

A review on catalyst development for dry reforming of methane to syngas: Recent advances



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ABSTRACT

The abrupt and massive deactivation of methane dry reforming catalysts especially Ni-based is still a monumental impediment towards its industrialization and commercialization for production of value-added syngas via Fischer-Tropsch process. The need for further and more critical understanding of inherent and tailored interactions of catalyst components for performance and stability enhancement during reforming reaction cannot be over-emphasized. This review provides a contemporary assessment of progresses recorded on synergistic interplay among catalyst components (active metals, support, promoters and binders) during dry reforming using state-of-the-art experimental and theoretical techniques. Advancements achieved during interplay leading to improvements in properties of existing catalysts and discovery of novel ones were stated and expatiated. Reaction pathways, catalytic activities, selection of appropriate synthesis route and metal/support deactivation via sintering or carbon deposition have over time been successfully studied and explained using information from these crucial component interactions. This perspective describes the roles of these interactions and their applications towards development of robust catalysts configurations for successful industrial applications.

1. Introduction

It was estimated at the beginning of 2016 that a total of 6879 trillion cubic feet natural gas (NG) has been discovered in its associated and non-associated form [1]. Fast depleting crude oil reserves and stringent environmental regulations on emission control has diverted attention to NG as a source of energy for heat, power and vehicular applications. Setbacks to NG for these applications are its characteristic low energy density, low critical temperature, high cost of storage and transportation. As a result of these challenges, utilization of abundant NG reserves as fuel is low resulting to flaring of large volume during exploration of crude oil. Anthropogenic production and emission of greenhouse gases (CH₄, CO₂, H₂O vapour, NO_x) have been established to be responsible for the menace of heat trapping in the Earth's atmosphere known as

global warming [2]. As at 2011, the World Meteorological Organization (WMO) assessment revealed the atmospheric concentration of CH₄ and CO₂ as 1.8 and 393.1 ppm respectively [3]. Despite the low methane concentration relative to that of carbon dioxide, its global warming potential (GWP) is 28–36 times higher than that of CO₂, hence contributing severely to Earth's radiative imbalance [4,5]. CO₂ emission poses the greatest threat due to its high energy absorbing efficiency attributed to its large-scale emission and long-term duration in the atmosphere. Capture, sequestration and utilization of CO₂ have been the most effective abatement strategies towards combating this trend [6]. Despite the successes attained in Carbon capture and sequestration (CCS), Utilization of immensely stored CO₂ has found limited application. In an effort to curb underutilization, reduce wastage and control generation of greenhouse gases from gas flaring, CO₂ and NG

Abbreviations: BET, Brunauer–Emmett–Teller; CCS, Carbon capture and sequestration; CFD, Computational fluid dynamics; CLDRM, Chemical looping dry reforming of methane; DFT, Density functional theory; DRM, Dry reforming of methane; EISA, Evaporation-induced self-assembly; FESEM, Field-emission scanning electron microscope; FTIR, Fourier transform infrared; GWP, Global warming potential; NG, Natural gas; PDOS, Projected density of state; RWGS, Reverse-water-gas-shift; TAP, Temporal analysis of products; TOF, Turnover frequency; TPD, Temperature-programmed desorption; WMO, World Meteorological Organization

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Table 1
Comparisons of existing and prospective methane reforming process routes (Modified from Abdullah et al. [34]).

Methane reforming type	Operating conditions	H ₂ /CO ratio	Reaction enthalpy (kJ/mol)	Advantages	Disadvantages	Existing plant
Dry reforming	1 atm, 650–850 °C, CH ₄ :CO ₂ = 1:1	1:1	260.5	1. Utilization of two gases with great greenhouse potential 2. Production of clean energy source and other vital chemicals	1. High cost of noble metals 2. Carbon formation and deposition 3. Catalysts sintering at high reaction temperature	1. Linde Pilot Dry Reformer research facility at Pullach near Munich.
Steam reforming	3–25 atm, 700–1000 °C, CH ₄ :H ₂ O = 1:1	3:1	225.4	1. Higher concentration of H ₂ in the product 2. High efficiency of operation 3. Industrial maturity	1. Large volume of gaseous emissions from steam generation 2. Additional costs from external heat exchange device	1. Topsoe Package Hydrogen Plants at Air Liquide, Belgium; Plants in USA. 2. Air Liquide Steam Methane Reformer, Chempark Dormagen site near Cologne, Germany.
Partial oxidation	100 atm, 950–1100 °C, CH ₄ :O ₂ = 2:1	2:1	− 22.6	1. Higher tolerance for sulphur impurities 2. Short contact time 3. More economical from lesser amount of thermal energy	1. High cost of pure oxygen demand 2. Possible explosion from CH ₄ /O ₂ mixture 3. Existence of hot spots on catalyst from exothermic reaction 4. Higher complexity of the process	1. Pearl GTL, Ras Laffan Industrial City, Hamad street, Ad-Dahirah, Qatar.
Autothermal reforming	CH ₄ :H ₂ O:O ₂ = 1:1:0.5	1:1 or 2:1 based on fraction of reactants introduced	Variable depending on feed composition	1. Energy conservation due to combined steam reforming and partial oxidation 2. Lower CH ₄ slip 3. Requires more compact reactors due to reduced contact time for reaction 4. Very flexible from adjustable feed compositions	1. Lower hydrogen yield 2. Significant reaction limitations on increasing water-to-oxygen feed ratio	1. OLTIN YO'L GTL, Shurtan Gas and Chemical Complex, Karshi, Uzbekistan.
Plasma	Room temperature - > 2000 °C	3:1	−	1. High conversion efficiency 2. Lower cost due to simple power supply and electrodes 3. Good potential for H ₂ generation without CO ₂ formation 4. Effective with or without catalysts application	1. Dependence on electrical energy for reaction 2. Difficult towards high pressure operations 3. Possibility of CH ₄ combustion at high temperature thus, reducing desired product selectivity	1. Union Steel Corporation of South Africa (USCO) plasma arc heated methane reformer, South Africa (1985–1987).

containing mainly CH₄ are converted to synthetic gas (syngas), an important platform chemical intermediate for production of useful chemicals and synthetic fuels through distinct processes such as steam reforming, autothermal reforming, dry CO₂ reforming, oxidative coupling, partial and electrochemical oxidation [7,8]. The choice of any of these processes depends on raw materials, target products and reaction conditions, each with its characteristic merits and setbacks as itemized in Table 1.

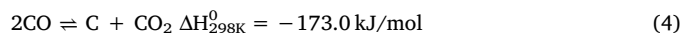
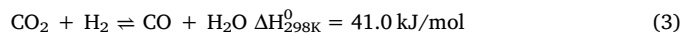
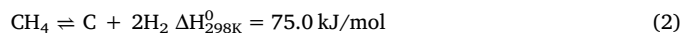
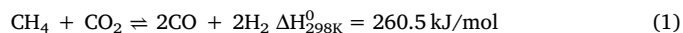
Methane conversion to synthesis gas (syngas) by CO₂ dry reforming is a catalytic induced process producing syngas (a gaseous fuel mixture containing primarily H₂, CO and traces of CO₂) used as a sustainable fuel alternative to fossil fuel and also a precursor for important chemicals such as methanol, ammonia and synthetic hydrocarbon fuel production [9,10]. Advantages of this technology are its suitability for low calorific value CO₂-rich NG, utilization and conversion of CH₄ and CO₂ which are both gases with significant greenhouse tendencies, production of eco-friendly fuel products and their subsequent conversion to liquid fuels through Fischer-Tropsch synthesis to address the inherent storage and transportation problems associated with gaseous fuels [11–13]. The utilization of cheap and readily available DRM catalysts with performance to maximally produce syngas has been the focal point of research and development in recent times. Despite its economic and environmental potentials, DRM is still an immature industrial process due to the problem associated with catalyst development with a long life-span on stream at a cheap price suitable for profit-oriented commercialization [14,15].

