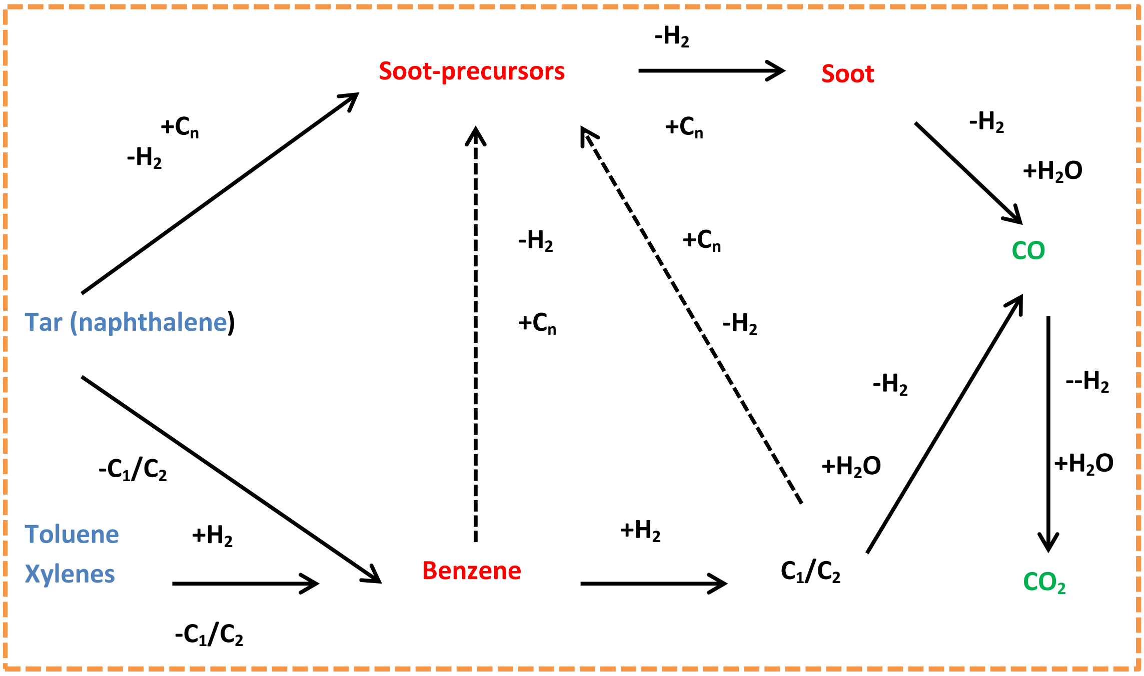


Figure 9: Thermal conversion reaction paths of aromatic hydrocarbons in the presence of H_2 and H_2O[83], C_1, C_2, C_n are hydrocarbons with 1, 2 and n carbon atoms

3.2. Model compounds as biomass tar

Model tar compounds such as toluene, phenol and naphthalene have been used to test the performance of modified catalysts as biomass tar representing compound [39,59,73,75,84–90]. Toluene is the most used compound, probably due to its high content in a typical biomass tar

(Figure 10) and having higher reactivity than naphthalene. Order of tar steam reforming reactivity are reported on Ni-based catalysts as benzene >toluene>anthracene>pyrene [88] and anisole>furfural>indene> phenol> toluene> methyl naphthalene [70] In addition, toluene is less hazardous and has a well-known chemistry at high-temperature reactions[91]. Generally, it is easy to represent tar with a model compound and monitor its conversion with a particular catalyst. This is due to the complex nature of tar, containing many individual components, which can even react with each other in some conditions [12].

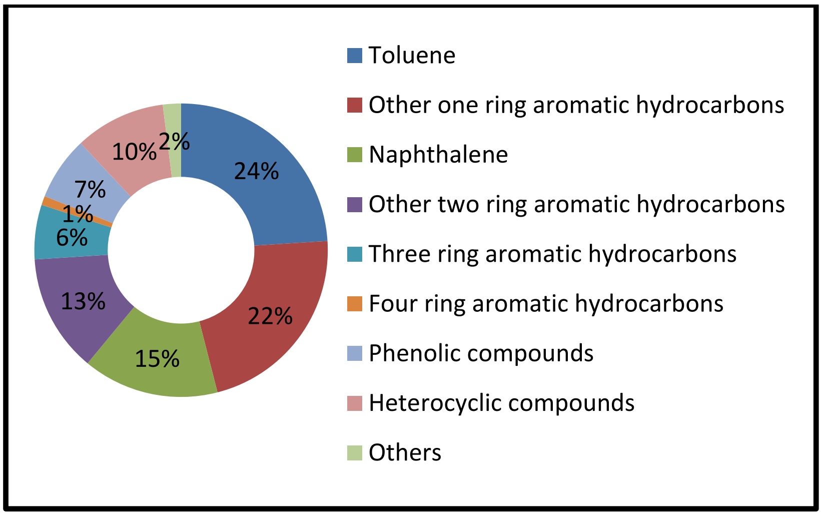


Figure 10: Typical biomass tar composition [43]

4. Modified nickel alloy for tar steam reforming

Combining nickel with other transition metals to compliment the nickel as a co-active metal catalyst for tar reforming has been proven to be an effective way to improve catalytic properties (a summary is shown in Table 1). Nickel can interact with other metals atomically to form an alloy, thereby altering the surface properties [92]. This synergistic effect improves the overall catalytic performance in terms of activity and stability. This section presents some of the co-metals found in the literature in used in the catalytic steam reforming process for tar reduction.

Generally, tar steam reforming mechanism over Ni-based catalyst is described as shown in Figure 11. Firstly, tar is adsorbed on Ni surface, enabling C-C scission, while the support adsorbs water to activate oxygen species via adsorption-dissociation mechanisms, this, through the support is spilled over to the Ni-active sites. At the metal-support interphase finally, oxygen species and C_1 reacts to form CO and H_2 according to different reactions (Figure11).

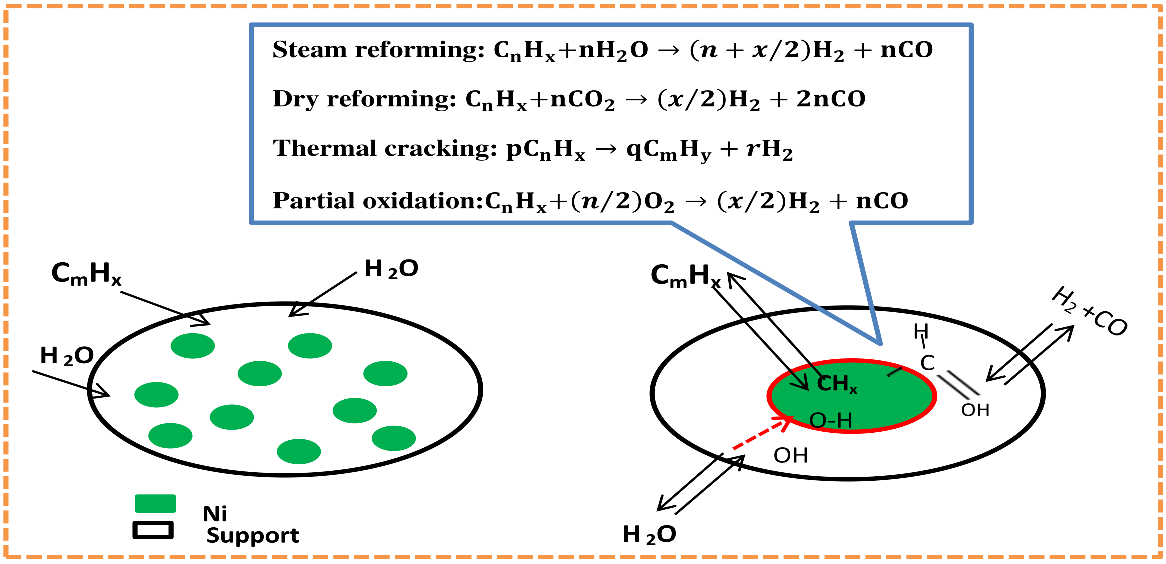


Figure 11: Mechanism of tar steam reforming over NI-based catalyst [93–95]

4.1. Bimetallic nickel- iron alloy catalyst

Monometallic Ni supported catalysts have been reported to have better activity for biomass tar reforming than monometallic Fe [96,97]. However, as a way to improve performance, the addition of Fe to Ni-based catalysts have been investigated in many studies [73,89,96–98]. Iron provides redox ability to the bimetallic catalyst, thereby enhancing its resistance to carbon deposition. Iron in the presence of an oxidizing agent, such as H_2O or O_2 forms FeO_x species, which further react with the carbon deposits through the redox mechanism, shown in Figure 12[99].

To demonstrate these promotional benefits of bimetallic Ni-Fe supported catalysts for biomass tar reforming have been investigated. Steam reforming of tar from pyrolysis of cedar wood at 873 K showed that Fe addition to Ni/Al_2O_3 at a molar ratio of Fe/Ni between 0 and 2 decreases tar content with optimum reduction at an Fe/Ni ratio of ≤0.5 [97]. Also, the addition of Fe to the Ni catalyst improves the H_2/CO ratio and the combined formation rate of H_2, CO and CH_4, thus confirming tar conversion.

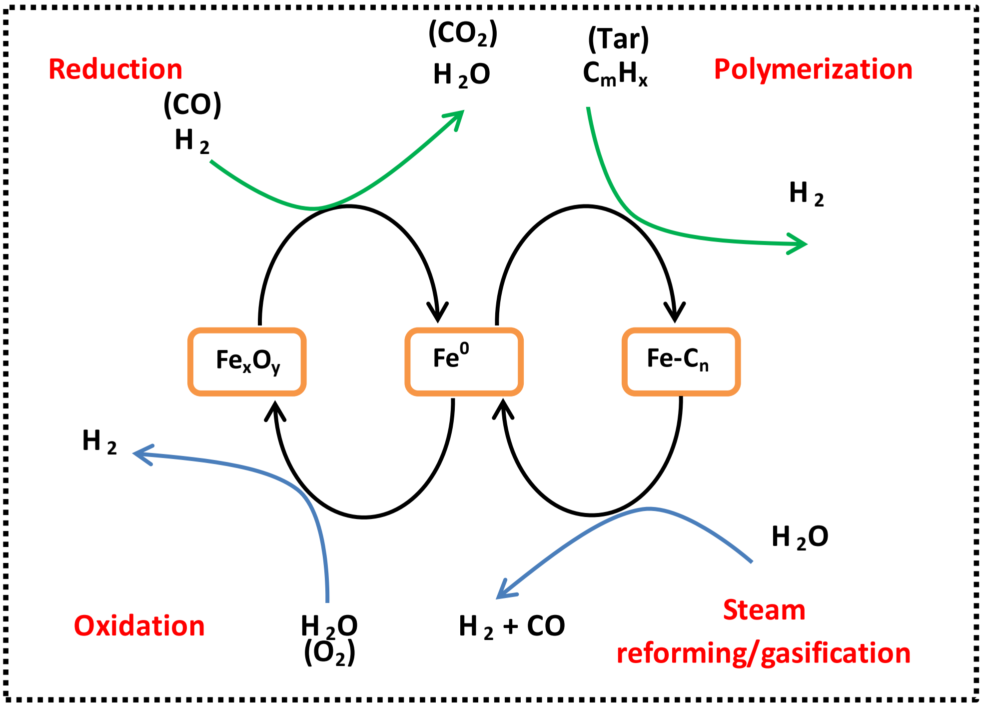


Figure 12: Redox mechanism of Fe during steam reforming of tar [100].

In addition, it was noted that coke deposition decreased with increasing molar ratio of Fe/Ni. The rate of formation of reforming gases was stable with Ni-Fe/Al_2O_3 (Fe/Ni ratio of 0.5) for 100 min reaction time. In comparison, after only 20 min, Ni/Al_2O_3 showed a high decline in the formation rate of the product gases, indicating a high rate of deactivation. The results suggest the role of Fe when alloyed with Ni improves catalyst activity and stability, which is due to the redox ability of Fe in providing oxygen to the surface. Ashok and Kawi [89] used a similar catalyst in the form of Ni-Fe/Al_2O_3−Fe_2O_3 as a catalyst for toluene reforming. The catalyst was prepared by calcination of the support (Al_2O_3−Fe_2O_3) at different temperatures (500 - 900 °C) and then impregnation of the metal onto the support. The toluene reforming performance of the catalysts at 650 °C revealed that the catalyst prepared at a calcination temperature of 500 °C exhibited the maximum conversion of more than 90% and maintained a stable conversion for 26 h. The Ni/Al_2O_3−Fe_2O_3 catalyst was not compared with an unmodified catalyst. Characterization of the catalysts revealed that the catalyst calcined at 500 °C in comparison with others had better Fe enrichment and stronger metal-support interactions. It was reported that Ni−Fe alloy particles increased the oxygen coverage on the surface and subsequently improved both activity and stability. Additionally, the carbon deposits on the used catalysts in relation to the calcination temperature followed the order of 500> 700> 900 °C with values of 21.2, 18.3 and 48.9 mg C/g_{cat}, of carbon deposition respectively. Dong et al. [101] also confirmed that

$NiO-Fe_2O_3-Al_2O_3$ catalysts at the optimum ratio of Ni/Fe of 9:1 were effective for the steam reforming of pyrolysis products of wood sawdust at 800 °C with increased H_2 yield with negligible coke deposits. The performance of the catalyst was linked to well-dispersed metal particles with crystal phases of $NiAl_2O_4$, α-Fe_2O_3, and γ-Fe_2O_3. The $NiAl_2O_4$ spinel resulting from the interaction between NiO and Al_3O_2 increases the thermal stability of the catalyst [102]. However, this interaction may also reduce the number of active sites that will participate in the tar reforming process. Thus, optimization of the metal-support interaction through testing of different catalyst compositions and operating parameters is therefore essential. Larger particle sizes are formed due to weak interaction of NiO with the support, which migrates and aggregates easily during high temperature reforming conditions, causing catalyst deactivation through sintering [103]. In addition to agglomeration, active metal with large particle sizes are also vulnerable to carbon deposition [104].

Table 1: Summary of steam reforming of biomass tar using Ni-based catalysts modified with a secondary metal

	Modified nickel based catalyst	**Unmodified nickel catalyst**	**Operating condition**	**Natureof tar**	**Tar conversion**		**StabilityTest**		**Carbon deposit**	**Improved properties of the modified catalyst**	**Ref**
					Modified	Unmodified	Modified	Unmodified			
1	Ni-Fe/Al_2O_3(Fe/Ni=0.5)*	Ni/Al_2O_3	S/C ratio of 0.57, 873 K	Tar from pyrolysis of wood	Formation rate of H_2 + CO + CH_4 is around 2900 μmol/min and H_2/CO=2.3	Formation rate slightly higher than 2000 μmol/min and H_2/CO=1.7	Stable within 100 min reaction time	Formation rate stable only within 20 min	Ni/Al_2O_3>>Ni-Fe/Al_2O_3	Ni-Fe alloy particle enhanced oxygen supply to the surface	[97]
2	Ni/Al_2O_3–Fe_2O_3	-	S/C ratio of 3.4, 650°C	Toluene	90%	-	Stable after 26 h	-	21.2 mgC $gcat^{-1}$ h^{-1}	Ni–Fe alloy particles promoting both Fe enrichment and metal support interactions	[89]
3	Ni–Fe/ activatedcarbon(AC) (Fe/Ni=0.1)*	Ni/activatedcarbon	LHSV= 0.87/h, S/C ratio of 2,	Toluene	93.8%	92.9%	Stable after 20 h	Stable after 20 h	Ni/AC has 76% carbon deposit higher than Ni–Fe/AC	Ni–Fe synergy improves the	[98]

			600◦C							resistance against sintering	
4	Ni-Fe/Zeolite(Ni/Fe=0.77)*	Ni-Fe/Zeolite	S/C ratio of 3, 600°C	Toluene	74%	35%	Stable Over 10 h	Unstable	Carbondepositionobserved<<Ni/Zeolite	Ni−Fe interaction prevents the formation of carbon	[73]
5	8%Ni-3%Fe/palygorskite	8%Ni/ Palygorskite	S/C ratio of 1, 550 °C	Toluene	80.5%	78.3%	Average conversion of 70.4% at 700 °C for 48 h	Decreased to 77.3% after only 120 min at 550 °C	10.3 and 6.9 mgC/gcat h for modified and unmodified catalysts respectively	Ni−Fe alloy improves dispersion and smaller particles	[96]
6	6%Ni–1%Fe/SBA-15	7%Ni/SBA-15	S/C ratio of 0.5, 600 °C	Cellulose	90%	70%	Rate of conversion stable than 7%Ni/SBA-15	-	Unmodified catalysts has 164% carbon deposit higher than the modified catalysts	Addition of Fe to Ni promotes metal-support interaction and dispersion	[105]
7	12wt%Ni–Co/Al_2O_3(Co/Ni=	12wt%Ni/Al_2O_3	550 °C	Tar from steam gasificati	Formation rate of H_2 + CO + CH_4 is around	Formation rate of H_2 + CO + CH_4 is	Stable within 60 min	N/A	Ni-Co/Al_2O_3>> Ni/Al_2O_3	Combining Ni and Co offers better	[106]

	0.25)*			on of wood	3000μmol/ min and H_2/CO=2.5	around 2200 μmol/min and H_2/CO=1.7				dispersion and reducibility	
8	7.48%Ni-2.51%Co/ZrO_2	Ni/ZrO_2	Phenol to steam molar ratio of 1:9, 600 °C	Phenol	Conversion 53.5% with H_2 yield of 50.4% w	Conversion of 32.4% with H_2 yield of 24.8%	Stable for 6 h	Only stable within 2 h	Addition of Co reduces the carbon deposit by 64%	Presence of Co increases the catalyst basicity property, thus, enhancing catalytic performance	[107]
9	15%Ni-4%Cr/SBA-15	15%Ni/SBA-15	S/C ratio of 0.95, 600 °C	Bio-oil	Around 100%	Around 95%	Maintained conversion of 97% after 5 h	Less 90% after 5h	317 and 37 mgC gcat−1 h−1 for unmodified and modified catalyst respectively	Improvement in both activity and stability are linked to smaller particle size promoted with the Cr addition	[108]

10	12%Ni-Cu/Mg/Al (CuNi/=0.25)*	12%Ni-Cu/Mg/Al	S/C= 0.38, 550 °C	Tar from steam gasification of wood	Formation rate of H_2 + CO + CH_4 is around 3500µmol/min and H_2/CO=2.0	Formation rate of H_2 + CO + CH_4 is around 3000µmol/min and H_2/CO=2.0	Stable within 120 min	Stable only after 60 min	83.6 and 8.6 mgC $gcat^{-1}$ for unmodified and modified catalyst respectively	Ni-Cu alloy particle enhances lesser particle size, better dispersion, and better oxygen affinity	[109]

*Molar ratio

Different support materials other than Al_2O_3 have been investigated. For example, the steam reforming of toluene with Ni–Fe supported on activated carbon (AC) was tested at a molar ratio of Fe/Ni of 0.08 to 0.2 and in terms of toluene conversion at 600 °C, followed the order of 0.1-Fe/Ni (95.7%)> 0.2-Fe/Ni (68.6)> 0.08-Fe/Ni (64.0%). The catalyst stability test undertaken over a time period of 20 h with 0.1-Ni–Fe/AC and Ni/AC showed an average conversion of 93.8% and 92.9%, respectively [98]. Therefore, the addition of Fe to Ni/AC showed almost no improvement in the toluene conversion. However, TEM observation of the spent catalysts revealed that Ni–Fe/AC had a lower average metal particle size of 19.0 nm compared with that of Ni/AC at 30.0 nm. Thus, indicating that the Ni–Fe/AC catalyst was less susceptible to particle agglomeration than the Ni/AC catalyst. In addition, compared to Ni–Fe/AC, a large amount of carbon deposits in the form of carbon flakes, carbon filaments and hollow carbon tubes are found on the Ni/AC catalyst as shown in Figure 13.

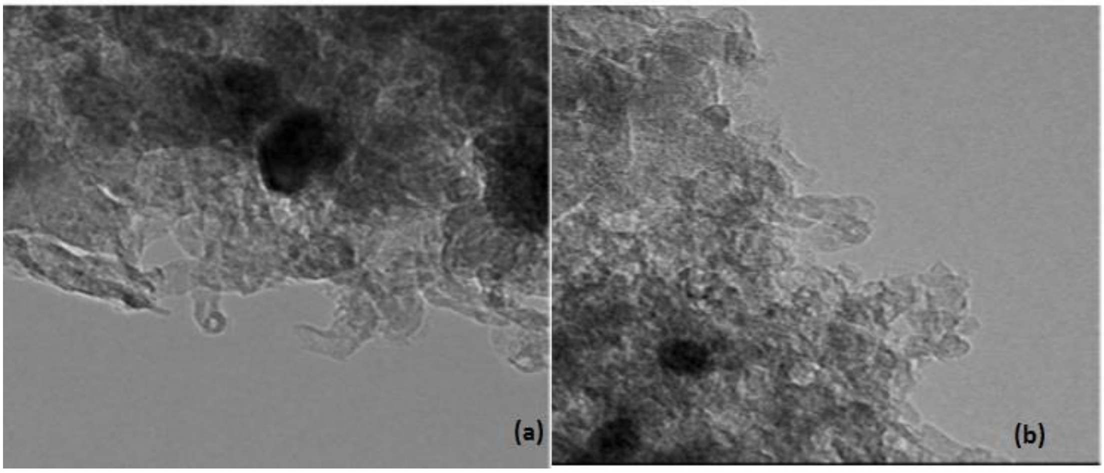


Figure 13: TEM images of (a) Ni–Fe/activated carbon(b) Ni–Fe/activated carbon catalysts after steam reforming of toluene at reaction for 600 °C for 20 h, modified from Yang et al. [98].

In a similar study by Ahmed et al. [77], the catalytic performance of Ni/zeolite with the addition of Fe at a molar ratio of Ni to Fe of 0.71 and 0.77 for the steam reforming of toluene was investigated at 873 K [73]. The results showed toluene conversions in the order of 0.77 Ni-Fe/ zeolite (74%)> 0.71 Ni-Fe/zeolite (60%)> Ni/zeolite (35%)> zeolite only (18%). Further addition of MgO using sequential impregnation to the Ni-Fe(0.77)/zeolite catalyst improved the yield of H_2, indicating an enhanced conversion of the toluene. The combined effect of increased basicity strength provided by MgO and better reducibility of Ni species enhanced by Fe was suggested to be responsible for the higher activity of Ni-Fe-Mg/zeolite and Ni-Fe/zeolite catalysts. The addition of 3% Fe to 8% Ni supported on a palygorskite support material indicates that the interaction between Ni and Fe improves the catalyst properties in terms of dispersion and smaller particle sizes [96]. Subsequently, steam reforming of toluene at 550 °C and an S/C ratio of 1 also showed that the modified 8%Ni-

3%Fe/palygorskite catalyst exhibited higher toluene conversion of 80.5% and increased stability. Comparison of the different catalysts with the palygorskite support alone showed toluene conversions of 80.5%, 78.3%, 77.3% and 69.7% for the 8%Ni-3%Fe/palygorskite, 8%Ni/palygorskite, 3%Fe/palygorskite and palygorskite catalysts respectively, as shown in Figure 14. The carbon deposits on the used catalysts also followed the same order as the activity, with the 8%Ni-3%Fe/palygorskite exhibiting the highest amount of deposits. Further increase in temperature to 700 °C showed that the modified 8%Ni-3%Fe/palygorskite catalyst could attain a maximum toluene conversion of 97% with a H_2 yield of 63%. The stability test for a time period of 48 h also confirmed that the catalyst was stable with an average conversion of 70.4% at 700 °C. Further analysis showed that the carbon deposits on the modified catalyst was graphitic carbon and the catalyst was able to regain its optimum performance after regeneration. Furthermore, the TEM analysis of the used 8%Ni-3%Fe/palygorskite catalyst revealed that the catalyst retained its original morphology in terms of well dispersed and small particles of Ni and Fe.

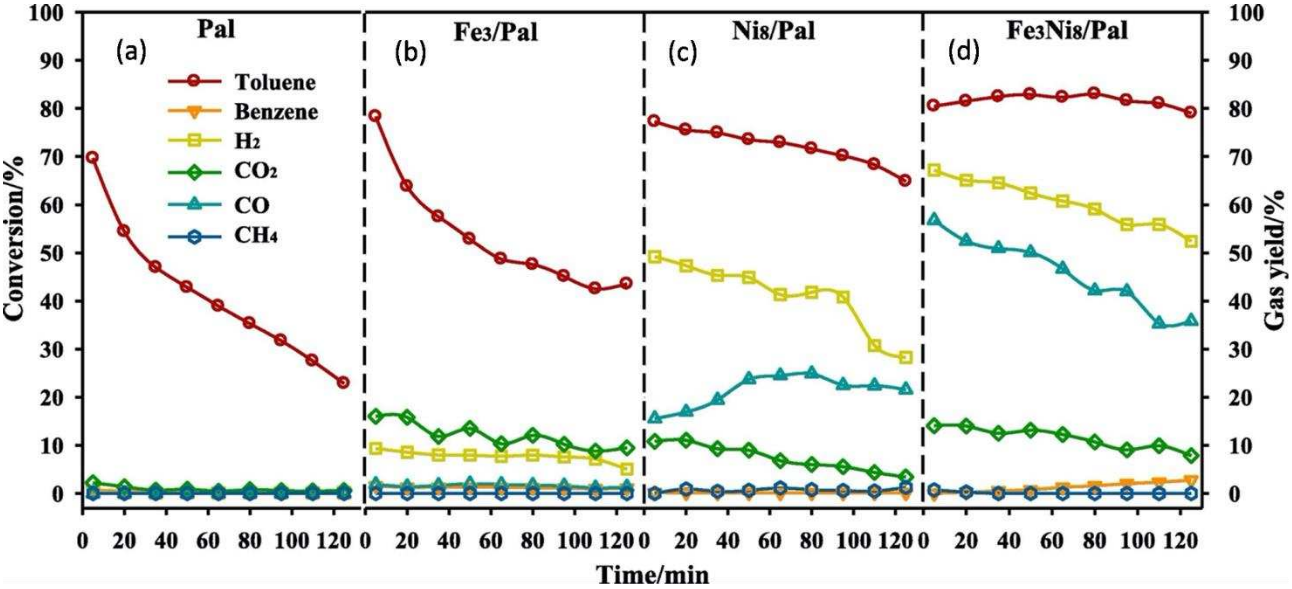


Figure 14: Steam reforming of toluene with (a) palygorskite (b) 3%Fe/palygorskite (c) 8%Ni/palygorskite (d) 8%Ni-3%Fe/palygorskiteat 550 °C and S/C ratio of 1.0, reproduce with permission[96].

Also, it has been reported that as compared to monometallic catalyst supported on mesoporous SBA-15 material, bimetallic Ni–Fe/ SBA-15 catalyst improves both stability and activity for the steam reforming of cellulose at 600 °C [105]. Among the three modified catalysts prepared using an incipient wetness impregnation method with Ni/Fe ratios of 6:1, 1:1 and 5:2, 6%Ni-1%Fe/SBA-15 showed the highest conversion of 90% with better catalyst stability over a time period of 180 min. On the other hand, the monometallic 7%Ni/SBA-15 catalyst displayed a cellulose conversion of only 70%. The most effective modified catalyst possessed well-dispersed nanoparticles of less than 3 nm in size and stronger metal-support interaction as indicated by the second hydrogen adsorption peak temperature (615 °C) as shown in the TPR profiles in Figure 15. These properties clearly linked the modified catalyst to its superior performance.

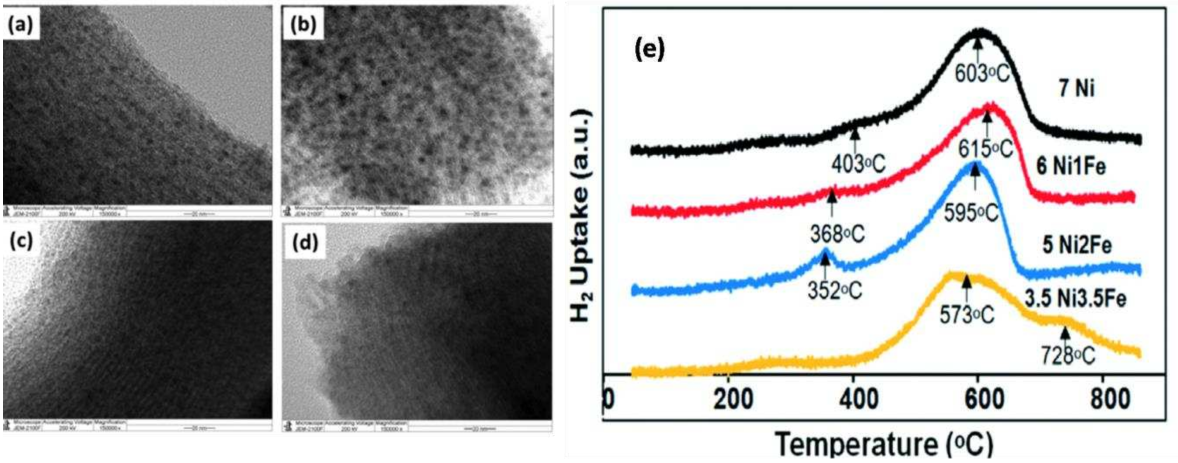


Figure 15: TEM images of fresh catalysts (a) 7%Ni/SBA-15(b) 6%Ni-1%Fe/SBA-15(c) 5%Ni-2%Fe/SBA-15(d) 3.5%Ni-3.5%Fe/SBA-15 (e) H_2-TPR profiles of Fe modified and unmodifiedNi//SBA-15 catalysts, modified from Kathiraser et al.[105].

The above studies show that the addition of Fe to Ni at the optimum ratio for steam reforming of biomass tar results in the formation of a Ni-Fe alloy. Fe provides oxygen to the Ni catalyst surface, which promotes metal–support interaction, better dispersion and smaller particle sizes of the active Ni metal. These subsequently improve catalyst activity and prevent the formation of carbon deposits responsible for catalyst deactivation. However, a high amount of Fe on the nickel surface will lead to a decrease in catalyst activity due to poor metal dispersion and larger metal particle size. This suggests that above the optimum addition of Fe to Ni, the reducibility benefit provided by Fe cannot compensate for the reduction in active nickel, since monometallic nickel has been reported to have higher catalytic activity compared with monometallic Fe.

4.2. Non-ferrous nickel alloy catalyst

In addition to Fe as a bimetallic candidate for the addition to nickel-based catalysts for improved tar reforming, other metals such as Co, Cu, Cr have also been explored and will be discussed in this section. Cobalt and nickel-based catalysts are inexpensive with a medium activity which is considered as a good alternative to the noble metals, however, they both suffer deactivation in the reforming process. Although cobalt is less prone to carbon deposits than Ni, the presence of Co on the Ni surface makes the deposited carbon more easily to be gasified [110]. To investigate the addition of Co to Ni, Wang et al. [106] carried out a study using a Ni-Co/Al_2O_3 catalyst for both steam gasification of cedar wood and reforming of toluene and its performance was compared to the monometallic catalysts, Ni/Al_2O_3 and Co/Al_2O_3. For catalytic steam gasification at a temperature of 823 K, the results indicated that Ni-Co/Al_2O_3 at an optimum Co/Ni molar ratio of 0.25 exhibited the highest rate of formation of CO, H_2, CH_4 with less tar yield and higher resistance to carbon deposits. The order of the catalysts performance was Ni-Co/Al_2O_3 (Co/Ni ratio of0.25)>Co(15 wt%)/ Al_2O_3> Ni(15 wt.%)/Al_2O_3, for the catalytic steam reforming of cedar wood. However, for the toluene reforming at 923 K, a different order was noticed as: Co (12 wt%)/Al_2O_3> Ni–Co/Al_2O_3(Co/Ni ratio of 0.25)> Ni(12wt%)/Al_2O_3. It was suggested that the addition of Co to Ni/Al_2O_3 improves tar reforming except for that of aromatic hydrocarbons (toluene) since tar from biomass pyrolysis contains a high amount of oxygenated hydrocarbons. The synergy that exists between Ni and Co as active metals offers a better metal particle dispersion and reducibility which enhanced both activity and catalyst stability for tar reforming. These results revealed the dependency of catalyst performance on tar composition. In fact, the amounts of carbon deposit on catalyst were also reported to vary according to the tar composition [70]. In general, oxygenated compounds tend to produce more carbon deposits than aromatic compounds [111].

On a ZrO_2 supported Ni catalyst, the introduction of Co affected the catalytic properties by increasing its basicity, the optimum molar ratio was found at a Ni/Co ratio of 1. The introduction of Co-Ni/ZrO_2 catalyst compared to the monometallic catalyst (Ni/ZrO_2) showed an increase in phenol steam reforming conversion of 65% and H_2 yield of 103%, while decreasing the carbon deposits on the catalyst by 64%. A decrease in activity and increase in carbon deposits was found with higher Co loadings beyond the optimum. Recently, results by Calles et al. [108] also reported the advantageous bimetallic effect of Ni-Co in relation to the catalytic reforming of aqueous bio-oil produced from the pyrolysis of de-ashed wheat straw. The aqueous bio-oil was comprised of a mixture of acetic acid, hydroxyacetone, furfural and phenol. Using 15%Ni-4%M/SBA-15 as the reforming catalyst at a temperature of 600 °C and S/C ratio of 0.95, where M represents Co, Cu or Cr, the test revealed that both Ni-Cr/SBA-15 and Ni-Co/SBA catalysts produced a aqueous bio-oil conversion of nearly 100% for a time period of 5h. The carbon deposits on the spent catalyst was found to follow the order of Ni-Cr/SBA-15 <Ni-Co/SBA-15 < Ni/SBA-15 < Ni-Cu/SBA-15. A large carbon deposit (Figure 16(b)) was found on the Ni-Cu/SBA-15 catalyst and the stability test over a time period of 5 h confirmed that the Ni-Cu/SBA-15 catalyst performance was below that of the unmodified catalyst (Ni/SBA-15) (Figure 16(a)). This result suggests that the bimetallic Ni-Cu/SBA-15 catalyst did not have any promotional effect. It was also observed that the carbon deposits on the catalyst for individual tar components was in the order of hydroxyacetone> acetic acid > furfural > phenol. It was noticed that the Ni-Cr/SBA-15 catalyst had the strongest metal-support interaction among all the catalysts. This interaction could have promoted the formation of small Ni crystallites on the surface, thus enhancing its performance.