In 2015, Linde group revealed the pioneer pilot plants for dry reforming of methane (DRM). It was a product of concerted research effort in partnership with BASF and others. The Linde Pilot Reformer (LPR) is located near Munich and it uses two catalyst materials; a Nickel-based and a Cobalt-based. The aim is to test-run the LPR to obtain data at longer-term and longer-scale using pilot facility to investigate and optimize different approaches which could be used towards design of a commercial plant for the DRM [16]. Obviously, the LPR not only inspired greater research efforts in DRM catalyst design and development, but it is a step further towards commercial utilization of DRM catalysts for syngas production [17,18]. The other two industrial pilot plants successfully implemented are the SPRAG and CALCOR projects [18].

Contemporary design of DRM catalysts involved principally the utilization of inherent properties of catalyst components and understanding their complex synergistic interactions for optimum performance and longevity using state-of-the-art theoretical and analytical characterizations. Different catalyst configurations, morphologies and topologies have overtime been tested to evaluate how synergistic component interactions affects active metal dispersion, basicity, redox property, oxygen mobility, particle size, size distribution, reducibility and mass transfer limitations of catalysts [19,20]. These interactions have been linked towards predicting the pathways for establishing DRM reaction kinetics, thermodynamics, mechanisms and reactor design. Trade-offs between catalysts cost and their respective activity, selectivity and stability is the main challenge facing syngas production by dry reforming. Base metals are cheap and abundant catalyst precursors currently applied in dry reforming of methane (DRM) as a replacement to noble metals but their accelerated deactivation due to catalyst sintering, coke formation and deposition on catalyst surface at reforming conditions constitute a major challenge. Catalysts from noble metal precursors such as Ir, Pd, Pt, Rh and Ru have proven to manifest higher activity, selectivity and stability during DRM. Their viability for large scale industrial application is however not economical, attributed to their high cost and scarcity [21,22].

In a typical DRM system, syngas is produced from endothermic reaction of CH₄ and CO₂ (Eq. (1)) at a lower syngas ratio (H₂/CO = 1) in comparison to steam reforming (H₂/CO = 3) or partial oxidation (H₂/CO = 2) making a suitable path way to Fischer-Tropsch synthesis [23]. This endothermic nature of DRM requires high temperature for activity

which implies high energy consumption and thus high operating cost. Production of syngas by DRM is however affected by competing side reactions which aid carbon formation and deposition on catalyst such as methane decomposition (Eq. (2)), Boudouard reaction (Eq. (4)) and reverse water-gas shift (RWGS) reaction (Eq. (3)) [12].



From the stoichiometry of the DRM reaction, CO₂ and CH₄ conversions are expected to be equal and the syngas ratio also to be unity. Presence of side reactions and the extent with which they occur are measured by the deviation from products formed from the ideal stoichiometry. RWGS reaction can be confirmed by presence of water at the outlet of the reactor and higher stoichiometric conversion of CO₂ than CH₄, Boudouard reaction by disproportionation of CO formation and CH₄ decomposition by CH₄ conversion higher than CO₂ conversion [21].

Suitability of different catalysts for DRM has been thoroughly investigated. However, their application has recorded limited successes for commercialization due to their susceptibility to deactivation caused by coke formation and sintering [24,25]. Research attention has shifted from noble metals to base metals for economic reasons. Ni-based catalysts have been found to be competitive with noble metals in their catalytic activities at affordable costs [19]. To overcome challenges of coke deposition and sintering of Ni catalyst, various factors have been considered and investigated for their reduction or elimination. These include nature of active metal, incorporating promoters with basic properties, interactions between active metals and support, particle size reduction, change in pre-treatment and preparation route and viability testing for different combinations of metals and supports [26–28]. Lots of researches carried out in DRM have shown that achieving an ideal carbon-resistant and heat stable catalyst by exclusive adjustment of a single parameter is difficult to achieve. Therefore, it is imperative to consider the collaborative association of various parameters in the design of a robust and efficient DRM catalyst. Attempts to improve coking resistance and catalytic activity have also been made via combination of two or more active metals, support and/or promoters [29].

Several astounding reviews have been produced on various breakthroughs recorded in catalysts development for DRM reactions with emphasis in the last decade mainly on catalysts configuration [30], noble metal catalysts [31], influence of process parameters [23], coke deposition and management [32], development of oxygen carriers in chemical looping DRM [33], Ni and Ni-based catalysts [34], low temperature dry reforming [35] and advances in synthesis of catalysts with mesoporous SBA-15 support [36]. Nevertheless, it is imperative to produce a research report on synergistic interactions of catalyst components such as active sites, basicity, oxygen vacant sites, metal-support interactions, oxygen carriers by chemical looping, core-shell configurations and deactivations using facts and findings from theoretical and experimental data. These aspects of DRM catalysts have been the focus of recent research outputs in search of efficient DRM catalysts.

2. Active sites

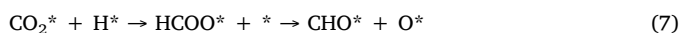
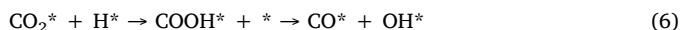
It has been established in literature that the presence of active sites facilitates dissociation of reactants to produce species that subsequently combine to yield the desired product [37]. DRM occur via bi-functional active sites approach such that the active sites for CO₂ are on acidic/basic supports while metals are active sites for CH₄ dissociation. Catalysts with an inert support such as silica follow a mono-functional pathway where both CO₂ and CH₄ are activated on active metals [31]. Various mechanisms have been proposed in an effort to explain the

Table 2

Energy to overcome activation barrier for forward and reverse elementary dry reforming of methane reactions [40,41].

No.	Elementary reaction	Pt		Ni	
		$E_{a,forward}$ (eV)	$E_{a,reverse}$ (eV)	$E_{a,forward}$ (eV)	$E_{a,reverse}$ (eV)
1	$CH_4^* + * \rightarrow CH_3^* + H^*$	1.01	1.19	0.91	0.90
2	$CH_3^* + * \rightarrow CH_2^* + H^*$	1.39	1.36	0.70	0.63
3	$CH_2^* + * \rightarrow CH^* + H^*$	0.45	1.70	0.35	0.69
4	$CH^* + * \rightarrow C^* + H^*$	2.27	1.20	1.33	0.81
5	$CO_2^* + * \rightarrow CO^* + O^*$	1.81	0.38	0.67	1.65
6	$CO_2^* + H^* \rightarrow COOH^* + *$	0.75	0.32	1.13	0.85
7	$COOH^* + * \rightarrow CO^* + OH^*$	1.55	0.65	0.57	1.65
8	$CO_2^* + H^* \rightarrow HCOO^* + *$	3.64	1.97	1.13	0.85
9	$HCOO^* + * \rightarrow CHO^* + O^*$	1.12	0.46	na	na
10	$CHO^* + * \rightarrow CO^* + H^*$	0.55	0.70	0.57	1.65
11	$CH^* + O^* \rightarrow CHO^* + *$	1.46	2.94	1.53	1.08
12	$CH^* + O^* \rightarrow COH^* + *$	1.725	4.205	na	na
12	$CHO^* \rightarrow CO^* + H^*$	0.55	0.70	0.20	1.48
13	$CH^* + OH^* \rightarrow CHOH^* + *$	0.70	1.46	1.48	0.80
14	$CHOH^* + * \rightarrow COH^* + H^*$	0.86	1.52	0.15	0.86
15	$C^* + O^* \rightarrow CO^* + *$	1.43	5.36	1.59	2.94
16	$C^* + OH^* \rightarrow COH^* + *$	0.76	3.68	1.46	2.01
17	$COH^* + * \rightarrow CO^* + H^*$	1.15	1.79	0.20	1.48
18	$O^* + H^* \rightarrow OH^*$	na	na	1.35	1.16
19	$OH^* + H^* \rightarrow H_2O^*$	na	na	1.33	0.92
20	$H_2O^* \rightarrow H_2O(g)$	na	na	0.29	0.00
21	$H^* + H^* \rightarrow H_2^*$	na	na	0.92	0.06
22	$H_2^* \rightarrow H_2(g)$	na	na	0.22	0.00
23	$CO^* \rightarrow CO(g)$	na	na	1.92	0.00