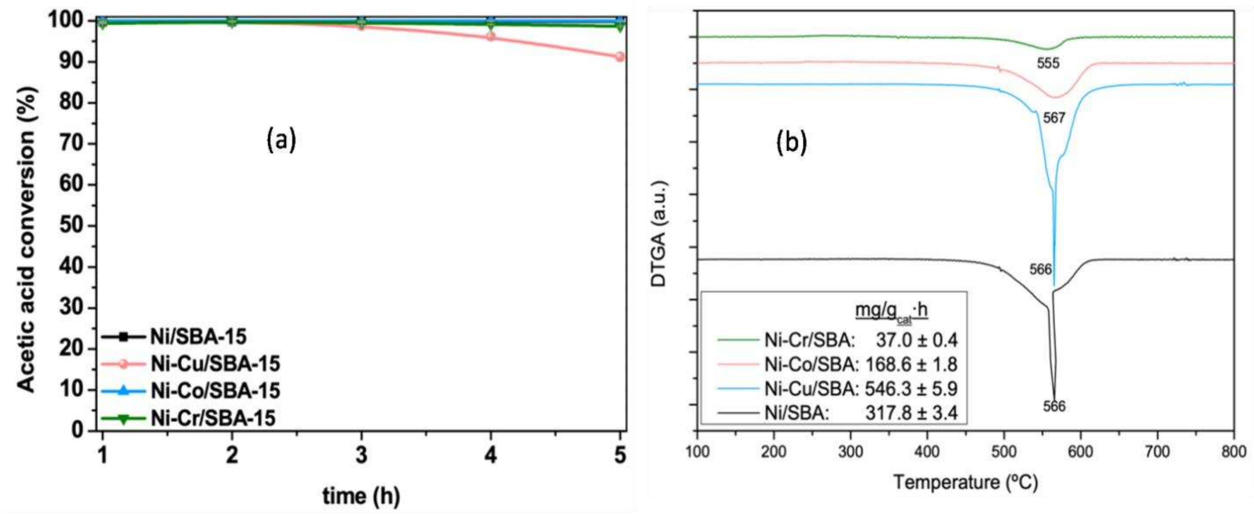


Figure 16 : (a) Steamreforming of aqueous bio-oil using Ni-M/SBA-15 catalysts at 600 °C (b) DTG Profile of the spentNi-M/SBA-15 catalysts after the reaction modified fromCalles et al. [108].

The previous studies have showed that Cu addition to the Ni-based catalyst could offer no improvement in both catalyst stability and activity. However, improved performance was reported for cedar wood steam gasification using a hydrotalcite-like catalyst material of Ni-Cu/Mg/Al with a molar ratio of Cu/Ni between 0.1 and 1.0 and at a temperature of 823 K [109]. The results (Figure 17) revealed an optimum addition of Cu at Ni/Cu ratios of 0.25, showing almost zero tar production and with the highest combined formation rate of CO, H_2, and CH_4. Compared to Ni/Mg/Al (without Cu), the Ni-Cu/Mg/Al catalyst maintained a stable rate of formation of gaseous products at a temperature of 923 K for a time period of 120 min. The performance of the Ni-Cu/Mg/Al catalyst was ascribed to Ni-Cu alloy that promoted lower particle sizes, better metal particle dispersion and better oxygen affinity as confirmed by STEM, EDX, XRD and H_2 chemisorption analyses. The difference between the poorly performing Ni-Cu/SBA-15 catalyst [108] and the improved performance of the Ni-Cu/Mg/Al catalyst could be attributed to the high Ni to Cu ratios used in the Ni-Cu/SBA-15 catalyst, which could not provide reasonable reducibility; suggesting that Cu addition to Ni may require a higher amount of loading than other metals considered (Cr and Co). Another possible reason for the effect of hydrotalcite-like compounds of Ni-Cu/Mg/Al, are related to promotion of metal particle dispersion and thermal stability [112,113]. However, the determination of appropriate ratios of metals in the hydrotalcite-like compound has also been confirmed for improved performance [114,115].

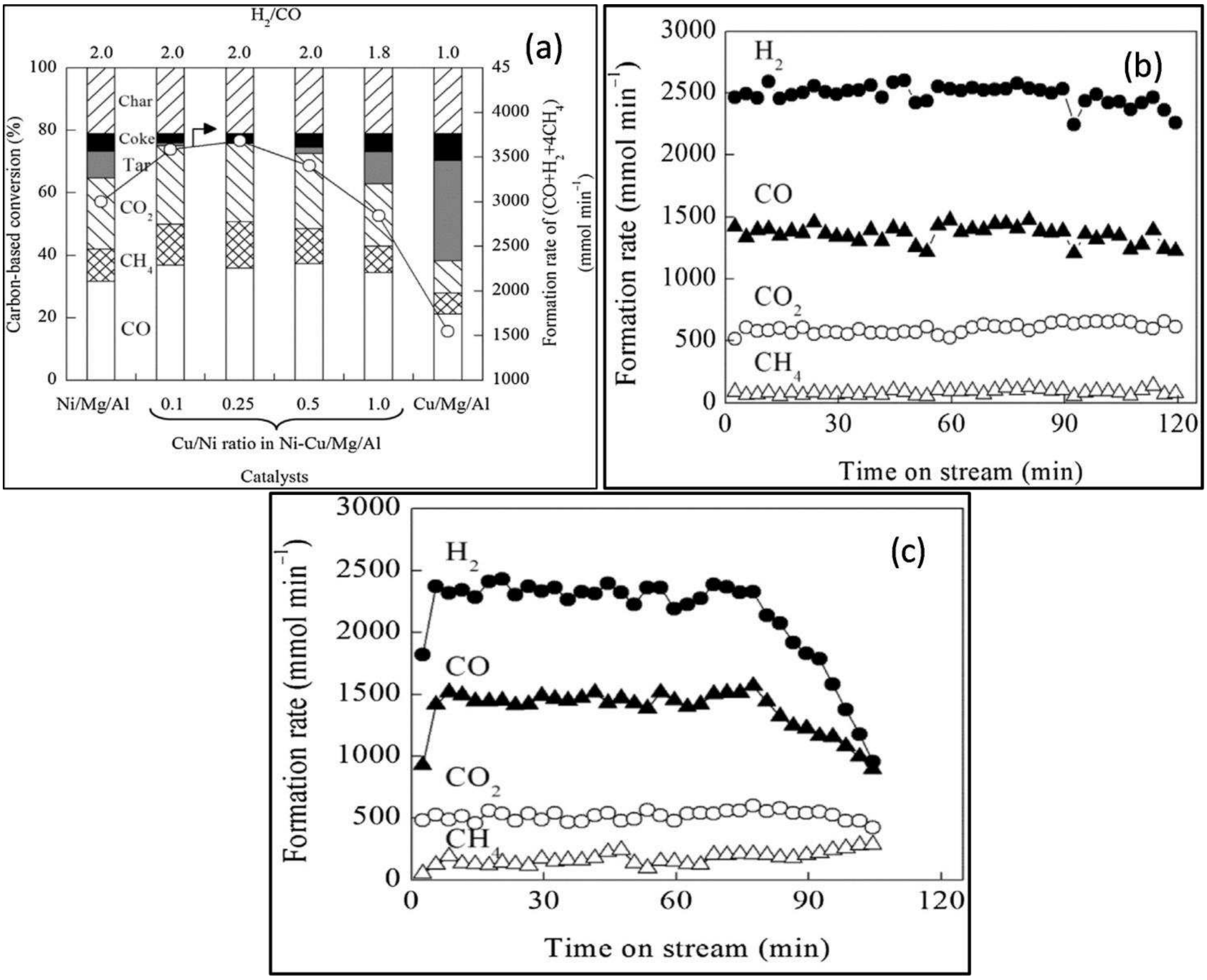


Figure 17: Performances of steam reforming of tar from cedar wood at 550 ◦C and S/C ratio of 0.38 for 0.5 h of (a) Ni-Cu/Mg/Al catalyst in comparison with Ni/Mg/Al and Cu/Mg/Al (b) Ni-Cu/Mg/Al catalyst for 120 min (c) Ni/Mg/Al catalyst for 100 min, modified from Li et al.[109]

5. Promoter-modified nickel catalysts for tar reforming

The summary of Ni-based catalysts considered in this section with modification with promoters is presented in Table 2.

5.1. Rare earth metals/oxides as promoters

The additions of rare earth metals/oxides such as cerium or lanthanum as promoters have been found to be effective to improve the catalytic performance of Ni-based catalysts for tar reforming. Cerium is one of the most abundant rare-earth metals and is considered as a promoter metal due to its redox properties, and the property to exchange oxygen via Ce^{3+} and Ce^{4+} promoted by its oxygen-storage capacity [116,117] and can undergo reactions (1) to (4) [118,119].

$$Ce_2O_3 + H_2O \leftrightarrow 2\ CeO_2 + H_2 \qquad (1)$$

$$Ce_2O_3 + 0.5O_2 \leftrightarrow 2CeO_2 \qquad (2)$$

$$2CeO_2 + CO \rightarrow Ce_2O_3 + CO_2 \qquad (3)$$

$2CeO_2 + C \rightarrow Ce_2O_3 + CO$ (4)

Lanthanum has the ability to chemisorb oxidants such as H_2O and CO_2, which is a beneficial property against carbon deposition [120],the mechanism is presented in reactions (5) and (6) [90]. The presence of La also decreases acidic sites on the surface of the catalyst and also improves H_2 yield through dehydrogenation of oxygenated compounds [84].

$La_2O_3 + CO_2 \leftrightarrow La_2O_2CO_3$ (5)

$La_2O_2CO_3 + C \leftrightarrow La_2O_3 + 2CO$ (6)

The increasing amount of La added to Ni supported on sepiolite (a complex magnesium silicate clay material) produced a decrease in the Ni crystal size as evidenced with a weaker and broader peak of Ni^0 in the XRD profile as shown in Figure 18a [84]. The hydrogen pulse chemisorption and TPR analytical results (Figure 18b) also showed that the addition of La to Ni increases metal-support interaction. Subsequently, the improved properties of Ni-La/sepiolite with an optimum addition at 10 wt% La resulted in a 92.1% conversion for the steam reforming of a phenol–ethanol mixture for a time period of 50 h producing a H_2 yield of 87.6%. In contrast, within 50 h reaction time, Ni/sepiolite (without La) exhibited a poor phenol–ethanol mixture conversion of only 20% and a H_2 yield of 14%. Post-reaction catalyst characterization by TGA showed a reduction in carbon deposits of about 45% were achieved with the addition of La on the Ni/sepiolite catalyst. In another study, the addition of only 1wt% La as the optimum amount to Ni/SBA-15 confirmed that La promotes smaller Ni particle sizes of 2.8nm leading to Ni migration into the pores of the support [121]. In comparison, the particle size for the Ni/SBA-15 (un-promoted) catalyst produced a particle size of 9.7 nm. Subsequently, results for the gasification of cellulose revealed that production of CO was increased while CO_2 was decreased with the increasing amount of La addition, thus, suggesting CO_2 adsorption. Also, the 1%Ni-La/SBA-15 catalyst maintained a very stable H_2 production for 4 h at 4000 mmol min^{-1}, while H_2 production of the un-promoted catalyst reduced to around 2500 from 3750 mmol min^{-1} after 4 h. The catalysts were also tested for steam reforming of toluene at 700 °C with a S/C ratio of 1, and it was found that after 30 h reaction, toluene conversion for the un-promoted Ni/SBA-15 catalyst was only 38% but increased to 97% with the La promoted Ni/SBA-15 catalyst. In addition, catalyst carbon deposits were reduced from 48 mg C $gcat^{-1}$ h^{-1} to 5 mg C with the used of Ni-1%La/SBA-15 (promoted catalyst). Increasing the loading of La beyond the optimum addition of 1 wt.% was reported to decrease catalyst stability.

The above studies have therefore confirmed that La addition to Ni-based catalysts for tar reforming/gasification produces smaller Ni crystal sizes, better metal dispersion, and improved metal-support interaction. These properties aid in CO_2 adsorption leading to a carbon resistant catalyst and enhancement of the water gas shift reaction.

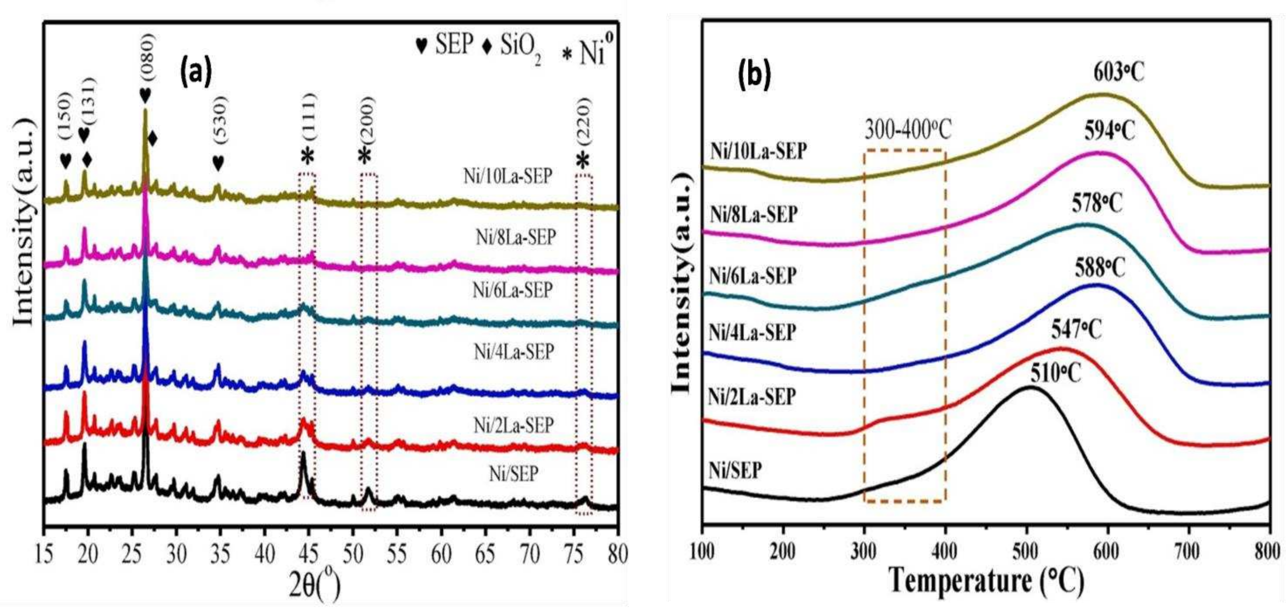


Figure 18: (a) XRD profiles of reduced Ni/sepiolite and Ni-xLa/sepiolite catalysts prepared using co-precipitation method (b) TPR profiles of reduced of Ni/sepiolite and Ni-xLa/sepiolite catalysts, modified from Chen et al.[84].

Table 2: Summary of steam reforming of biomass tar using Ni-based catalysts modified with promoters

Modified nickel based catalyst		**Unmodified nickel catalyst**	**Operating condition**	**Nature of tar**	**Tar conversion**		**Stability Test**		**Carbon deposit**	**Improved properties of the modified Catalyst**	**Ref**
					Modified	Unmodified	Modified	Unmodified			
1	Ni-10wt% La/sepiolite	Ni/sepiolite	600 °C, S/C ratio of 1.7, WHSV = 5.4 h−1	Phenol – ethanol mixture	92.1% conversion with 87.6% H_2 yield.	60% conversion with 45% H_2 yield after 50 h	Stable	14% conversion and 20% for H_2 yield after 50 h	Modified catalyst showed 81% less carbon deposit than Ni/sepiolite	Addition of La to Ni increases metal dispersion, active metal surface and metal-support interaction.	[84]
2	5%Ni-1%La/ SBA-15	5%Ni /SBA-15	700 °C and S/C ratio of 1	Toluene	97%	65%	Stable Within 30 h	38% after 30 h	Rate of carbon deposit is 48 and 6 mgCg/cat-h for unmodified and modified respectively	Promoting effect of La aids CO_2 adsorption and water gas shift reaction due to increase in Ni crystal sizes, metal dispersion, and metal-support interaction	[121]
3	14.9% Ni-2%Ce /Al_2O_3	14.9% Ni-Al_2O_3	900 °C S/C ratio of 6, WHSV =12 h−1	Bio-oil from maize stalk fast pyrolysis	71.4%H_2 yield.	69.9% H_2 yield.	Reduced to about 25% from75% H_2 yield after 10 h at 850 °C.	N/A	Decreased in coke deposit by 3.8% with Ni-Ce /Al_2O_3 compared to Ni-Al_2O_3 after reaction at 800°C	The addition of cerium improves the catalyst resistance to carbon deposit	[122]
4	5%Ni-5%Ce/ mayenite	5%Ni/ Mayenite	800 °C, S/C =4	A mixture of toluene and naphthalene	Around 92%	Around 95%	Reduced to about 85% after 8 h	Stable for 8 h	Both catalysts exhibited almost similar carbon deposit	The addition of Ce has a negative effect which may be due to %5wt not being the optimum addition	[123]
5	4%Ni-30%CeO_2 /Al_2O_3	4%Ni/ Al_2O_3	600 °C, S/C=0.5	Tar from gasification of wood	H_2 formation rate of around 2100 µmol/min and H_2/CO=2.8	H_2 formation rate of around 1500 µmol/min and H_2/ CO=1.9	N./A	N/A	Ni-CeO_2/Al_2O_3< Ni/Al_2O_3	CeO_2 redox property improves the dispersion of Ni metal particles and catalyst resistance to carbon deposit	[118]

6	3%Ni–1%Ce/olivine	3%Ni/olivine	S/C = 5 790°C;	Toluene	88%	59%	Reduced to around 65% after 7h	Reduced to around 10% after around 3 h	29% and 3% carbon deposit for unmodified and modified catalyst respectively	The addition enhances water gas shift reaction and resistance against carbon deposits	[124]
8	Ni-CeO_2(3 wt%)/SBA-15	Ni/SBA-15	S/C ratio of 3 850 °C,	Toluene	98.9%	Around 80%	Stable after 29 h	N/A	0.21% and 0.01% carbon deposits after 4h reaction for unpromoted and promoted catalyst respectively	Surface area and pore volume were increased with CeO_2 which enhanced activity and resistance against carbon deposits	[125]
9	10%Ni-Mn(1%)/ dolomite	10%Ni/ Dolomite	800 °C,S/C ratio of 3	Toluene	62.6% toluene to CO and CO_2	50% toluene to CO and CO_2	Stable after 320 min	25% after 320 min	No carbon deposit was observed on Ni-Mn/dolomite, while Ni/dolomite showed presence of graphitic carbon	The oxygen vacancy created by the presence of Mn help to gasified carbon to more valuable gases	[39]
10	0.1%Pt/4%Ni/30%CeO_2/Al_2O_3	Ni/30%CeO_2/Al_2O_3	550 °C, S/C =0.5	Steam reforming of tar from wood pyrolysis	Formation rate of H_2 + CO + CH_4 is around 3200 µmol/min and H_2/CO=2.7	Formation rate of H_2 + CO + CH_4 is around 2600 µmol/min and H_2/CO=2.5	N/A	N/A	Carbondeposit on Pt/Ni/ CeO_2/Al_2O_3<<Ni/ CeO_2/Al_2O_3	Pt addition improves Ni reduction and eliminates the need to active NiO at high temperature.	[126]
11	5%Ni-0.85% Pt/$La_{0.7}Sr_{0.3}AlO_{3-\delta}$	5%Ni /$La_{0.7}Sr_{0.3}AlO_{3-\delta}$	600°C GHSV =12,000 h^{-1}	Toluene	59.1%	57.5%	N/A	N/A	57 and 8 mg/ g-cat for unpromoted and promoted catalyst respectively after 10 min	Formation Pt-Ni alloy and electron donation from Pt to Ni improves both activity and reduction of carbon deposit	[127]
12	9%Ni/$La_{0.7}Sr_{0.3}AlO_{3-\delta}$	9%Ni/ $LaAlO_3$	650 °C, S/C ratio of 2	Toluene	Average 92.55% for 120 min	Average 89.61% for 120 min	Stable	Stable	Incorporation of Sr into the catalyst reduces carbon deposit from 80 to 30 mg/g·catalyst	Addition of Sr to $LaAlO_3$ increases surface oxygen	[128]

13	Ni/Sr/ La_2O_3 (Ni/Sr=1.49)	Ni/La_2O_3	650°C, S/C ratio of 1	Toluene	Around 75%	Around 50%	Stable for 8 h	Stable for 8 h	Carbondepositon Ni-Sr/La_2O_3 is about 100% higher than that of Ni/La_2O_3	Introduction of Sr enhances water adsorption, thus higher activity, although Ni-Sr/La_2O_3 had higher carbon deposits, the results confirmed it is not responsible for catalyst deactivation	[129]
14	$5\%Ni/La_{0.7}Sr_{0.3}AlO_{3-\delta}$	$5\%Ni/LaAlO_3$	600°C S/C ratio of 2	Toluene	58.2%	25.8%	N/A	N/A	Rate of carbon deposits is 57 and 800 mgC g cat−1for promoted and unpromoted catalysts respectively	Sr presence aids in the mobility of oxygen lattice to the catalyst surface, which helps to inhibit carbon deposition	[130]
15	2.28%Ba/5%Ni/ $LaAlO_3$	5%Ni/ $LaAlO_3$	600°C S/C ratio of 2	Toluene	Around 45 %	Around 30%	Around 30 % after 2 h	Around 20 % after 2 h	Rate of carbon deposits at 740 and 139 mgC g cat−1 for unpromoted and promoted catalystrespectively	The sequential impregnation of Ba on $LaAlO_3$ along with Ni promotes dispersion, reducibility, adsorption of H_2O and its activation to the catalyst surface	[131]
16	$La_{0.8}Sr_{0.2}Ni_{0.8}Fe_{0.2}O_3$	$LaNi_{0.8}Fe_{0.2}O_3$	750°C S/C ratio of 1	Toluene	Around 85%	Around 70%	Around 70% after 8 h	Around 50% after 8 h	Rate at around 5.5 and 42 mg C/mg.h for promoted and unpromoted catalystsrespectively	Sr presence enhanced water adsorbed leading to higher activity at low S/C	[132]
17	3%Ni–1%Ce–1% Mg/olivine	3%Ni–1%Ce/olivine	S/C 3.5 790°C	Toluene	93%	75%	Stable within 7h and reduced to 80% in the presence of H_2S after 7 h	Stable only for around 2.5 h and reduced to 25% in the presence of H_2S after around 4 h	Modified catalyst has 167% less carbon deposits than Ni-Ce/olivine	MgO inclusion improves the catalyst resistance to both carbon deposits and sulphur poisoning	[124]
18	2.5%(Ni20CaO60$CeO_2$20)	2.5 wt%(Ni20$CeO_2$80)	700 ◦C	Toluene	66% but reaches	56%	93 % after 48h at 800	Unstable	N/A	The use of two metal oxides as promoters	[133]

	/CARBO HSP	/CARBO HSP			100% at 800 ◦C		◦C			improves both activity and stability	

The use of 3wt% cerium as a promoter to Ni-Al_2O_3 was investigated forthe catalytic reforming of bio-oil derived from fast pyrolysis of maize stalk. It was found that for a 1h test at 700 °C H_2 yield increased by 2.8% and by 2.1% at 900 °C in comparison to the un-promotedNi-Al_2O_3[122]. There was no stability time period test to compare between the two catalysts, but for the Ce promoted catalyst a decrease in H_2 yield from about 75% to 25% yield after 10 h time period at a catalyst temperature of 850 °C was reported. However, the initial tests undertaken at 700 °C indicated a decrease in coke deposition of 3.8% with the addition of the Ce promoter, suggesting the promotional effect of Ce against carbon formation. Similarly, H_2 selectivity was enhanced (Figure 19a) with Ce addition on a $Ni_2Mg_4Al_2$ hydrotalcite structure for toluene steam reforming [134]. The Ce promoted catalyst exhibited higher intensities for both moderate and strong basic site peaks (Figure 19b). The redox ability of Ce promotes CO_2 interaction with Mg oxides/hydroxides basic sites to form surface carbonate.

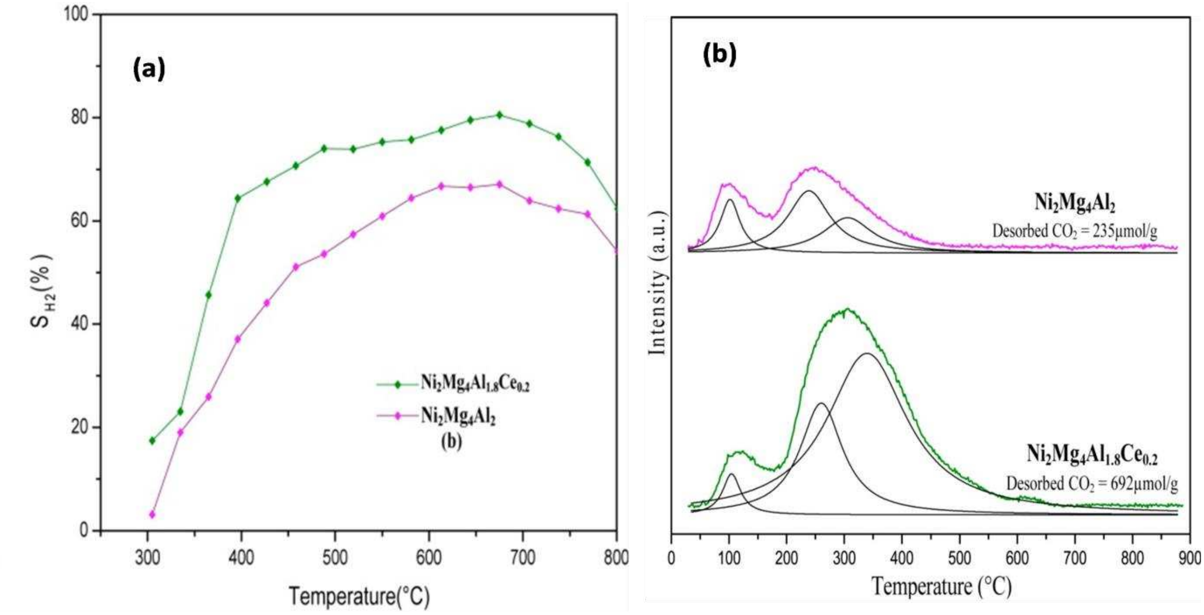


Figure 19: Comparison between $Ni_2Mg_4Al_{1.8}Ce_{0.2}$ and $Ni_2Mg_4Al_2$ catalysts (a) H_2 selectivity from toluene steam reforming at 300-800 °C, steam/toluene ratio of 14(b) CO_2-TPD profiles, modified fromAbou et al.[134].

The studies demonstrated by Zhang et al [124] for toluene conversion also showed that the addition of 1%Ce to 3%Ni/olivine enhanced the water gas shift reaction and inhibits the formation of carbon. Consequently, Ce addition improved the toluene conversion from 59% to 88% for the catalytic steam reforming process. In another study, the addition of 5 wt.% Ce to Ni supported on mayenite was shown to have increased the catalyst surface area due with improved porosity, and also enhanced the nickel particle-support interaction [123]. The catalytic performance for reforming at 800 °C showed that the promoted Ce/Ni/mayenite catalyst exhibited around 92% conversion for a mixture of toluene and naphthalene and reduced to about 85% after an 8 h time period. The un-promoted catalyst showed a conversion of 95% for 8 h, which was higher than that of the promoted catalyst. The negative effect of Ce addition on activity here could be attributed to the 5 wt.% of Ce loading used in these studies which may not be the optimum addition. However, the introduction of thiophene (50 ppm) as a source of sulphur to the model tar compound indicated a superior performance of the Ce/Ni/mayenite catalyst as compared to the un-promoted Ni/mayenite. Ceria could have oxidised the sulphur to sulphates and sulfonate, thereby lowering its effect. Sulphur oxidation provides an oxygen-shielded structure which inhibits the interaction of sulphur with active metal [135]. Thus, a higher presence of surface oxygen will promote sulphur oxidation, therefore, the introduction of Ce to Ni/mayenite may have increased the surface oxygen. Kimura et al [118] carried out steam gasification of cedar wood and examined the addition CeO_2 to Ni/Al_2O_3 as a catalyst for tar reduction. The catalyst was prepared using two methods with varying content of CeO_2 from 0 to 50%: co-impregnation (CI) and sequential impregnation (SI). Irrespective of the catalyst preparation methods and at 773K, the addition of CeO_2 improved the formation rate of H_2, and resulted in a reduction in tar content and also resistance to carbon deposit formation. However, the formation rate of CO was observed to be unchanged with all catalysts. The optimum performance was achieved with the $4\%Ni/30\%CeO_2/Al_2O_3$ (CI) catalyst. In general, catalysts prepared using co-impregnation showed higher catalytic performance than those catalysts prepared using the sequential impregnation preparation method. The characterization results revealed by TEM and EXAFS indicated that the $4\%Ni/30\%CeO_2/Al_2O_3$ (CI) catalyst had better dispersed Ni metal particles and had the strongest metal-support interaction based on TPR analysis. The promotional effect of CeO_2 could be linked to its redox property which enhanced the gasification of the carbon deposits to form more CO. Since the rate of formation of CO was unchanged while H_2 yield was increased with the CeO_2 addition, this suggests that the rate of the carbon gasification is equal to the rate of CO consumption through the water gas shift reaction. Therefore, the addition of CeO_2 to Ni/Al_2O_3 also enhanced the water gas shift reaction. A similar trend is described by Tao et al. [125] for a comparison of the activity of a CeO_2 promoted $Ni-CeO_2/SBA-15$ catalyst with Ni/SBA-15 for toluene reforming. It was found that $Ni-CeO_2$(3 wt%)/SBA-15 catalyst exhibited the highest performance at a catalyst temperature of 850 °C with 98.9% toluene conversion, which was stable for 29 h and had negligible catalyst carbon deposit formation. In addition to the redox property, the presence

CeO_2 addition to nickel-based catalyst, also improves surface area and pore volume, as shown in Table 3, these could be the combined effect for its enhanced catalytic performance.

It is believed that MnOx could play a similar role to CeO_2 in supplying oxygen to the Ni species [46]. This is confirmed by a study conducted by Koike et al. [136]for the catalytic steam reforming of tar from biomass pyrolysis at a catalyst temperature of 823 K. The addition of MnO_2 at ≤ 20 wt% to 12 wt% Ni/Al_2O_3 decreased both the rate of tar formation and carbon deposits on the catalyst. Also, the addition of MnO_2 increased the H_2/CO ratio and the rate of formation of CO, H_2 and CH_4. At the optimum MnO_2 addition of 20 wt%, zero tar yield was recorded, the catalyst also exhibited the highest catalytic stability as compared to Ni/Al_2O_3. The water-gas shift reaction was also enhanced in the presence of the MnO_2 promoter as evidenced by an increase in the H_2/CO ratio with increasing MnO_2 loading. On a Ni/dolomite catalyst, the addition of Mn also increased H_2 production from 62% to 79% and recorded the highest toluene conversion to CO and CO_2 of 62.6%, while comparison using Ca and K additions showed only a slight improvement [39]. In addition, the Mn promoted catalyst was stable over a 5 h reaction time at a catalyst temperature of 800 °C with no carbon deposit formation (based on XRD and TGA analyses).

Table 3: Catalytic properties of Ni-/SBA-15 and Ni-CeO_2/SBA-15catalystsbefore reaction and carbon deposits after 4 h of steam reforming of toluene at 850 °C [125].

Catalyst	BET Surface area (m^2/g)	Pore volume (cm^3/g)	Carbon deposit (wt %)
Ni/SBA-15	261.1	0.43	0.21
Ni-CeO_2(1 wt%)/SBA-15	301.6	0.48	0.02
Ni-CeO_2(3 wt%)/SBA-15	307.7	0.51	0.01

As indicated by the above studies, the addition of Ce or CeO_2 and MnO_2 enhanced tar reforming ability of Ni-based catalysts by promoting water gas shift reaction. Also, their presence enriched the Ni surface with oxygen due to their redox properties, hence improving Ni catalyst resistance to carbon deposits. Furthermore, the addition of cerium is also found to provide resistance against sulphur poison.

5.2. Noble metals as promoters to Nickel-based catalysts for biomass tar reforming

Noble metal catalysts are well known to have a higher resistance to carbon deposits than nickel catalysts under biomass gasification/tar reforming reactions. The nature of the carbon formed on the noble metals catalyst are also different from that formed on Ni catalysts during tar reforming [137]. However, due to the high cost of noble metals, the Ni-based catalyst has been the preferred industrial catalyst for reforming. Modification of Ni catalysts with small amounts of noble metals such as Pt, Rh, Ru, or Pd is demonstrated as a way to improve the carbon resistance of the Ni catalysts.

Using a Pt promoted Ni-dolomite catalyst (1%Pt-10%Ni/dolomite) for coconut shell steam gasification at 800 °C displayed higher gaseous products and less tar yield compared to Fe and Co promoted catalysts (1%Fe-10%Ni/dolomite and 1%Co-10%Ni/dolomite) [137]. The product distribution also showed that Pt addition promoted methane reforming. Furthermore, the carbon deposits after 2h reaction time for the different catalysts was in the order of Ni/Pt/dolomite (6.5%) <Ni/Fe/dolomite (8.3%) <Ni/Co/dolomite (9.3%) <Ni/dolomite (16.5%). The superiority of the catalyst with Pt addition was linked to improved pore volume and reducibility. In addition to the synergy that exists between Ni and CeO_2 which enriches oxygen to the Ni surface and reduces formation of coke, a further improvement may be through the addition of Pt. For example, as reported by Nishikawa et al. [126], further addition of Pt (0.1 wt%) to a $Ni/CeO_2/Al_2O_3$ catalyst improves Ni reduction due to the formation of a Pt-Ni alloy as revealed by EXAFS analysis. As a result, steam gasification of cedar wood was enhanced in terms of lower tar yield and higher formation rate of H_2, CO and CH_4 in the order of the catalysts a, $Pt/Ni/CeO_2/Al_2O_3$> $Ni/CeO_2/Al_2O_3$> Ni/Al_2O_3. It was observed that between catalyst temperatures of 823 and 923 K the $Pt/Ni/CeO_2/Al_2O_3$ catalyst recorded zero tar yield. In particular, the difference in the performance of the catalysts was more pronounced at a lower temperature (823 K). Furthermore, the $Pt/Ni/CeO_2/Al_2O_3$catalyst showed similar catalytic performance with or without H_2 reduction. Also, both $Ni/CeO_2/Al_2O_3$ and Ni/Al_2O_3 catalysts showed a lower catalytic activity without H_2 reduction. Thus, the use of Pt/Ni/ CeO_2/Al_2O_3 eliminates the need to active NiO at high temperature through H_2 reduction.