interactions between reactants for reforming and active sites on catalysts through experiments, characterizations, DFT and micro-kinetic computations [38,39]. Energy requirements to overcome Ni activation barriers for each elementary step for forward and reverse reaction were determined and compared with that of a regular noble metal in Table 2, both based on *in silico* DFT calculations obtained from the work of Niu et al. [40] and Zhu et al. [41]. Activation barriers for Ni catalysts are lower than those of Pt for most of the steps, implying stronger tendencies for conversion at same reaction conditions. For successful and sustainable bond dissociation, it is preferable to have barrier energy for forward reaction to be lower than the reverse. Activation energies for the Ni and Pt metals in each step are endothermic, which is responsible for their suitability in DRM reactions at elevated temperatures. According to DFT, dissociative adsorption pathway of CH_4 takes place directly on the active metal surface [38,40,42] producing H_2 and CH_{4-x} species at the beginning. CO_2 is activated on active metals or supports; however, pathway for its activation is debatable nonetheless. Niu et al. [40] proposed three plausible pathways to CO_2 activation and dissociation (Eqs. (5)–(7)) of which the pathway with the lowest activation barrier is more likely to occur.



Presence of mobile lattice oxygen on catalyst supports which originated from carbonates on basic supports and hydroxyls on acidic supports have been found to immensely contribute to DRM activity. Mobile lattice oxygen species aid the activation of C–H bond on CH_4 molecule. Lattice oxygen with less activity towards C–H bond activation but active to surface carbon deposit prevents the accumulation of graphitic and filamentous carbon on metal surface [43].

The activity of well-defined nickel aluminates prepared by Pechini method with different spinel compositions were studied based on structure and composition of their active sites [44]. From results obtained, the nature of active sites, activity and possibility of carbon formation during DRM reactions are dependent on the type of spinel formed. Four-fold coordinated Ni phases on $NiAl_4O_7$ and $NiAl_2O_4$ are

discovered to be the active sites for dry reforming with low carbon deposition which is in contrast to $Ni_2Al_2O_5$ spinel. From the work of Sutthumporn et al. [45], comparative studies on effect of partial substitution of different metal (Bi, Co, Cr, Cu and Fe) on Ni^{3+} sites of $La_{0.8}Sr_{0.2}Ni_{0.8}O_3$ perovskite catalysts were carried out on DRM activity. Cu-substituted catalyst produced the highest initial activity and mobility of lattice oxygen albeit a low stability of Ni due to poor metal-support interaction. Fe-substituted on the contrary showed the highest stability, less mobility of lattice oxygen species, lattice oxygen species having less activity for activation of C–H bond and more active towards formation of $La_2O_2CO_3$ on reaction with CO_2 . Vasiliades et al. [46] also proved that abundant lattice oxygen of $Ce_{0.38}Zr_{0.62}O_{2.8}$ supported Ni catalyst play a crucial role in carbon-path towards CO formation and inhibition of inactive carbon deposition. CH_4 -TPR and H_2 -TPR are effectively used in evaluating the role of surface and lattice oxygen groups on catalyst activity using CH_4 [45,47] and H_2 [46,48,49].

3. Surface acidity/basicity of catalyst

The acidity/basicity of catalyst surface has been found to play a decisive role on the performance of catalysts for DRM [50]. The acidity and basic properties of the global catalyst structure are contributed by one or a synergistic effort from the support, active metal or promoting agent. Acidity of catalyst was said to inhibit dissociative chemisorption of CO_2 onto catalyst surface due to accretion of dehydrogenated carbon deposits on catalyst surface resulting to aging and graphitization of carbon deposits making it inactive. Concentration of these inactive carbon residues block catalyst sites responsible for CO_2 adsorption and activation leading to swift catalyst loss of activity [51]. Basicity of catalyst however was found to improve adsorption of CO_2 which facilitates gasification of carbon deposited preventing any possibility for growth and graphitization. Chemisorbed CO_2 becomes activated on catalyst support in the presence of surrounding Ni and other active metal particles to form intermediate carbonate species which on contacting CH_4 molecules result to formation of CO [52,53]. Attraction of acidic CO_2 molecules is driven by the basic nature of catalyst, thus increasing the CO_2 surface coverage and reduction in carbon deposition through Boudouard reaction [54].

Basic catalyst property was observed to increase the activity of DRM by lowering the activation energy of the reactants as depicted in the work of Abdullah et al. [34]. CH_4 is more stable than CO_2 and thus, require higher energy for activation. Activation barrier was found to be sensitive to catalyst basicity making it also a fundamental determinant for catalyst activity. Basicity can be increased by application of supports or promoters with strong basicity.

Das et al. [55] investigated effects of acidic/basic SiO_2 and Al_2O_3 based support on Ni catalyst activity by establishing a synergistic correlation between support acid-base properties with catalyst activity and deactivation. Their findings revealed that excessive acid sites on support favours catalyst deactivation by coke formation and deposition, excess of basic sites support the occurrence of RWGS reaction and formation of metallic oxides via oxidation which are also causative to catalyst deactivation. Concentration and distribution of acidic and basic sites were varied based on methods adopted for catalyst supports preparation. It was discovered that homogenous acidic and basic sites distribution at a moderate concentration obtained from one-step synthesis of support improves the CH_4 reforming process with less side reactions and high stability of catalyst. Stepwise synthesis produces irregular distribution of acidic and basic sites at high concentration favouring formation of side reactions and fast catalyst deactivation. It was concluded that a balance must be established on a moderate acid-base sites providing minimum equivalent activation energy for CH_4 and CO_2 towards dry reforming at the least chance of catalyst deactivation.

In an effort to control acidity of catalyst supports, various promoters have been introduced to the catalyst structure to improve basicity which eventually reduce coking and deactivation. From the work of Alipour et al. [56], basic oxide promoters from alkaline earth metals (MgO , BaO and CaO) were doped on Al_2O_3 support by impregnation to influence basicity of Ni catalyst. Their introduction subdued carbon formation and deposition while also boosting catalytic activity. Similarly, Mg and Ca were added to Ni catalyst on Al_2O_3 support by one-pot synthesis [57], Na on MCM-41 supported Ni [25], La, Mn and Al on Ni supported on Fe modified clay [58] and MgO coated on Ni/SBA-15 [59]. There are however few exceptions to this trend as obtained from the work of Titus et al. [60] where MgO-ZrO_2 supported NiO catalyst was prepared at different MgO loadings. On characterizing the acidity and basicity of the support using TPD- NH_3 and TPD- CO_2 respectively, there was no correlation between MgO loadings and acid-base properties. Densities of acidic and basic sites are found to be more dependent on calcination temperature. These findings were further supported in the work of Ozdemir et al. [61] on effects of calcination temperature on structural and catalytic properties of $\text{Ni/MgAl}_2\text{O}_4$. Calcination temperature enhances basicity to acidity ratio which as a result improves metal oxides support interaction. Increasing the calcination time causes severe Ni sintering which results to higher turnover frequency (TOF) but also at higher carbon deposition.

Catalyst acidity and basicity in relation to its overall properties is a function of the mean electronegativity and/or the nature and extent of adjustment experienced on the surface acidic and basic sites for DRM [62]. These can be characterized based on their respective interactions with probe molecules such as CO , NH_3 , and pyridine for acidic sites and CO_2 for basic sites on temperature-programmed desorption (TPD) and density-functional theory (DFT) computations. Selection of a particular probe molecule is accompanied by its distinct advantages and disadvantages. CO being a weak electron donor is frequently used for probing acidic sites of metallic oxides based on their electrophilicity and availability of localized d-electrons for back-donation into the $\text{CO } \pi$ orbital. NH_3 and pyridine with more basicity than CO interacts stronger with surface acid sites and stronger sensitivity towards probing Brønsted acid sites. CO_2 is popularly applied for studying surface basicity forming carbonates on interaction with basic O_2 -groups.