Mukai et al. [127] also demonstrated that Pt addition to Ni supported on $La_{0.7}Sr_{0.3}AlO_{3-\delta}$ perovskite-type oxide for toluene reforming eliminates pre-treatment through H_2 reduction. In addition, the Pt promoted catalyst showed improvement in H_2 yield and reduction in carbon deposits. The improved performance was correlated with the formation of a Pt-Ni alloy and electron donation from Pt to Ni as revealed by STEM-EDX, XAFS, and XPS analyses. Based on these studies [126], Nishikawa et al. [138] further compared a $Pt/Ni/CeO_2/Al_2O_3$ catalyst with the addition of other noble metals; Pd, Rh, and Ru to $Ni/CeO_2/Al_2O_3$ for the steam gasification of cedar wood. At a catalyst temperature of 823 K, the order of reactivity of the $Ni/CeO_2/Al_2O_3$ catalysts modified with the noble metals was 0.1wt% Pt> 0.1wt% Rh> 0.5wt%

Ru> 0.1wt% Pd. The TPR profiles of the catalysts showed that Pt had the strongest interaction with Ni among all the noble metals, and thus, was responsible for its higher catalytic activity. Moreover, all the noble metal promoted catalysts have lowered carbon deposition of <5wt%, which compares to 12 wt% formed on $Ni/CeO_2/Al_2O_3$ after the reaction. However, in another study for oxidative steam gasification of cedar wood [139], the promoting effect of Pd on Ni/Mg/Al hydrotalcite-like compound was found to be superior to Pt and other noble metals: Au, Ru, Rh and Ir. All the promoted catalysts showed higher catalytic activity than the non- promoted catalyst. The TEM analysis of the catalysts (Figure 20d) showed that the Pd-Ni/Mg/Al catalyst maintained high metal dispersion after 2 h reaction time with negligible increase in Ni crystal sizes. This is in contrast to the Ni/Mg/Al (un-promoted catalyst) which showed disappearance of Ni metal particles due to oxidation of Ni^0 after 2 h reaction time (Figure 20c). The optimum loading of Pd is as low as 0.05 wt% leading to better reducibility and dispersion of Ni active particles. This shows the effectiveness of noble metals as promoters at even very low amounts. However, there is a need to compare their performance with other promoters such as transition metals that have higher loadings as their optimum addition.

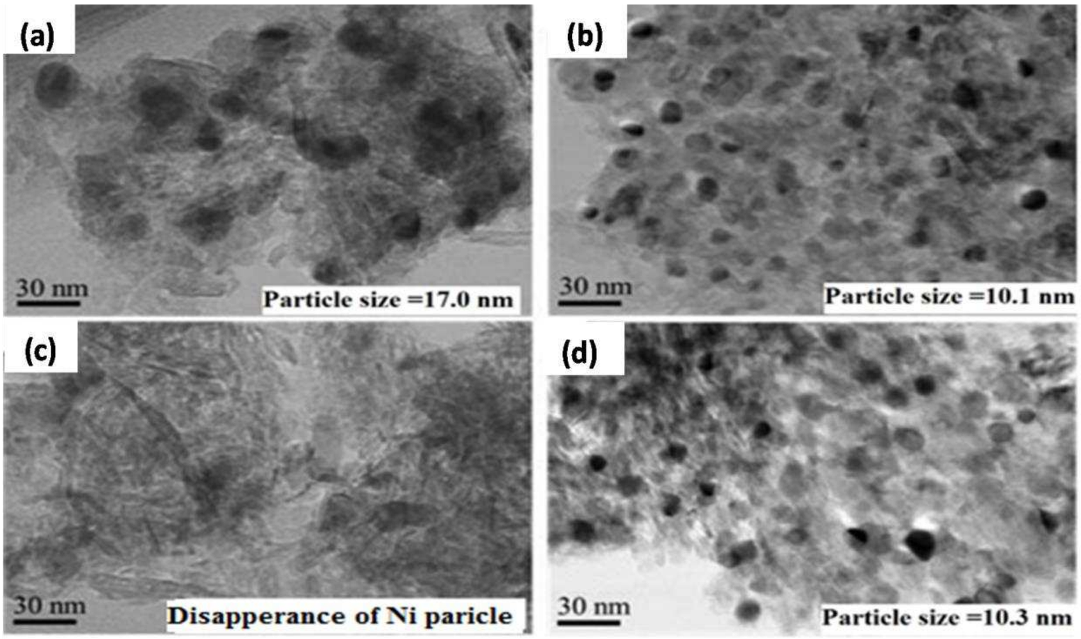


Figure 20: TEM images of (a) Ni/Mg/Al after reduction pre-treatment (b) 0.05%Pd-Ni/Mg/Al after reduction pre-treatment and images after 2 h reaction oxidative steam gasification of cedar wood at 873 K of (c) Ni/Mg/Al (d) 0.05%Pd-Ni/Mg/Al, modified from Chen et al.[139].

Considering the above studies that compared the addition of different noble metals as promoters, it can be established that Pt and Pd have a superior promoting effect over Rh, Au, Rh and Ir. The results by Profeti et al. [140] also support this claim, where Pt and Pd are found to be superior promoters than Ir and Ru on Ni/CeO_2–Al_2O_3 catalyst for the steam reforming of biofuels. While the superiority between Pt and Pd may depend on the nature of the support used, this is because both studies [138,139] used cedar wood, the only variable was the composition of the catalysts. However, Profeti et al. [140] further reported that the Pt-Ni/CeO_2–Al_2O_3 catalyst had the highest activity for the steam reforming of glycerol, while Pd-Ni/CeO_2–Al_2O_3 exhibited better performance for steam reforming of ethanol.

In general, noble metal additions to Ni-based catalysts in low amounts have been found to stimulate an interaction that stabilized Ni active sites in a reduced state with better dispersion. This interaction improves the activity of Ni-based catalysts and their resistance to carbon formation.

5.3. Alkali and alkaline earth metals

Alkali and alkaline earth metals are known as catalyst promoters due to their unique basic property which tends to help catalyst stability during reforming by limiting deactivation due to carbon deposits [132].

5.3.1 Incorporation of alkaline earth metals into perovskite containing Ni structure

Several findings have shown that alkaline metals can be incorporated into a perovskite structure to enhance their catalytic performances. Perovskite structure is known for the provision of highly dispersed active metal particles formed from the precursor of metal oxides matrix [141]. The perovskite structure is represented by ABO_3, where the A-site corresponds to a rare-earth metal such as La, Ba, Ca, or Sr, while the B-site corresponds to a transition metal such as Ni, Co, Fe, or Cu as the active site [142]. The A-site metal interacts with the active metal to increase the stability of the structure [143]. Another metal can be substituted into either the A or B site to further improve the perovskite catalytic properties [144,145], for example, creating an oxygen deficiency on the surface [146].

The partial substitution of La^{3+} in $LaAlO_3$ by Sr^{2+} to form $La_{0.7}Sr_{0.3}AlO_{3-x}$ perovskite supported on Ni increases the surface oxygen due to mobility of lattice oxygen [128]. The surface absorbed oxygen reacts with carbon or its intermediates. Thereby, reducing the carbon deposits for example, it has been reported carbon reduction from 80 to 30 mg/g·catalyst after toluene steam reforming at a catalyst temperature of 650 °C and S/C ratio of 2. While the -OH from H_2O dissociation supplies the lattice with oxygen to continuously maintain oxygen availability in the cycle (Figure 21c). The further presence of alkali and alkaline earth metals: K, Ca and Mg on $La_{0.7}Sr_{0.3}AlO_{3-x}$ perovskite support was reported to further suppress sintering of Ni. In addition, their presence leads to more absorbed oxygen from the lattice forming on the catalyst surface, as indicated by an increase in the area of the second peaks in XPS the spectra (Figure 21a). Accordingly, the presence of K, Ca and Mg resulted in further reduction in carbon deposits by over 60% (Figure 21b).

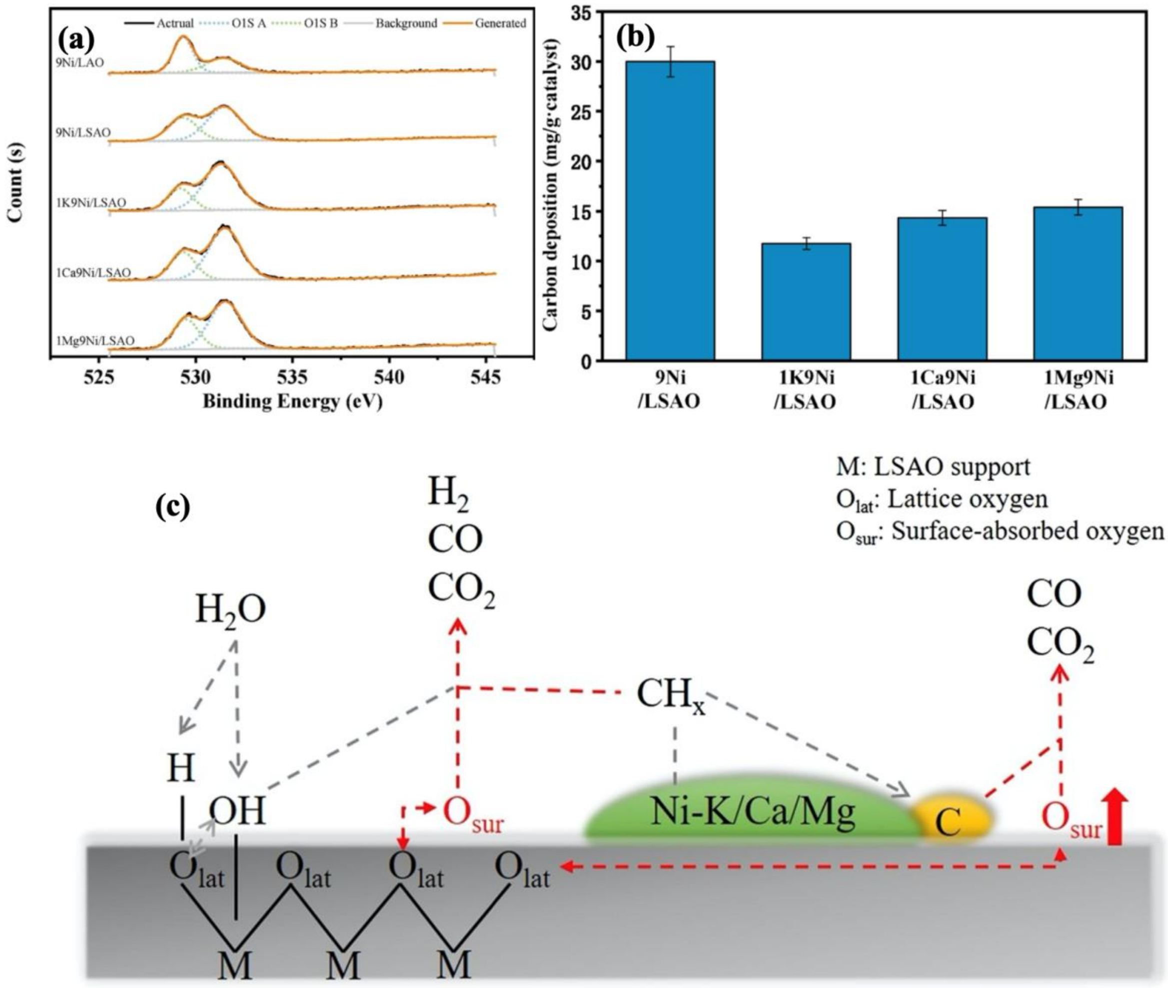


Figure 21: (a) XPS spectra from top to bottom of fresh catalysts: 9Ni/LAO, 9Ni/LSAO, 1K9Ni/LSAO, 1Ca9Ni/LSAO and 1Mg9Ni/LSAO (b) carbon deposition on various catalysts after toluene steam reforming at 650 °C, S/C ratio of 2.0 after 120 min reaction (c) Mechanism of carbon deposition resistance in the presence of alkali and alkaline earth metals. LAO and LSAO represent $La_{0.7}Sr_{0.3}AlO_{3-x}$ and $LaAlO_3$ respectively, while 9 and 1 stand for wt%Ni., modified from Zhang et al.[128].

A similar observation was made by Sekine et al. [130], who showed that compared to $Ni/LaAlO_3$, the use of a $Ni/La_{0.7}Sr_{0.3}AlO_{3-x}$catalyst reduces carbon deposits in addition to improving toluene conversion. However, $Ni/LaAlO_3$ displayed better performance in terms of H_2 yield and toluene conversion than Ni catalysts supported on other perovskites: $LaFeO_3$,

$BaTiO_3$, $SrTiO_3$ and $SrCeO_3$. Furthermore, Ni/$La_{0.7}Sr_{0.3}AlO_{3-x}$was also found to be superior to catalysts with substitution with other alkaline earth metals: Ni/$La_{1-x}M_xAlO_{3-\delta}$ (where M represents Ba or Ca),and the order of their effectiveness was reported as Sr> Ba> Ca. In addition, the study also established the superiority of Ni/$La_{0.7}Sr_{0.3}AlO_{3-x}$ (Sr substituted perovskite) over Sr doped catalyst using (Ni/Sr/$LaAlO_3$) a sequential impregnation method. Again, on a different perovskite: $LaNi_{0.8}Fe_{0.2}O_3$, the substitution of Sr was confirmed to be superior to Mg and Ca substitutions for the steam reforming of toluene. The mechanism is shown in Figure 22[132]. Both TPSR-H_2O and TPD-H_2O analyses showed that the alkali metal substitution increases the water adsorption ability of the catalyst. This property enhanced the reforming of the toluene at a lower S/C ratio of 1 with high catalytic activity and less carbon deposition as compared to $LaNi_{0.8}Fe_{0.2}O_3$. Further, TPD-O_2 and XPS results also showed that the $La_{0.8}Sr_{0.2}Ni_{0.8}Fe_{0.2}O_3$ catalyst had the highest mobile lattice oxygen among all the catalysts. In particular, the TPD-O_2 peaks of the Sr promoted catalyst was found at temperatures of around 700–800 °C, conforming to the toluene steam reaction conditions. As a result, the carbon deposits on the Sr promoted catalyst decreased with increasing reaction temperature; while the deposits on the $LaNi_{0.8}Fe_{0.2}O_3$catalyst increased with increasing reaction temperature.

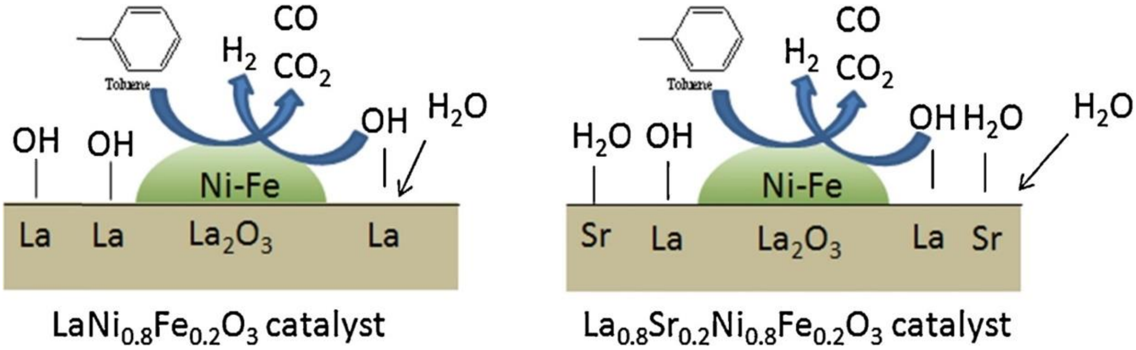
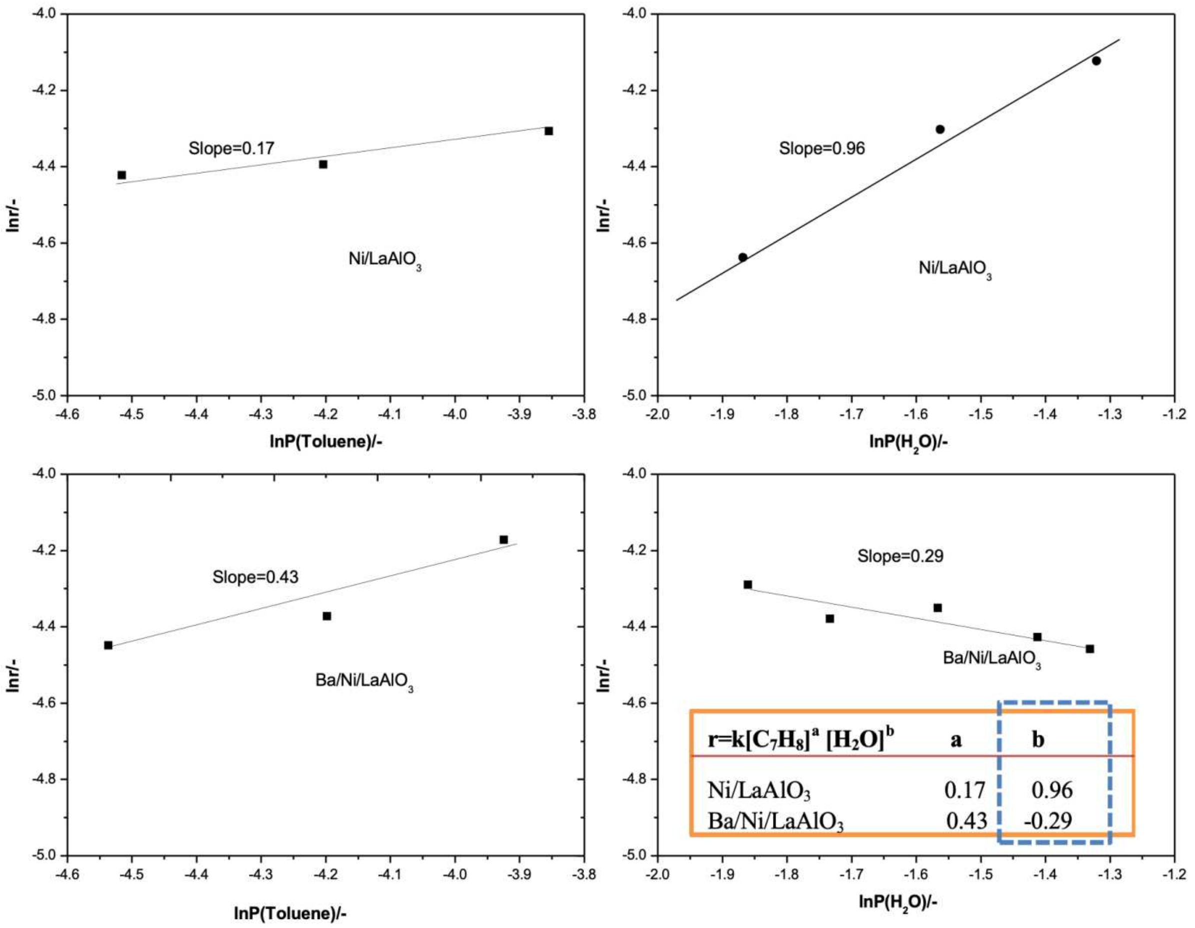


Figure 22: Toluene steam reforming mechanisms on $LaNi_{0.8}Fe_{0.2}O_3$ and $La_{0.8}Sr_{0.2}Ni_{0.8}Fe_{0.2}O_3$ perovskite structure, reproduce with permission[132].