Catalyst deactivation as associated with acidity or basicity of catalysts has been theoretically studied using the density functional theory (DFT) computations. Effects of carbon deposition on Ni catalyst were

studied with DFT taking into consideration carbon accumulation on Ni surface and sub layer. The results depicted that both sub-surface and surface carbon deposits disrupt chemisorption and dissociation of methane species in comparison to clean Ni surface [63]. From the projected density of state (PDOS) analysis, deposited carbon atoms modified Ni electronic structure thus drastically reducing the activity of the bonded Ni particles. The computations also reveal that the presence of C atoms increase CH_4 activation barrier necessary for dissociation due to C-Ni induced electronic deactivation and a repulsive C- CH_4 interactions. Ni polluted with carbon has a characteristic down shift of its D band leading to less reactivity.

Strong basicity of catalyst favours RWGS reaction leading to water formation as a by-product [55]. Water molecules are found to inhibit activity of certain catalysts depending on the basicity of the support or active metals as investigated in the work of Lalik et al. [64] using DFT calculations. The relationship between water poisoning and deactivation of SiO_2 and Al_2O_3 supported metallic and bimetallic catalysts were established on DFT using the Turbomole code (local cluster model) for its implementation. Effects of water on each metal cluster were computed based on binding energies of water-metal and water-water energy interaction. Alumina support catalyst having a stronger basicity showed more susceptibility to water poisoning and deactivation than silica supported counterpart.

4. Oxygen vacancy

Oxygen vacancy is a prototype representation of inherent point defects on metallic oxide catalysts developed in the process of synthesis due to exposure to elevated temperatures and a reducing atmosphere [65]. Stability and diffusivity of oxygen vacancies play a crucial role in physical and chemical properties of metallic oxide supported catalyst [66]. Consequently, ability of catalyst support to release oxygen under a reducing environment and storing oxygen under oxidizing atmosphere causes the formation and filling of oxygen vacancies [67,68]. Supports and promoters are mostly materials with high capacity for oxygen storage which when combined with active metals increase mobility of oxygen atoms through the crystal lattice and promote formation of oxygen vacancies [52]. Presence of oxygen vacancies in DRM catalyst serve as sites for CO_2 activation and C–O bond cleavage, thereby increasing the pool of oxygen atoms on catalyst surface [31]. Mobile oxygen species also reduce the chance of catalyst deactivation due to carbon accumulation by oxidizing surface carbon to CO .

In recent times, efforts have been put into the maximization of oxygen vacancies for increased CO_2 dissociation and activation to produce CO . Quest for catalyst supports with special redox properties and exceptional O_2 storage capacity (OSC) is still ongoing in the field of catalysis for DRM. High O_2 retention potential of substances results to higher reducibility thus, more mobile oxygen atoms flow from the lattice to the catalyst surface for oxidation of carbon deposits and creation of vacancies on supports for CO_2 activation. Ceria and ceria-containing materials have been extensively applied as an excellent support for CO_2 activation. This is attributed to their strong reducibility, high OSC, release of mobile oxygen pool and generation of extensive vacant sites as depicted in Fig. 1. From the work of Makri et al. [49], the effects of lattice oxygen and oxygen defect sites on reactants activation with respect to their reaction rates were investigated. The high lattice oxygen content and defects from $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2.8}$ support was also responsible for the noticeable low carbon formation and deposition. Ay and Uner [67] investigated the activities of CeO_2 supported Ni-Co bimetallic catalysts on DRM. Coke deposition was observed to decrease with increase in calcinations temperature of catalyst caused by reduction of Ce^{4+} to Ce^{3+} in association with the formation of oxygen vacancies. The influence of ceria-zirconia on alumina supported Ni catalyst was investigated in the work of Faria et al. [69]. From results obtained, addition of $\text{CeO}_2\text{-ZrO}_2$ at the proportion $\text{Ni/Ce}_x\text{Zr}_{1-x}/\text{Al}_2\text{O}_3$ ($x = 0.5, 0.75$ and 1.0) improved the OSC of the global catalyst

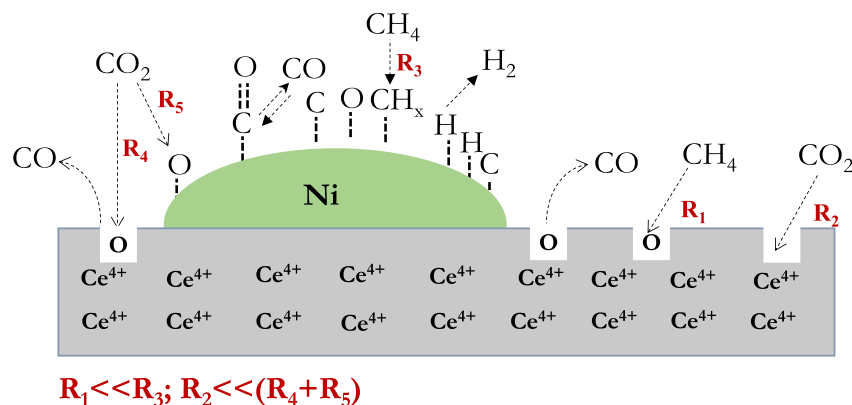


Fig. 1. Schematic representation of mechanistic reaction step for CH_4 and CO_2 activation on 5 wt% $\text{Ni}/\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2-\delta}$ catalyst. Modified from Ref. Makri et al. [49].

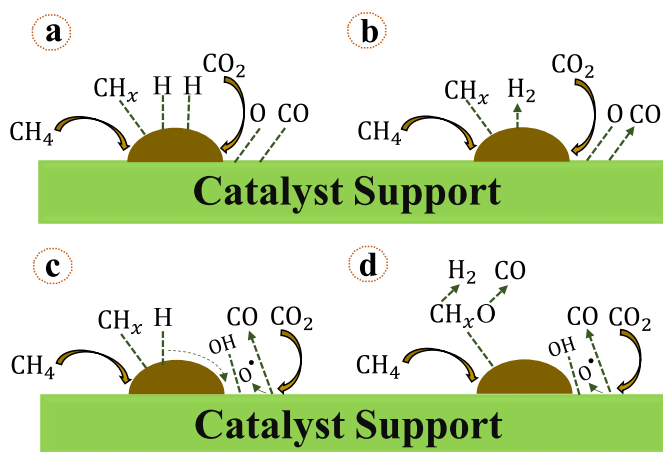


Fig. 2. Mechanistic steps for methane reforming reaction involving: (a) chemisorption and dissociation of CH_4 and CO_2 on metal-support interface, (b) fast rate of H_2 and CO desorption, (c) hydrogen and oxygen spillover forming surface hydroxyls, (d) oxidation of hydrogen-depleted CH_x species by surface hydroxyls and oxygen groups to produce H_2 and CO . Modified from Ref. Aramouni et al. [20].

structure which is an indication of large surface coverage of CeZrO_2 on alumina causing increased labile oxygen mobility and development of large oxygen vacancies as depicted from X-ray diffraction (XRD) and temperature-programmed reduction (TPR) data. Synergy between ceria and zirconia as catalyst support, binder or promoter in solid solutions yielded abundant oxygen vacancies which enhanced catalyst redox property and also improving significantly the metal-support interaction [49,70–72].

For further understanding on the presence and role of oxygen vacancies in DRM activity, application of DFT computations for this study has gained serious attention lately. Insights into relative stability and localization of f electrons of oxygen vacancy on catalyst support surface and sub-surface sites is still a controversy. Fan et al. [73] used DFT calculations to study O_2 and H_2O interactions with reduced CeO_2 support surface with the aid of their various adsorption energies, geometries and reaction barriers. It was observed that diffusion of sub-surface oxygen vacancies to the surface are promoted by adsorption of O_2 on the supporting ceria surface. Diffused oxygen vacancies to the surface sites are healed by adsorbed O_2 thus oxygen adatom are left behind on support surface. The prospects of production, diffusion and aggregation of oxygen vacancies on neutral amorphous SiO_2 was investigated by Munde et al. [74] through application of an electric field using DFT to optimize their geometries, compute their electronic structures and finally study the properties of active and neutral oxygen vacant sites. The electric field application reduced the energy barrier for intrinsic

electron trapping on silica surface. DFT has also been used effectively to study interplay between oxygen vacancies and Fe/CeO_2 [75], Mo/TiO_2 [76], Ni/ZrO_2 [77], Ni/CeO_2 [78], $\text{V}_2\text{O}_5/\text{TiO}_2$ [79]. Other than metal oxides, thermal and chemical resistant refractory compounds like hexagonal boron nitride (h-BN) nanosheets and halloysite clay with abundant vacant defect sites have been successfully applied in tuning electronic state and activity of 2D Ni catalysts during DRM reaction [80,81]. The defect-induced efficiency of these catalysts is attained by confinement of Ni nanoparticles in the defect sites of the support. Cao et al. developed a coke-resistant catalyst by Ni enclosure on h-BN vacancies thus, improving metal-support interaction via redox mechanisms which favour reactant chemisorption and activation. Lu et al. conducted similar work by confining Ni on defect sites of halloysite clay nanosheets. This phenomenon is a potential pathway for development of DRM catalysts with excellent carbon resistance.

5. Metal-support interaction

It is an established fact from literature that positive interaction between active metal and support play a crucial role in enhancement of catalytic activity and reduction of catalyst deactivation via coke formation and active metal sintering especially at high temperature DRM [9]. The support properties determine the DRM reaction pathway especially for Ni-based catalysts by initiating the adsorption and activation step (Fig. 2). Activation of CH_4 on active metal and CO_2 activated on mildly acidic (Al_2O_3) or basic (CeO_2 , La_2O_3) support is a typical bi-functional DRM reaction pathway whereas catalyst supported on inert silica-based materials follow the mono-functional pathway such that both CH_4 and CO_2 activation are on active metal surface [31]. Catalysts with strong metal-support interaction develops thermal resistance to Hüttig and Tamman temperature limitations which is a semi-empirical indicator of temperature at which sintering starts [52]. Strong interaction between metal and support enables the dispersion of active metal to maintain its uniform small size at high DRM temperature [77,82]. The stronger the metal-support interaction, the higher the temperature needed for the metal to break free and combine with the neighbouring metal particle thereby inhibiting agglomeration. Weaker interaction between active metal and inert support makes it more suitable than acidic/basic supports for bimetallic catalysts. This is because it was reported to provide better metal-metal interaction [31].

Catalyst synthesis methods were used to control the location and localization of active metals in the support skeletal structure which subsequently explain the interaction that transpires. In recent times, different synthesis routes have been applied towards developing catalysts with excellent coke and sinter resistance by Ni particles immobilization with varied degree of success. Notable ones are via alloy formation with a promoter [83–86]; confinement within mesosilica shell structure [87]; polyol-assisted immobilization in channels of mesoporous SiO_2 [88]; sublimation-deposition [89]; and aerogel

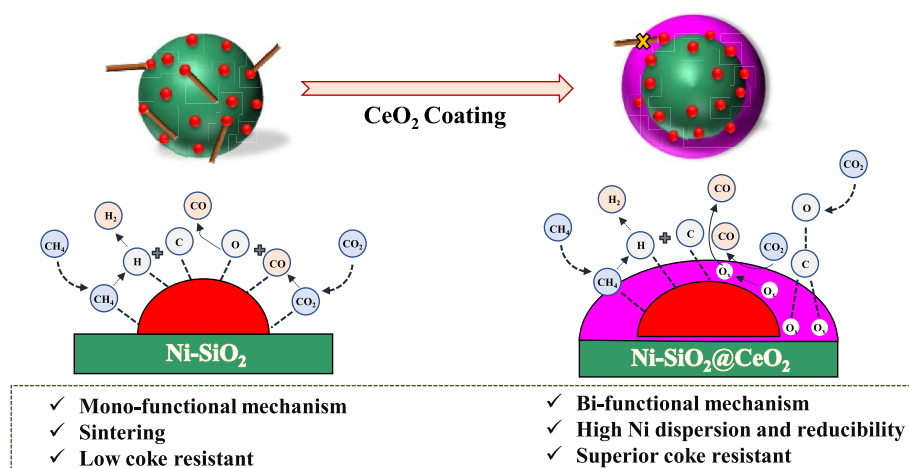


Fig. 3. Core-shell structure of silica-supported Ni catalyst encapsulated in ceria for protection against sintering and coke deposition. Modified from Ref. Das et al. [197].

confinement [90,91]. Wang et al. [92] investigated the effect of metal-support interaction of Ir/Ce_{0.9}Pr_{0.1}O₂ catalyst by tuning their different mode of synthesis on catalytic performance and stability. Ir/Ce_{0.9}Pr_{0.1}O₂ synthesized by deposition-precipitation produced the highest performance and stability, followed by sequential precipitation and lastly by co-precipitation. The best performance is attributed to Ir/Ce_{0.9}Pr_{0.1}O₂ having Ir nanoparticles uniformly dispersed on catalyst surface while for the other two, Ir was partially or fully confined in Ce-Pr-O mixed oxide matrix. Aghamohammadi et al. [93] conducted similar research to evaluate the influence of metal-support interaction on catalyst Ni/Al₂O₃-CeO₂ prepared by facile sol-gel and impregnation method. Their results indicated a higher distribution of active phase with smaller particle size in sol-gel method than impregnation as obtained from FESEM, BET and FTIR results. Effect of addition of CeO₂ promoter on Ni/Al₂O₃ metal-support interaction is more evident in sol-gel preparation than impregnation.

Weak metal-support interaction has been a major challenge also to noble metal catalysts despite their strong resistance to coke formation and deposition. Their catalytic activity and stability over long exposure to reaction conditions decline due to noble metal sintering caused by their ease delocalization on support surface thereby facilitating their agglomeration. Increase in interaction between noble metals and support have been achieved by introduction of promoters to the catalyst structure as obtainable from the work of Wang et al. [92]. Beltran et al. [94] compared the performance of Rh supported on Al₂O₃ with that promoted by ZrO₂ addition. It was concluded that the interaction between Rh and support is a function of surface coverage of Al₂O₃ with ZrO₂ and the phase orientation of ZrO₂ in the grafted support system. These imply that high alumina coverage with zirconia signifies strong metal-support interaction and the interaction of Rh is stronger with the tetragonal phase of ZrO₂ than the monoclinic phase of which the former increases with increased zirconia loading in the grafted support and thus increased metal-support interaction.

DFT calculations have been increasingly applied to provide further insights on metal-support interactions with the aim of opening new and better routes for tuning the existing interactions. Activation and decomposition of CH₄ is the most challenging step during the DRM process as a result of high stability of its C–H bonds. However, calculations from DFT predicts low activation energy requirement for splitting C–H bonds of adsorbed CH₄ molecules on catalyst with strong metal-support interaction. Strong perturbation of electrons in the active metal particles which are produced by the support of different stoichiometry and reducibility is the driving force responsible for the chemical change towards CH₄ adsorption and decomposition for DRM [95,96]. This phenomenon investigated at molecular level using DFT indicated that

small coverage of active metals on support is responsible for the low energy barrier C–H bond dissociation which is a function of the surface coverage of metal on support. Further works on the effect of metal-support interaction on CH₄ activation via DFT studies are obtained from the works of Das et al. [97] for Ni on surface modified alumina and Larmier et al. [98] for cobalt on Y-alumina.