These studies considered above have pointed to the superiority of Sr substitution into perovskite supported Ni catalysts for tar reforming compared to other alkaline earth metals (Ba, Ca and Mg). However, it is essential to note that partial substitution into perovskite Ni-based catalyst for improved tar reforming is not limited to the use of alkaline earth metals. It was reported that due to substitution of Ce (rare earth metal), a $La_{0.6}Ce_{0.4}NiO_3$catalyst exhibited improvement in surface area, smaller particle sizes, better metal particle dispersion and reducibility [146]. As a result, better conversion of toluene was achieved with a yield of 57.26% and 76.62% for CO and H_2 respectively at 800 °C. Also, as compared to $LaNiO_3$,the substitution of Mn in $LaNi_{0.5}Mn_{0.5}O_3$as a catalyst for steam reforming of toluene leads to higher catalytic activity and stability in both the presence and absence of H_2S [147].

5.3.2 Doping of alkaline earth metals on Ni supported catalyst

Here, the alkaline earth metals are not substituted into the perovskite but rather used as a promoter on the surface of the supported Ni catalyst. It was reported that Ba was the most effective promoter on $Ni/LaAlO_3$ (perovskite) [131]. The catalytic activity for toluene steam reforming at a S/C ratio of 2.0 at a temperature of 873K was investigated and the formation of catalyst carbon deposits followed the order as $Ni/Ba/LaAlO_3 >$ $Ni/Ca/LaAlO_3 >$ $Ni/Sr/LaAlO_3$. It was found that highly dispersed Ba on $Ni/LaAlO_3$ provided the strongest basic strength; which promotes H_2O adsorption and activation to the catalyst surface. The activation of H_2O to the catalyst surface is considered the rate-determining step for toluene steam reforming; in which the reaction order is lowered from 0.96 to -0.26 in the presence of Ba as shown in the Arrhenius plots of Figure 23. Oemar et al. [129] also doped (without substitution) Sr on Ni/La_2O_3 and noticed an enhancement of adsorption of water in the presence of Sr as revealed by TPD-H_2O analysis. The authors found that compared to catalysts prepared using a co-impregnation method, the sequential impregnation method of preparation had enhanced Sr surface enrichment. Subsequently, the catalyst prepared using the sequential impregnation method had higher catalytic activity and stability for the steam reforming of toluene at a lower S/C ratio of 1. However, at similar calcination temperatures and regardless of the method of preparation, the catalysts doped with Sr performed better than the un-doped catalysts. Apart from the water adsorption capacity promoted by the presence of Sr, other physicochemical properties of the fresh catalysts confirmed that Sr also increases surface area and the dispersion of Ni particles. These may have been the reason for the higher performance of the catalyst with the better Sr surface enrichment.



$r=k[C_7H_8]^a\ [H_2O]^b$	a	b
Ni/LaAlO$_3$	0.17	0.96
Ba/Ni/LaAlO$_3$	0.43	-0.29

Figure 23: Arrhenius plots used in determining rate order for steam reforming of toluene at 873K on catalysts: Ni/LaAlO$_3$ and Ba/Ni/LaAlO$_3$,modified from Higo et al. [131]

5.3.3 Alkaline earth metal oxides

Alkaline earth metal oxides possess unique properties of high basicity, and thermal stability, which make them suitable candidates as promoters for Ni-based catalysts. For example, the promoting effect of MgO, CaO, SrO and BaO were investigated with a Ni-Fe/ Carbo HSP catalyst for the reforming of toluene [138]. It was reported that MgO showed a higher catalytic activity compared with the other oxides for toluene conversion, and the trend in terms of toluene conversion was MgO >>CaO>SrO>BaO[148]. The FTIR spectral analysis of the oxides after moisture adsorption showed a very large O-H signal at 3699 cm^{-1} on the MgO promoted catalyst (Figure 24a) corresponding to Mg(OH)$_2$, thus suggesting the role of H$_2$O adsorption in the catalyst performance. The optimum catalyst composition was found to be 1.17% total loading of 45%Ni-21%Fe-34%MgO supported on Carbo HSP. As displayed by the SEM image (Figure 24b), the modified catalyst has a distinct morphology: highly dispersed with low agglomeration of the particle. Subsequently, the optimized catalyst indicated no carbon deposit with nearly 100% conversion of a toluene/ethylene mixture for

48 h reaction time at 750 °C. Both Ni3Fe alloy phase and MgO contributed to the enhanced catalytic performance. From the different tests, it appears that the Ni3Fe alloy phase accounts for the catalyst resistance to coke formation, while resistance to sintering is due to the presence of MgO.

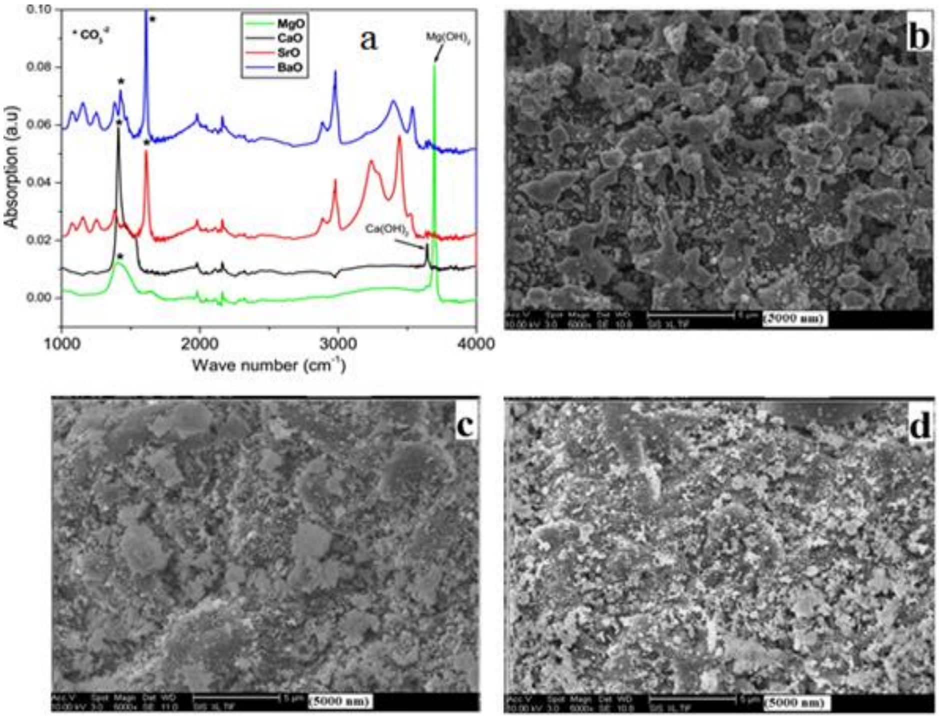


Figure 24: (a) water adsorption IR spectra of MgO, CaO, SrO and BaOoxides,SEM images of fresh reduced Carbo HSP supported catalyst of (b) 1.17%(Ni45Fe21Mg34) (c) 0.77%(Ni68Fe32) (d) 0.75%Ni, modified from Baidya et al.[148]

Similarly, Nogueira et al. [142] also confirmed that MgO addition to Ni/Al_2O_3 is responsible for the sintering resistance property of the catalyst, allowing it to produce stable steam reforming of acetic acid with 91% conversion for a 24 h reaction time at 600 °C catalyst temperature. In addition, the presence of MgO leads to the formation of $MgAl_2O_4$, which inhibits coke formation.

Similar to MgO, the combination of the promotional effect of both CaO and CeO_2 on the surface of Ni/CARBO HSP support resulted in 100% steam reforming conversion of toluene at 800 °C which only declined by 7% after 48 h reaction time [133]. It was found that the use of CeO_2 alone as the promoter results in rapid catalyst deactivation, while using CaO maintained its resistance to deactivation. The results suggested that the basic nature of CaO enhances higher metal dispersion and resistance to carbon deposition, while CeO_2 acts as a redox provider that promotes H_2O dissociation on the catalyst surface. In addition to both sintering and coke formation resistance, the presence of MgO further contributes to Ni-based catalysts, in that Zhang et al [124] demonstrated that the presence of MgO also prevents sulphur poisoning of the catalyst. This was noticed from experiments with a further addition of Mg to Ni–Ce/olivine which resulted in an increase in toluene conversion from 75% to 93% at 790°C and with a S/C ratio of 3.5 over a 7 h reaction time period. The results showed that as compared to 3%Ni/olivine and 3%Ni–1%Ce/olivine, the catalyst still maintained 90% conversion in the presence of 10 ppm of H_2S. Whereas, both %Ni/olivine and 3%Ni–1%Ce/olivine showed a very poor conversion of 20% at around 3 hr and 25% at around 4 hr reaction time periods respectively.

The basicity properties of alkaline earth metal oxides were found to enhance H_2O adsorption resulting in inhibition of carbon deposition. In addition, MgO is an effective promoter to reduce sintering of Ni-based catalysts for tar reforming and it also prevents sulphur poisoning.

6. Effect of modification of support on Ni-based catalysts for tar steam reforming

Herein, the effects of modification of the support material with promoters are presented. Nickel-based catalysts are generally supported on metal oxides to provide both mechanical strength and good surface area for the active metals. The activity of a catalyst is influenced by the type of support used, mostly due to the interaction between the support and the active metal which affects metal particle dispersion, oxygen vacancies and reducibility of the catalyst [149]. It can even determine the type of carbon deposits formed on a catalyst [104]. Typically, the support is catalytically inactive in a chemical reaction, but in some cases, it can participate in the reaction due to the active metal-support interaction. In addition,, the support can also interact with reactants to enhance adsorption [53]. Nevertheless, some supports such as Al_3O_2 favors the formation of coke due to their acidic nature. In addition, the high operating temperatures employed in biomass gasification may lead to the support collapsing or result in the formation of larger metal clusters which causes sintering due to reduction in metal dispersion. Catalyst supports are therefore modified with promoters to mitigate some of these effects for better performance of the tar reforming catalyst or by lowering the reaction temperature [137]. The use of two or more metal oxides as catalyst support can result in a change in structural, textural and redox properties of the catalyst. In some cases, mesoporous materials such SBA-15, ZSM5, MCM-41 and MCM-22 are used to improve the Ni catalytic properties, mainly due to their high surface area and enhancement of active metal dispersion [84].

6.1. Mayenite as support for Ni-based catalysts

Incorporation of a thermally stable material such as mayenite ($Ca_{12}Al_{14}O_{33}$) into a support matrix can limit the rate of carbon formation, since such materials contain an appreciable amount of free oxygen species. For example, mayenite possesses a unique structure of cubic crystals composed of sub-nanometre size cages connected in three dimensions. Two out of twelve cages are occupied statically by O^{2-} and O^{-} ions, as shown in Figure 25 [150]. Thereby compensating the positive charge in the cage framework with the chemical composition of $[Ca_{24}Al_{28}O_{64}]^{4+}$. As such, those anions are in a free motion mode inside the cages, they are therefore referred to as “free oxygen ions”. The free oxygen ions on the nickel catalyst surface react with carbon and sulphur to prevent deactivation [151]. Based on the above properties, mayenite is found to be an excellent material as a support to nickel for tar reforming catalysts for preventing coke deposits and H_2S poisoning and has been investigated in many studies [151–153]. Mayenite is also reported to act as a spacer support to prevent sintering [154]. $Sr_{12}A_7$ as a free oxygen material for use as support for Ni catalysts has also found to exhibit excellent activity for biomass tar steam reforming [155].

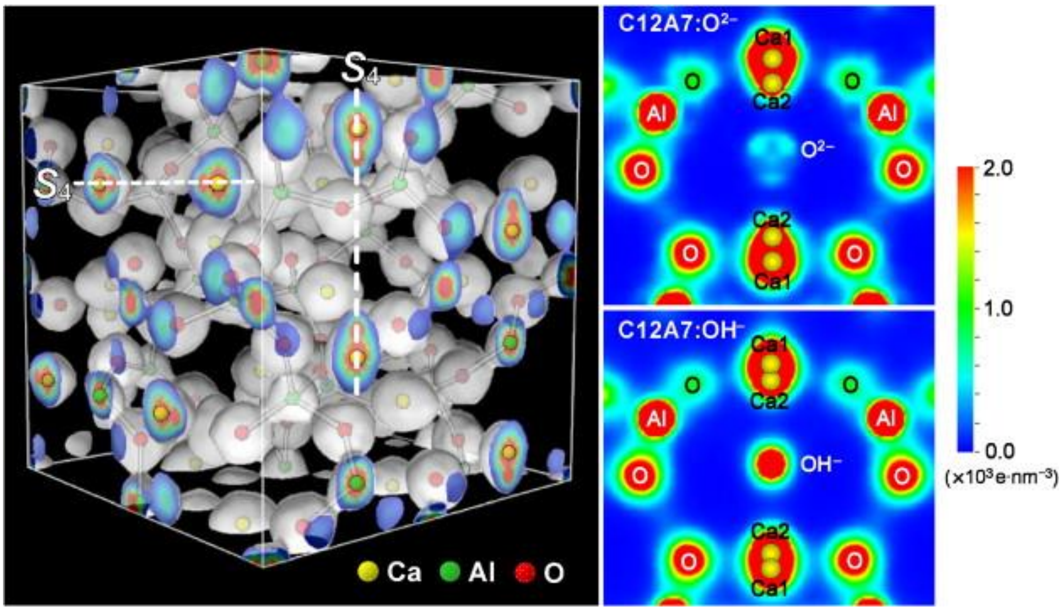


Figure 25: Superimposed electron density map of the crystal structure of mayenite displayed by maximum entropy method (MEM) analysis reproduced with permission[150]

In addition, a combination of $Ca_{12}Al_{14}O_{33}$ and CaO as support material for impregnated nickel catalysts enabled CaO to promote the water–gas shift reaction by capturing CO_2, whereas, $Ca_{12}Al_{14}O_{33}$ provided the catalyst with stability properties. Due to such properties, the modified catalyst exhibited the highest toluene conversion of 99% for 4 cycles (800 s for a cycle), dropping to 80% conversion and with no evidence of sintering after 9 cycles [156].

These studies confirmed the benefit of the thermal stability of mayenite and serve as a good support modifier for the prevention of sintering of Ni-based catalysts for tar reforming.

6.2. The use of CaO and MgO as support modifiers

The large surface area, abundance and natural occurrence of metal oxides like CaO and MgO in the form of minerals make them attractive materials as a catalyst support or modifiers/promoters. Besides contributing basicity to a support, they also provide CO_2 sorption which helps in shifting the equilibrium towards more H_2 production in tar reforming through the water gas shift reaction [157].

It is also reported that interaction between Ni, CaO and Al_2O_3 could exist in a solid solution form of Ca(Ni,Al)O, which inhibits Ni crystallite growth [157]. Experiments on catalytic reforming of toluene showed that the optimum catalyst (Ni–Ca–Al(8:62:30)) showed around 70% toluene conversion for 24 h reaction time with the highest H_2 production and lowest CO_2 selectivity (Figure 26). This was a significantly better performance compared to Ni/Al_2O_3(Figure 26). Furthermore, according to DT/TG, XRD and CO_2−TPD analyses of the used Ni–Ca–Al (8:62:30) catalyst had the lowest carbon deposition rate, lesser agglomeration of Ni and highest basicity. Similarly, the interaction between MgO and Al_2O_3 as a catalyst support has been shown to be beneficial in inhibiting coke formation due to formation of $MgAl_2O_4$ spinel [102].

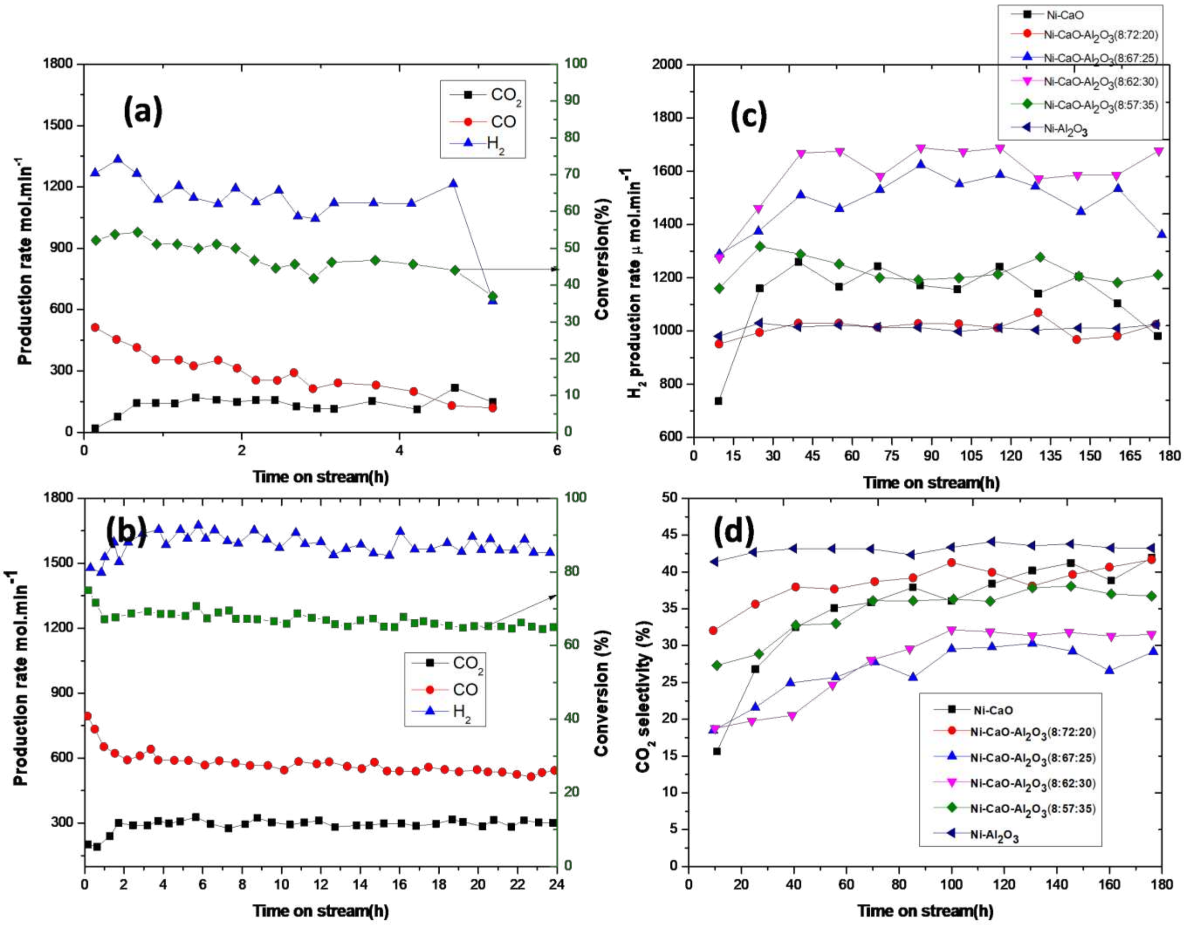


Figure 26: Steam reforming of toluene at S/C ratio of 1 and 650 °C of (a) Ni–Al(8:92),(b) Ni–Ca–Al(8:62:30) and (c) Rate ofH_2 production for various catalysts (d) CO_2 selectivity for various catalysts, modified from Ashok et al.[157].

The effect of CaO doping with a molar ratio of 1-2 on nickel supported mixed oxides of Fe_2O_3 and Al_2O_3 has also been investigated [158]. At 650 °C and S/C ratio of 2, the catalytic activity of the catalysts in terms of toluene conversion wasNi/CaO(1.5)–Fe_2O_3–Al_2O_3> Ni/CaO(1)–Fe_2O_3–Al_2O_3> Ni/CaO(0.5)–Fe_2O_3-Al_2O_3> Ni/CaO(2)–Fe_2O_3–Al_2O_3> Ni/Fe_2O_3–Al_2O_3. In particular, the highest activity Ni/CaO(1.5)–Fe_2O_3–Al_2O_3 catalystshowed a toluene conversion of 78.78% and with a H_2/CO ratio of 3.75, and the highest formation rate of H_2 and CO_2. The catalyst also maintained excellent stability for 22 h reaction time. The XPS results suggested that the presence of CaO promoted the surface catalytic activity of Fe, as it was found that the optimum catalyst had the highest surface Fe concentration. Furthermore, based on BET analysis, the introduction of CaO also increased the surface area and produced smaller crystallite sizes of the Ni particles (Table 4). While TPR profiles revealed that the addition of CaO limits the interaction of Fe with Al_2O_3, which enhances its interaction with

Ni. The presence of CaO is also suggested to have facilitated H_2O dissolution at a lower S/C ratio of 2 as confirmed by TPSR tests with water.

Table 4: Some physical catalytic properties of Ni-Fe-Al and Ni/Ca–Fe–Al catalysts and rate of carbon deposit on the catalysts after 4 h steam reforming of toluene at 650 °C and S/C ratio of 2.

Catalyst	Ni crystallite size (nm)	BET Surface area (m^2 /g)	Carbon formation rate (mg C/g cat h)
Ni/Fe–Al	22.7	14	30.4
Ni/Ca(0.5)–Fe–Al	21.3	38	26.1
Ni/Ca(1.0)–Fe–Al	22.1	31	19
Ni/Ca(1.5)–Fe–Al	21.4	27	14.5
Ni/Ca(2.0)–Fe–Al	23.7	20	17.8

Dolomite contains appreciable amounts of both CaO and MgO. Research recently conducted by Tan et al [90] shows that the use of dolomite as a promoter on different metal oxide supports of Al_2O_3, La_2O_3, CeO_2, and ZrO_2 strengthened the basicity and enhanced the metal-support interaction. Among all the catalysts investigated, Ni/dolomite/La_2O_3 showed the highest carbon conversion of model tar (phenol + toluene+ naphthalene) of 77.7% and a H_2 yield of 66.2%. The presence of the dolomite was to eliminate the formation of amorphous coke on the Ni/dolomite/La_2O_3, although the filamentous forms of the carbon were still present but was reduced from 12.2 to 11 wt%. Filamentous carbon has less effect on catalyst deactivation than the amorphous form. The performance of the catalyst was linked to the inherent CaO and MgO contained in the dolomite, aiding in eliminating the carbon deposits on the catalyst surface.

These results therefore confirmed the role of CaO in improving catalytic activity, H_2 selectivity and inhibition of coke formation through facilitation of H_2O dissolution, strengthening catalyst basicity, and enhancement of the surface enrichment of secondary metals on the nickel catalyst surface.

6.3. Mixed oxides of CeO_2–ZrO_2 as support for Ni-based catalysts

ZrO_2 is amphoteric in nature, enabling it to react as both an acid and a base, and such a property allows the Lewis acid sites on the $ZrO_2$to enhance metal dispersion, as metal atoms prefer to be associated with the Lewis acid sites of the support. Whereas the basic sites promote CO_2 adsorption on the support [159]. A combination of zirconia and ceria as a support are known as high oxygen storage capacity (OSC) materials with excellent thermal stability [160]. The interaction between the two metal oxides in the form of $Ce_xZr_{1-x}O_2$ creates lattice strain, thus causing oxygen mobility that improves the redox properties and increases the carbon deposition resistance of a catalyst [161].

There have been several studies of ZrO_2 and CeO_2as support materials in association with Ni-based catalysts. For example, the activity of catalysts in relation to benzene steam reforming conversion has been tested with different 15%Ni/metal oxide catalysts at temperatures between 550 and 700°C. The order of the catlysts in terms of benzene conversion was found to be Ni/ZrO_2 <Ni/CeO_2 <Ni/ϒ-Al_2O_3 <Ni/CeO_2(75%)–ZrO_2(25%) [86]. Equally, Ni/CeO_2(75%)–ZrO_2(25%) maintained excellent conversion (>80%) for a 5 h reaction time period, significantly higher than the other catalysts. In addition, lower carbon deposits (0.1%) were observed on the Ni/CeO_2–ZrO_2 catalyst after the reaction, which resulted in better catalyst stability, while the carbon deposits on the Ni/ϒ-Al_2O_3 catalyst was much higher at 17.4%. Excellent redox ability for oxygen storage and transfer exhibited by both CeO_2 and ZrO_2 for the Ni/CeO_2–ZrO_2 catalyst arethe major contributing factor to its superior performance. However, the highest surface area of 148.6 m^2 g^{-1} was recorded with the Ni/ϒ-Al_2O_3catalyst compared with 31.4 m^2 g^{-1} for the 15wt% Ni/CeO_2(75%)–ZrO_2(25%) catalyst. It is also important to note that the combination of CeO_2 and ZrO_2 improves the individual surface area of CeO_2 and ZrO_2. This suggests that the combined factors of surface area and the redox properties of the support determine the catalytic performance. In addition to enhancing the redox property by combining CeO_2 and ZrO_2 as the catalyst support, an additional property has been reported by Matas et al. [162]. They found that differences in the type of support can alter the location of the carbon deposits on a catalyst surface. This effect was found to have enhanced the catalytic performance of steam reforming of phenol at a temperature of 700 °C and a S/C ratio of 20 [162]. It was observed that after the reaction, TPO profiles of the used catalysts showed that the location of the carbon deposits on the Ni/Ce-ZrO_2 catalyst were distributed equally on both the nickel surface and the support. In comparison, TPO analysis of the Ni/K-La-ZrO_2 catalyst showed a large amount (~80%) of the carbon deposits were found on the nickel surface. To further enhance the catalytic activity of CeO_2–ZrO_2 as a Ni-based catalyst support, manganese ions from M_nO_x could be incorporated into the ceria lattice. This addition is reported to have increased the oxygen storage and mobility capacity of the CeO_2–ZrO_2 supported Ni catalyst surface [163]. The synergy that exists between the mixed oxides as revealed by catalyst characterization appears to have also increased reducibility, thereby promoting oxidation of carbon on the catalyst surface. As a result, experiments examining the catalytic steam reforming of naphthalene was maintained for a 6 h reaction time period due to a negligible carbon deposits (Figure 27).

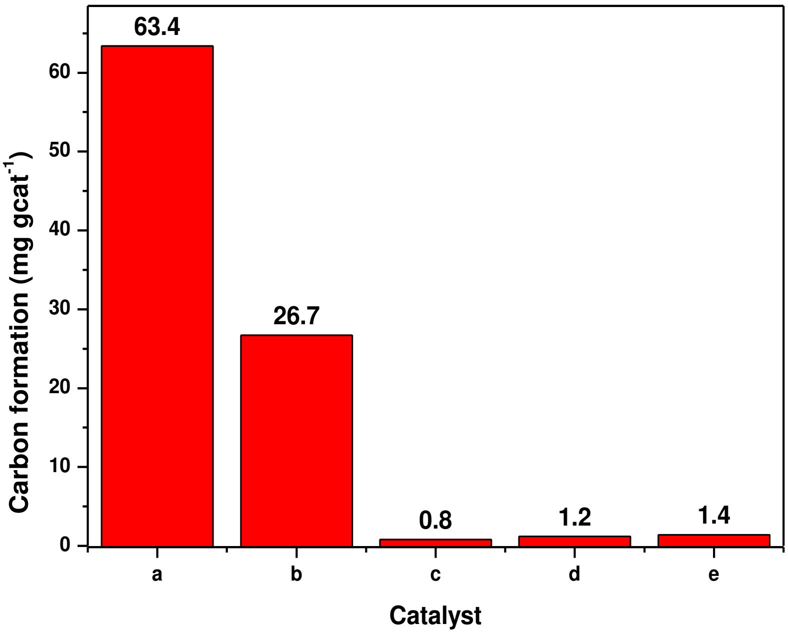


Figure 27: Amounts of carbon deposit after 6 h steam reforming of naphthalene at 700 °C and S/C ratio of 2 on catalyst (a)15%Ni/α-Al_2O_3(b)15%Ni/$Ce_{0.75}Zr_{0.25}O_2$(c)15%Ni/$Ce_{0.75}Zr_{0.15}Mn_{0.1}O_2$(d)15%Ni/$Ce_{0.75}Zr_{0.05}$ $Mn_{0.2}O_2$(D) 15%Ni/$Ce_{0.75}Mn_{0.2}O_2$[163].

The surface area of CeO_2–ZrO_2 support material for Ni catalysts may be further improved for tar reforming by encapsulation within the porous structure of a SiO_2 layer [164]. The SEM morphology of the catalyst showed regular spheres of SiO_2 (Figure 28a), while the HR-TEM image (Figure 28b), further revealed SiO_2 was coated onto the core material: Ni/CeO_2-ZrO_2. Based on the XPS analysis, the SiO_2 interacts with Ni to form a Ni-O-Si structure as core-shell catalysts. As such, the encapsulated catalyst is found to have improved the catalytic performance of the catalyst in terms of toluene conversion from about 60% to 80% at a temperature of 700 °C. However, there was no reaction time stability test to demonstrate the effect of the SiO_2 encapsulation on the catalyst performance. Furthermore, the increasing amount of SiO_2 on the catalyst caused a reduction in oxygen mobility (Figure 28(c)), which may affect the oxidation of carbon deposits on the catalyst surface.

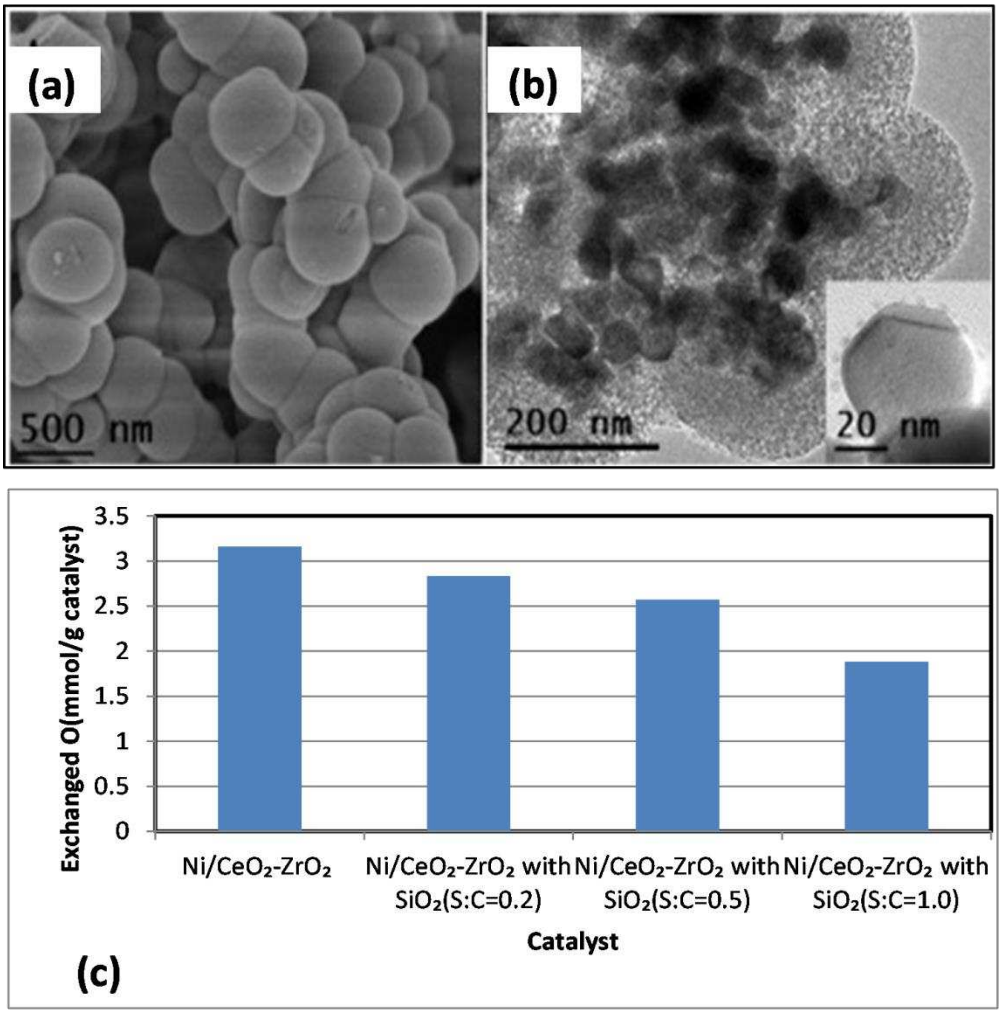


Figure 28: Image addition of SiO_2 at shell to core (S:C) mass ratio of 0.5 to Ni/CeO_2-ZrO_2 by (a)SEM (b) HR-TEM (c) Oxygen exchange capacity of catalysts with and without encapsulating SiO_2, images modified from Zhao et al. [164]

The excellent redox ability exhibited by the interaction of CeO_2 and ZrO_2 is found to improve both catalyst activity and stability of nickel-based catalysts for tar reforming. In addition, the properties of CeO_2-ZrO_2 as a support can be further enhanced by incorporating M_nO_x or encapsulating it with a porous structure such as SiO_2. However, encapsulation could negatively affect the resistance to catalyst carbon deposits.

7. Relationship between real biomass tar and model tar compound

To have a good understanding of NI-based catalysts as steam tar reforming catalysts, here, the performance of using the same catalyst for real biomass tar and model tar compound are compared.

Di Carlo et al., [165] conducted steam gasification of hazelnut shells at 850 °C, the concentration of the individual tar generated were measured without any catalyst usage as shown in Figure 29A. Employing $Ni/Ca_{12}Al_{14}O_3$ as catalyst effectively converted the individual tar components with 84 to 94% conversions (Figure 29B), with phenol and 1-ring components having the highest conversions. These results are compared with using the same catalyst but with toluene as model tar compound, and about 100% conversion is achieved [152,153].