6. Core-shell configuration

For practical and large-scale application of catalytic DRM, catalyst deactivation due to thermal sintering, severe carbon deposition and re-oxidation are still the main setbacks to cheap and readily available Ni and Ni-based catalysts as alternatives to exorbitant noble metal catalysts. Several researches have been carried out to proffer solutions to these setbacks, several of which are clearly described in the review of Abdullah et al. [34]. In recent times, attention has shifted towards development of catalysts with a core-shell structure by tuning the synthesis method [99]. The core-shell structure was achieved through coating of active metal with a support shell mostly with high surface for effective metal surface dispersion [100–102]. Encapsulation of nickel surface within the pore structure of the support protects the active phase from coke deposition and also limiting agglomeration of confined and dispersed nickel particles [57]. The structure is produced by an initial reaction to form seeds of active metal particles as the ‘core’ and subsequent addition of separate reactants to form the ‘shell’ coating the core [103,104] as a protective shield illustrated in Fig. 3. Due to their structural set-up, core-shell structural property is also referred as yolk-shell in some literature [35,90,99,105–107]. The motive is to synthesize nickel-based catalysts having an inherent control of its size and particle distribution to achieve sintering and coking resistance [108,109]. The core-shell morphology can be confirmed through characterization by transmission electron microscopy (TEM), as obtained in the work of Ding et al. [110] for Ni@SiO₂ catalyst.

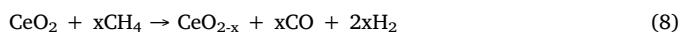
Jabbour et al. [111] conducted astonishing performance comparisons of Ni/Al₂O₃ catalysts prepared by one-pot evaporation-induced self-assembly (EISA) method with impregnated and non-porous nickel-alumina catalysts. Core-shell Ni/Al₂O₃ obtained after in situ surface reduction produced the highest stability and activity along a run of 40 h at 800 °C DRM. These are attributed to the strong Ni-support interaction facilitated by encapsulation and uniformly dispersed Ni particles thus reducing the propensity of coke formation. High dispersion of Ni particles was also obtained during one-pot EISA synthesis within Ni_x% (x: 5–10 wt %) and Ni₅% M₅% (M: Ca or Mg) supported on Al₂O₃ with high activity and stability [57]. The method was also effective on composite NiSiAl oxide frameworks such that nickel and alumina are

encapsulated in mesoporous silica skeleton thereby sustaining their stability and catalytic activity over 100 h at 700 °C than NiAl solid solution. The confinement is responsible for uniform dispersion of Ni and impeding transformation of amorphous Al_2O_3 to $\gamma\text{-Al}_2\text{O}_3$ [112]. Furthermore, Synthesis of core-shell catalyst by one-pot aids the formation of more basic sites on support structure than other methods as reported in the work of Wang et al. [59] where MgO was coated on the walls of mesoporous Ni/SBA-15 through one-pot synthesis after 10 wt% Ni impregnation. Synthesized catalyst was compared with Ni/MgO-SBA-15 prepared by conventional impregnation in which MgO coated Ni/SBA-15 produced more medium basic sites, higher surface area and superior order in its mesoporous structure than MgO impregnated sample as obtained from characterizations. Stronger basicity of MgO-coated catalyst than MgO-impregnated is attributed to better dispersion of MgO by in situ coating over impregnation.

Most of catalyst prepared with core-shell morphology were carried out on mesoporous supports with high surface area for monodispersion of Ni in the core. Notably are active metals encapsulated in the core of pure SiO_2 [102,104,108,113]; Al_2O_3 [57,114–116]; MCM-41 [25]; SBA-15 [117]; Fibrous KCC-1 [118,119]; and $\text{SiO}_2\text{-Al}_2\text{O}_3$ [112]. Ordered structures of solid solutions have also been synthesized with core-shell structure by one-pot to provide uniform dispersion and confinement of small Ni particles [109,120]. Besides being time and energy efficient, one-pot synthesis has proven to generally enhance catalytic activity, reduce active metal sintering and inhibit coke deposition. This method is therefore imperative to the quest for industrial and commercial production of syngas through DRM.

7. Redox potential

Reduction/oxidation (redox) potential of materials have been exploited for improved activity and stability of catalysts during DRM reactions. Profound investigations have been carried out to evaluate the extent and effects of redox properties of different materials as a catalyst support or promoter on performance during dry reforming. Materials prominently known and tested for redox potential are TiO_2 , CeO_2 , and ZrO_3 [121]. CeO_2 as a support or promoter for catalysts has proven to be the best and most widely used among others for application on Ni-based catalysts. This is attributed to its higher oxygen storage capacity (OSC) providing the required catalyst stability via coke gasification [122–124]. It has been established also that mixed redox oxides promote lesser carbon deposition than their respective individuals especially the filamentous or graphitic carbon that can result to permanent catalyst deactivation [125,126]. Materials with redox properties improve catalyst stability by reacting directly with carbon-containing reactants and intermediates to produce CO and H_2 , thus minimizing carbon formation and deposition [127]. Redox oxides such as CeO_2 have been reported to undergo reduction during DRM at high temperature from CeO_2 to a non-stoichiometric CeO_{2-x} (Eqs. (8) and (9)) and are re-oxidized back to CeO_2 by reacting with produced CO_2 and H_2O (Eq. (10)) [128].



High OSC of redox oxides aids easy storage and release of oxygen due to the stable and variable transition state of their constituent metals. Their oxygen-cushion effect allows mobility of lattice oxygen thus, creating an oxygen pool and oxygen vacant sites needed for DRM reactant activation and gasification of deposited carbon by oxidation to form CO [123,129].

Several researches have shown that redox oxide properties can be used to enhance performance and stability. These are used as support structure such as Ni/ CeO_2 [130,131]; Pd/ CeO_2 [132]. Higher activity

was attributed to strong interaction between the support oxides and loaded metal while the stability is from the oxygen transfer properties of the support. Singha et al. [132] reported high catalyst activity of Pd/ CeO_2 at low temperature of 350 °C, redox property and strong interaction of CeO_2 are responsible for the result obtained. Addition of redox oxides as promoters has helped to significantly mitigate catalyst deactivation due to carbon deposition and sintering especially to vulnerable Ni-based catalysts at high temperature. Reducibility of ceria (CeO_2) increases the lifespan of highly unstable Ni/ Al_2O_3 catalyst due to its characteristically low acidity and high OSC. This will go a long way in minimizing carbon formation or oxidizing the eventual carbon formed [133]. The reduced form of redox promoters has been found to also improve activity of Ni catalysts via facilitating reduction of Ni^{2+} to Ni^0 , increase intensity of basic sites and aid creation of active sites at low temperature [35]. This phenomenon was also noticed when Ni atoms in the B-site of perovskites are partially substituted by metals with redox properties. From the work of Valderrama et al. [134], Mn substitution of Ni in the LaNiO_3 perovskite oxide widens reduction temperature of Ni^{3+} to Ni^0 leading to the formation of more and highly dispersed Ni^0 particles on $\text{La}_2\text{O}_3\text{CO}_3\text{-MnO-Mn}_2\text{O}_3$ matrix which is the site responsible for higher activity and resistance to coking. Metal oxides with distinct and synergistic redox properties have been used as support for Ni catalysts [135]. Ni loading on $\text{TiO}_2\text{-CeO}_2$ at optimal Ti/Ce ratio improve catalytic performance and stability during DRM. The enhanced stability is attributed to the super-reducibility of the catalyst while higher activity is as a result of great dispersion of Ni crystallites on Ni/ $\text{TiO}_2\text{-CeO}_2$. Besides their redox properties, performance of CeO_2 have been found to be morphology dependence which validated its application over the past decade as catalyst support [136,137]. Shape and size of ceria are tuned by changing their synthesis route and formulations depending on the target application.