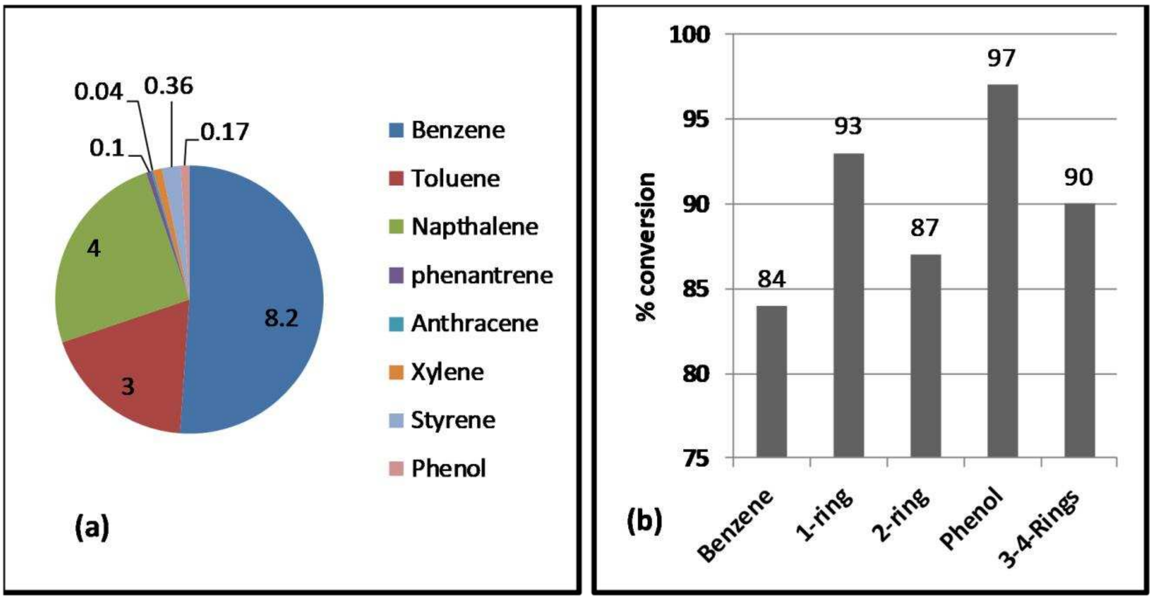


Figure 29: (a) composition of tar from steam gasification hazelnut shells at 850 °C (b) tar conversion with the use of $Ni/Ca_{12}Al_{14}O_3$[165]

The activity of Ni-Fe/activated carbon [98] and Ni-Fe/coal gangue ash[166]using toluene as model compound yielded 93.8% and 85.7% conversions respectively. In comparison with real biomass tar, 92.3% conversion was achieved during the in situ two-stage pyrolytic gasification of rice husk at 800 °C using Ni-Fe/rice husk char catalyst. The porous carbon presence increases the catalyst's surface area, thereby contributing to the sorption ability of the catalyst. This property together with char devolatilization increases the gas yield ($CO + CO_2 + CH_4 + C_2$) with LHV of 12.10 MJ/m^3 [167]. As described by Figure 30, tar is adsorbed on char matrix after its interaction with active sites on the surface, leading to polymerization reaction, thereby releasing permanent light components thereby releasing permanent light components and soot. The soot covers and blocks the active sites access with the tar. As such, if the carbon consumption rate is less than the rate of carbon deposition, then, catalytic deactivation will occur due to soot accumulation.

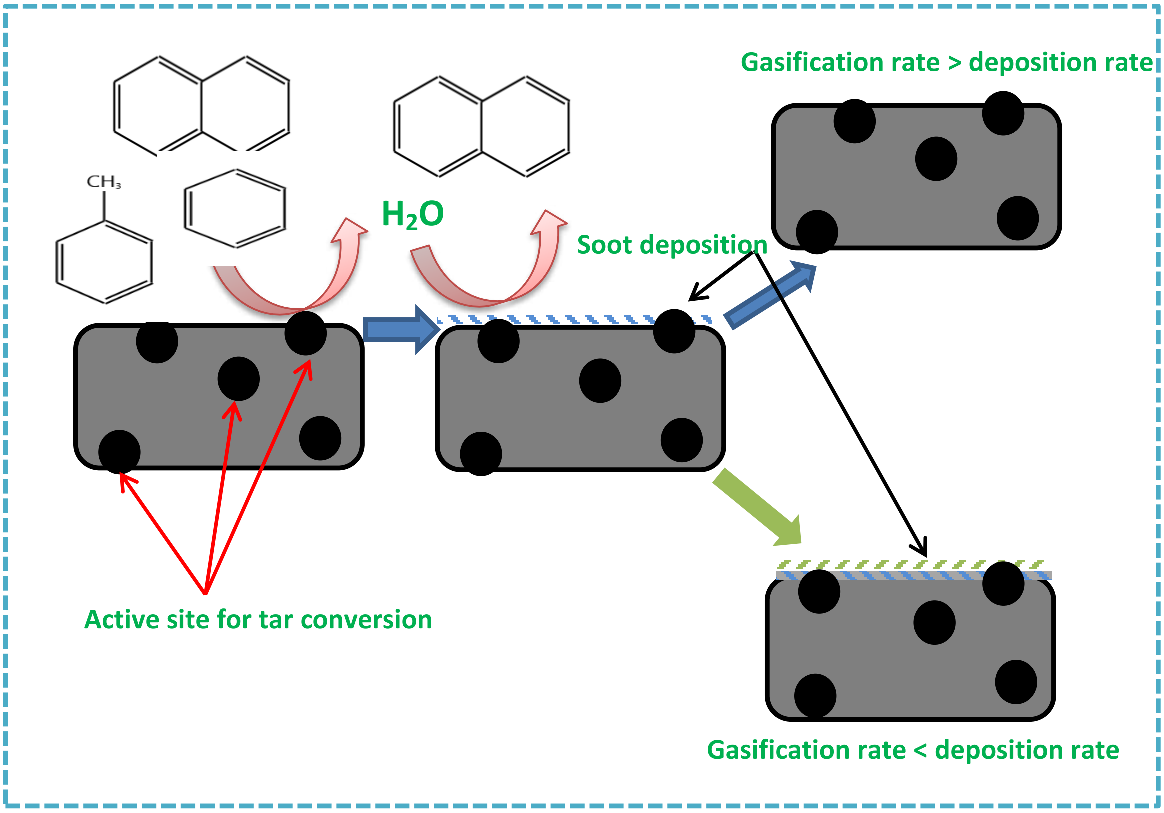


Figure 30: Mechanism of tar steam reforming over carbonaceous supported Ni-based catalyst[168,169].

Also, Daorattanachaiet al. [170]found the addition of Re to Ni-supported sewage sludge char catalyst to have improve metal dispersion and prevention of particle agglomeration. The catalyst showed 100 % and 90% conversions when tested for both steam reforming of real biomass tar from wood and naphthalene respectively. After the reaction, the amounts of carbon deposit (1.5 mmol·gcat^{-1}) on the catalyst used for real tar is higher than that for model compound (naphthalene) with 1.2 mmol·gcat^{-1}. Similar results were found by Laosiripojanaet al., where both the carbon deposit on Ni–Fe/$La_{0.8}Ca_{0.2}CrO_3$/MgO–Al_2O_3 and tar conversion were higher during the steam reforming real tar (wood) than that on model compound (toluene)[171]. This can be explained due to the complex nature of real tar containing different and higher hydrocarbons than just one model tar compound. The higher hydrocarbons can undergo other reaction such as polymerization, hence producing more carbon deposit. Again, it is reported that oxygenates are more reactive than aromatics but produces more carbon deposit[111].

It is important to note that the activity of modified Ni-based catalyst showed good relation between using real biomass tar and a model tar compound. However, the former due to its complexity tends to deactivate catalyst faster. Again, considering that the compositions of tar due vary depending on the biomass type, it will be difficult then to compare a particular model compound with all biomass tar.

8. Activation energy

One of the roles of modified catalysts is to lower the activation energy requires to break the C-C, H-O, C-O or C-H bonds. This section presents the Kinetics parameters most importantly the activation energy of modified catalysts in comparison with that of unmodified catalysts for steam reforming of tar.

The kinetic expression equation that describes tar steam reforming reaction is given by equations 7 and 8[60,172].

$$-r_{tar} = k_{app}\, C_{tar}^{n} C_{H_2O}^{m} \tag{7}$$

$$k_{app} = \frac{[-in(1-X_{tar})]}{\tau} = k_{0,app}\, e^{\frac{E_{app}}{RT}} \tag{8}$$

Where $-r_{tar}$ is the rate of disappearing of the tar, C denotes concentration, n and m reaction order. Usually, the reaction is a pseudo-order to tar concentration only with first-order reaction assumption. k_{app} represents apparent rate constant, which describes the sum of individual reactions involved in the tar steam reforming reaction and is given by the Arrhenius equation. Other parameters are X_{tar} as tar fractional conversion, R as the universal gas constant. The two kinetic parameters are $k_{0,app}$ as the apparent pre-exponential factor and E_{app} as the apparent activation energy, which is determined using the Arrhenius plot. Lastly, τ is the space-time, defined as the ratio of catalyst weight to gas flow rate, which is derived from the plug flow integral reactor model.

Compared to other catalysts, as shown in Figure 31, supported char Ni catalysts have the lowest $E_{app}$for steam reforming of tar from wood. This emphasizes the importance of Ni-based catalyst in steam reforming. For modified catalysts, the addition of Ba to $Ni/LaAlO_3$ promotes activation and adsorption of water on the catalyst surface, these subsequently lower the E_{app}value from 121 to 60.8 kJ mol^{-1}. Other catalysts reported are compared in Figure 31, where modified catalysts showed lower activation than unmodified catalysts. Kinetics parameters are influenced by catalyst type, reaction conditions and tar model compound [173], for instance, it was found that E_{app}, for naphthalene >> benzene[174].

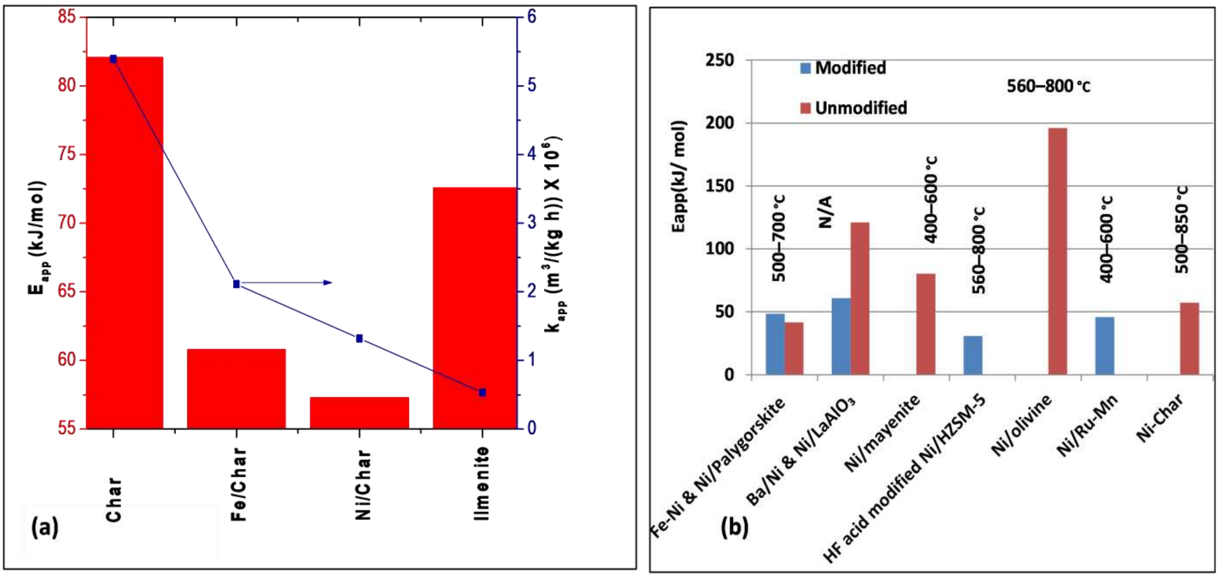


Figure 31: Comparison of activation energy between (a) Ni/Char and other catalysts [172] (b) some modified and unmodified NI-based catalyst[59,96,131,153,175–177] N/A=not available, HF=hydrofluoric acid

9. Summary and future outlook

Modifications of nickel-based catalysts are carried out in an attempt to prolong their reaction lifetime and improve their catalytic activity for tar reforming. The surface of the active nickel metal is modified with another transition metal to form an alloy or to act as a promoter. In some cases, the catalyst support may be modified for the improved catalytic property. Below is a summary of those modified catalysts, based on the literature reviewed in this article:

The low cost of transition metals such as Fe Co, Cu, Cr makes them an excellent alternative to the use of more expensive noble metals as catalyst promoters. An alloy is formed as a bimetallic active surface when these metals are added to Ni-based catalysts as a secondary metal. The formation of this alloy improves catalytic performance by enhancing Ni dispersion, lowers Ni particle size, and improves the oxygen affinity of the surface Ni. The presence of Co with Ni also increases the basicity of a catalyst. The improved properties of the modified catalysts were attained mostly at optimum additions of the secondary metal, which were achieved through catalyst design and optimization. In particular, the use of the transition metal Fe is predominant in the literature, where it may be concluded that an alloy of Ni-Fe compared to monometallic Ni was found to have improved tar reforming on different supports: Al_2O_3, activated carbon, zeolite, palygorskite, and SBA-15 as reported in several different articles. However, there is no available literature that compares the performance of the bimetallic Ni-Fe catalysts on different supports as a dedicated research article. Moreover, a wider range of support materials such as $MgAl_2O_4$, MCM-41 and natural phyllosilcate montmorillonite (MMT) could be explored in the future with Ni-Fe as the active metals for the improved catalytic reforming of tar.

The excellent redox properties of rare earth metals/oxides such as cerium or lanthanum have enabled them to be used as successful promoters that facilitate H_2O dissolution and CO_2 adsorption. These properties were found to improve the catalytic performance of Ni-based catalysts for tar reforming through the enhancement of smaller Ni crystal sizes, metal dispersion, metal-supported interaction and promotion of the water gas shift reaction. However, the superiority of cerium or lanthanum is not well established for biomass tar reforming due to lack of adequate literature.

The addition of noble metals as promoters to Ni-based catalysts in small amounts (Pd as low as 0.05 wt%) improve the metal-support interaction, reducibility and dispersion of the Ni active particles. These relationships were beneficial in both catalytic activity and their resistance to carbon formation. The additions of Pt and Pd as promoters have a superior promoting effect compared with Rh, Au, Rh and Ir. The partial substitution of alkaline earth metals into A-site of perovskite (ABO_3) Ni-based catalysts were also found as an effective way to improve catalyst activity. The substitutions enhance both the lattice surface oxygen and water adsorption, thereby improving activity and resistance against carbon deposits. In this regard, Sr seems to be a better promoter with respect to Ba, Ca and Mg. These partial substitutions into the perovskite structure offer a flexible opportunity for future catalyst development in the search for more robust biomass tar steam reforming catalysts. Metals as such Pb, Rh, Zn, Mn, Cu, Cr can be explored in the future as candidates for the partial substitution into either the A- or B-sites of perovskites.

Incorporation of a promoter into the support material improves the catalytic performance of Ni-based catalysts by altering the metal-support interaction or the interaction between support and support-modifier. These interactions subsequently affect the metal dispersion, oxygen vacancies and reducibility of the catalyst. On nickel-based catalysts, CaO and MgO were found as good support modifiers that enhanced CO_2 capture and H_2 selectivity through the water gas shift reaction. Material such as mayenite ($Ca_{12}Al_{14}O_{33}$) improves the thermal stability of Ni-based catalysts in tar reforming due to their free oxygen capacity. A combination of CeO_2-ZrO_2 as support material improves the oxygen storage capacity, which helps to reduce carbon deposits on the catalyst. In addition, the redox property of CeO_2-ZrO_2 can be further strengthened by adding another metal oxide such as M_nO_x. Natural mixed oxides such as pumice, vermiculite and perlite could be utilized in the future as low cost support modifiers. Additionally, mixed oxides in the form of Fe_2O_3/ZrO_2, La_2O_3/ZrO_2 and Fe_2O_3/La_2O_3have not been reported in the literature as support modifiers for Ni based biomass tar reforming catalysts.

In addition, more inter-comparative investigations are deemed necessary to unequivocally ascertain the best set of catalysts for tar reforming from biomass gasification. For example, comparing different sets of noble metals as promoters at lower metal loadings to that commonly used transition metals. Also, comparison between several methods of catalyst preparation followed by detailed comparison of their catalytic activities for catalytic tar reforming would advance knowledge. Similarly, an examination of different structures of Ni containing the same catalyst composition, for example, comparison between hydrotalcite-derived structure to that of perovskite structure. It is also important to emphasise the need to compare the performance of each developed modified catalyst with that of a conventional catalyst (Ni/Al_2O_3) for easy assessment of catalyst activity. In general, most of the reported research has used only one model tar compound to test the performances of the modified Ni catalyst. However, the performance of a catalyst depends on the composition of the tar. Even the amount and mechanism of carbon deposits on the catalyst differ based on the tar composition. Therefore, for a deeper understanding of the catalyst behaviourand for a wider application of the modified Ni catalyst, a systematic performance test is proposed (Figure 32): from using one model tar compound to using real tar produced from biomass gasification of complex composition. Moreover, operating temperature should also be a key factor in choosing a model tar compound for the performance tests. In addition to focusing on improving catalyst activity and stability, more focus is needed on the ability of the catalyst to reform tar at a lower temperature (<700°C). This will make the area of high-temperature tar conversion more acceptable and enhance its practical application at commercial/industrial level. Again, with the current world attention on the potential future hydrogen economy and its importance, more catalyst development is needed with higher selectivity towards H_2 from the steam reforming conversion of tar.

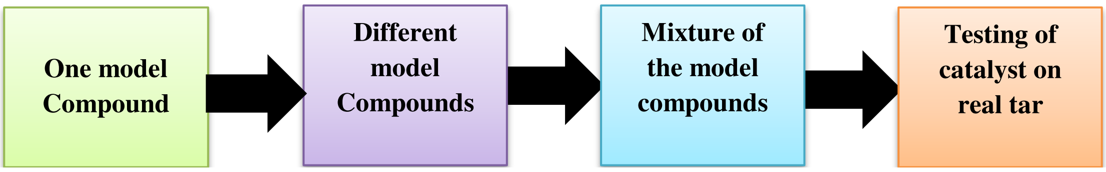


Figure 32: A proposed systematic approach for testing the performance of newly developed modified Ni-based catalyst for steam tar reforming.

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