With the aid of DFT computations, role of redox CeO_2 in Pt-Co/ CeO_2 during DRM was studied [138]. CeO_2 was found to favour CO_2 activation by supplying the catalyst surface with oxygen defects thus, promoting DRM with high entropy to recompense its higher activation barrier. Similar trend was noticed with CeO_2 -supported Pt-Ni for dry reforming of ethane and butane [139]. DFT attributed the increased activity from Pt addition to formation of bimetallic surface which decrease activation energy for reactant dissociation via reduction of NiO to Ni^0 and CeO_2 from Ce^{4+} to Ce^{3+} . Resistance of anatase TiO_2 (0 0 1) to carbon formation was also evaluated using DFT calculations measured by surface coverage of carbon on catalyst. These computations were carried out on the basis of surface OH^- groups present, relative stability of (0 0 1) and (1 0 1) anatase surfaces and possibility for surface reconstruction of the (0 0 1) phase. From the computations, C and CH were less stable than CH_2 and CH_3 on TiO_2 surface and hydrogenation of CH, CH_2 and CH_3 radicals at substantial rate took place right from 900, 900 and 600 K respectively [140]. These findings clearly indicate strong and sustained coking resistance of the highly reducible TiO_2 anatase during DRM. Using Ni/ Al_2O_3 as a research basis, Foppa et al. [141] discovered that supporting transition metals on redox oxides for enhanced stability prompts modification of the original metal reactivity. Multi-scale DFT/microkinetic modelling was used to evaluate the reactivity of Ni/ Al_2O_3 interfaces formed. It was deduced that the role of this interfaces in DRM cannot be fully comprehended in terms of adsorption/dissociation energies and elementary steps only. It is imperative to also take into account the population of surface species and preferred reaction pathways.

8. Chemical looping dry reforming of methane catalysts

Chemical looping dry reforming of methane (CLDRM) is a contemporary innovative technology which uses the principle of chemical looping combustion (CLC) to carry out CH_4 reforming by exposure of catalysts to the reactants (CH_4 and CO_2) in a cyclic form (Fig. 4). This is an attractive, auspicious and alternate technology for DRM such that

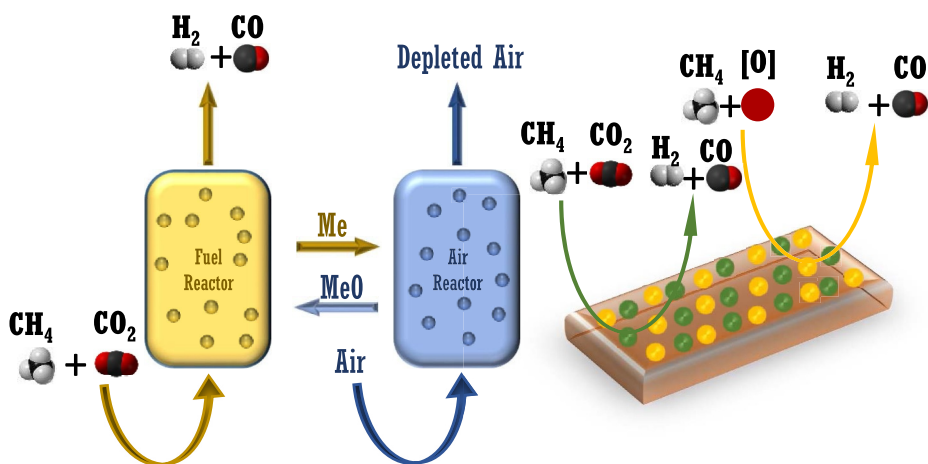
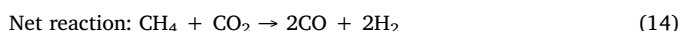
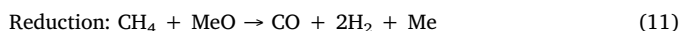


Fig. 4. Schematics of DRM by chemical looping technology. Modified from Ref. Kang et al. [191].

heterogeneous metallic oxide (MeO) catalyst serves as an oxygen vector that reacts with CH_4 to selectively produce syngas and gets reduced in the process [142]. The reduced catalyst (Me) is re-oxidized in the second stage by CO_2 which is a catalyst regeneration process [33,143,144]. The catalyst regeneration is simply the recovery of most lattice oxygen consumed from CO_2 to form an intermediate oxygen carrier state ($\text{MeO}_{1.8}$) thus reducing CO_2 to CO. The $\text{MeO}_{1.8}$ recovers the remaining lattice oxygen via air oxidation in the air reactor to be finally at its initial state (MeO) [145,146]. CLDRM process is similar to the conventional DRM such that the net reaction of both pathways produces syngas having the same stoichiometric ratios (Eq. (11)) but CLDRM is targeted at the optimization of CO_2 activation while high yield of syngas is the main target for DRM [145]. Eq. (11–14) depicts the catalytic redox CLDRM reaction steps. From the reaction pathways, CLDRM evade direct contact of CH_4 , CO_2 and catalyst thereby eliminating the possibility of side reactions like RWGS, Boudouard and coking reactions which are the major drawbacks of DRM [147]. Coking is avoided during regeneration cycle due to carbon oxidation, RWGS is suppressed when produced H_2 is not in contact with CO_2 , and thus selectivity to syngas production is optimized.



Several researches have been recently conducted over selection of an efficient metal oxide and improvement of its activity. Nickel-based oxides are most frequently used as CLDRM oxygen carriers and catalysts due to their documented high CH_4 conversion and prolonged thermal stability over harsh conditions [142]. Low syngas selectivity and associated high cost of nickel has hampered its widespread applications. The prospect of Fe-based oxides has been studied as an alternative to nickel oxides because of their relatively lower price but at a penalty of lower reactivity in comparison to Ni [148]. Support materials are being introduced to iron oxides to overcome these setbacks. Lately, synergistic effect between Fe and Ni is being harnessed due to the fact that Fe is very reactive to CO_2 but low reactivity towards CH_4 while Ni is highly active for CH_4 dissociation but is not oxidized with CO_2 . More et al. [149] investigated the effect of Fe-Ni alloy on CLDRM and discovered that the reactivity of each metal combined synergistically during CL reforming process. It was also discovered that activation of carrier for CH_4 conversion is effective even at low of Ni loadings, which is made possible due to repeated re-oxidation of Ni by CO_2 in the presence of Fe.

9. Catalysts deactivation

Long-term stability of catalyst is a significant challenge in the development of new and robust catalysts for industrial syngas production through DRM. Regardless of the active metal and support structure applied, serious deactivation has been reported during DRM reactions involving Ni and Ni-based catalysts. This is attributed generally to carbon species deposition, sintering and/or oxidation of active metal particles [150]. Despite the fact that catalyst deactivation is inevitable during dry reforming, its immediate and far-reaching effects can be reversed, postponed or even avoided [151]. There have been decades of conspicuous development reported in the science of catalyst deactivation notably via books [152–154] and comprehensive reviews [32,151,155,156]. These efforts were carried out with the sole aim of providing a critical understanding of deactivation process models, design of highly stable catalyst and optimization for slower catalyst deactivation. In a typical DRM reaction conducted at high temperatures, catalyst deactivation is mostly caused by growth of active crystallite size, carbon and coke formation, collapse of support pore structure and/or solid-state reactions between active metal phase with support or promoter [157].

9.1. Carbon/coke formation

The only distinction between carbon and coke is that carbon is formed as a result of CO disproportionation while coke is a product of hydrocarbon condensation or decomposition on catalysts surface consisting of typically polymerized long-chain hydrocarbons [3]. Tendency of deactivation by carbon deposition from steam reforming of methane (SRM), DRM and partial oxidation are compared and estimated based on their stoichiometric O/C and/or H/C ratios in the feed [23,158]. The lower the feed H/C and/or O/C ratio, the greater the possibility of carbon deposition. As such, DRM (H/C = 2, O/C = 1) is the most susceptible to carbon deposition in comparison to SRM (H/C = 6, O/C = 1) and partial oxidation (H/C = 4, O/C = 1). In addition, feed composition, catalyst type and reactor conditions are also very crucial in determining the rates and chemical structures of carbons and cokes formed during DRM reaction [159]. Wang et al. [27] discovered that feed composition (CH_4/CO_2 ratio) greatly influenced the chemical inertness and morphology of accumulated carbon. Out of the whisker, amorphous and encapsulating carbon visibly deposited on Ni-CaO-ZrO₂ catalyst as visible in high-resolution transmission electron microscopy (HRTEM) result on the spent nickel catalyst sample, encapsulating carbon was found to be the most likely carbon connected to the catalyst deactivation. Reaction temperature [157], nature of support [160] and promoters [161,162] have been found to determine the type of carbon

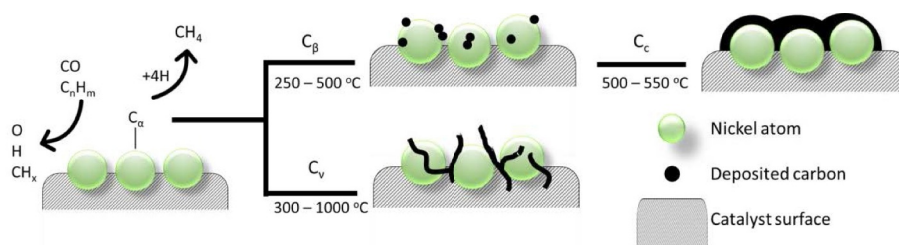


Fig. 5. Carbon formation, deposition and transformation pathways on Ni-based catalyst. Produced with information from Ref. Argyle and Bartholomew [165].

formed and their resultant effect on deactivation.

Deactivating carbon (coke) formed are deposited on supported metal surface through (1) encapsulation of metal particles as a result deactivating them completely, (2) monolayer chemisorption or physical adsorption in multilayers in both cases blocking accessibility of reactant gases to active metal sites, (3) continuous build-up of active filamentous carbon in pores of support materials to the point of stressing and subsequently fracturing the support. Thereby causing attrition of catalyst pellets and plugging of reactor void space [32]. Carbon formation, deposition and transformation mechanisms on metallic catalysts developed by CO disproportionation and hydrocarbon cracking are illustrated in Fig. 5. CO when in contact with active metals dissociates to produce adsorbed atomic carbon species, C_a with repeating units reacting together to form polymeric carbon filaments, C_b . At elevated temperatures, C_a and C_b which are highly reactive are converted to less active graphitic carbon, C_v . As a matter of fact, some carbon form cause catalyst deactivation while some do not, depending on their relative deactivation rate. Deactivation rate is measured as a difference in the rate of coke/carbon formation and gasification ($r_d = r_f - r_g$). Carbon/coke is deposited when the rate at which carbon precursors are formed is higher than their rate of gasification ($r_f > r_g$). Therefore, catalyst deactivation by carbon/coke formation is avoided in temperature regions where their formation rate is less than gasification rate [163]. Carbon/coke formation is also known to be sensitive to nature of metal crystallite and support structure since the formation of a carbon type involves the formation of C–C bonds on the number of available sites [156].

According to DFT, coke formation is dependent on the extent with which C–H oxidation pathway dominates with respect to the overall oxidation reaction and also the barrier to CO dissociation. Probability of coke formation is measured as the rate ratio of C–H oxidation pathway to C oxidation. For Ni-based catalysts, DFT revealed that flat Ni surface (Ni (1 1 1)) is the most resistant to coke formation. Stepped surfaces of nickel (Ni (2 1 1)) and nickel carbide (Ni₃C (1 1 1)) however are very vulnerable to coke formation. Dominance of C–H oxidation and high energy barrier of CO dissociation are responsible for the coking resistance of Ni (1 1 1) surface [163].

9.2. Metal sintering

Catalyst sintering, another thermal induced catalyst deactivation leading to reduction in catalyst surface area as a result of metal particle growth. Sintering can also be attributed to support pore collapse on metals of the active phase. It is a result of surface energy reduction of kinetically favoured crystallites and their size-dependent movement on catalyst support [156]. Metal sintering predominantly occur at high DRM reaction temperatures usually higher than 700 °C and are generally promoted by the presence of moisture produced mostly from RWGS reactions. The pathways to the growth of active metal crystallites during DRM at high temperature proceeds in two principal mechanisms on support as described in the schematic diagram in Fig. 6 namely: (1) atomic migration by coarsening and Ostwald ripening and (2) crystallite migration in the form of coalescence [164]. During atomic

migration, metal atoms are detached from the crystallite and migrated over the support surface before eventually got captured by larger crystallites. Agglomeration due to crystallite migration involves mobility of whole crystallite across support surface through collision and coalescence. From a practical point of view, the possibility of both mechanisms occurring simultaneously through some intricate physico-chemical steps cannot be overlooked. These steps involve: (1) disengagement of metal atoms from its crystallite, (2) adsorption and entrapment of the metal atoms in the pores and external surfaces of catalyst support, (3) diffusion of entrapped atoms across support pores and surfaces, (4) wetting of support pores and surfaces by metal particles, (5) nucleation of metal particles, (6) coalescence between metal particles and (7) capture of metal atoms by larger metal particles [165]. Processes involved in metal sintering occur at a slow rate especially at mild reaction temperatures but are however generally difficult to reverse. This is why prevention of sintering is less complicated than its cure.

9.3. Regeneration of spent catalyst

To address the inevitability of DRM catalysts getting deactivated after some time of reaction due to particles sintering and coke formation, it is therefore imperative to choose among available alternatives of discarding, recycling or regenerating the catalysts. Regeneration is the most preferred option for economic and environmental reasons but regeneration ability is totally dependent on the reversibility of the cause and source of deactivation [165,166]. Reactivation of sintered catalysts has proven to be strenuous due to its irreversibility with the exception of some selected noble metals. Deposition of most carbonaceous materials are reversed with relative ease by in-situ/ex-situ, onsite/offsite or batch/continuous heat treatment and oxidation [32,113,164]. Regeneration by temperature-programmed oxidation (TPO) takes place in the presence of gasifying agents such as air [167,168]; CO₂ [169]; O₂ [170]; steam [171] and hydrogasification [172] at temperatures ranging mostly from 300 to 500 °C and followed by reduction. The low gasification temperature was to allow recovery of catalyst without causing destruction or modification to the catalyst pore structure or disruption in its composition.

Recently, Theofanidis et al. [169] studied carbon removal by gasification from Fe–Ni catalyst on MgAl₂O₄ support with the regeneration process studied by operando time-resolved XRD and temperature-programmed oxidation (TPO) in a mechanistic pathway shown in Fig. 7 showing the sensitivity of distant and localized carbon to gasification. Gasification by O₂ (Fig. 7b) is characterized by (1) oxidation of active Ni and Fe particles, (2) gasification of carbon species on metal surface via lattice oxygen, (3) migration of particles to the point of contact between active metals and isolated carbon species which is made possible due to increase in local temperature from oxidation of surface carbon and (4) oxidation of the isolated carbons by lattice oxygen from oxides of active metals. During gasification by O₂, Ni and Fe are oxidized to NiO and Fe₂O₃ prior to oxidation of carbon species. CO₂ gasification (Fig. 7a) occur in two distinct and parallel processes: (1) CO₂ dissociation over Ni surface resulting to oxidation of carbon by surface



Fig. 6. Pathway to sintering of catalyst via crystal growth by (A) atomic migration, (B) crystallite migration. Modified from Argyle and Bartholomew [165].

oxygen, O_s (2) oxidation of Fe by CO_2 , followed by oxidation of carbon deposited by lattice oxygen from the Fe_3O_4 thus, reduced back to Fe. Amorphous and graphitic carbon types were noticeable on the catalyst during gasification with the aid of temporal analysis of products (TAP) pulse response, a transient response technique. Carbon gasification due to O_2 spillover was considered negligible during regeneration.

Regeneration ability of spent Ni hydroxyapatite-based catalyst using air and CO_2 as gasifying agent after DRM was investigated and compared in situ at a temperature of $700^\circ C$ from the work of Vasconcelos et al. [167]. Results obtained from both gasification atmospheres after three successive reaction cycles showed high regenerability with small portion of noticeable deactivation proven to be irreversible. The irreversible deactivation was found to be triggered by core-shell coke formation and nickel particles agglomeration.

The choice of method for carrying out regeneration depends largely

on the type, design and configuration of catalyst reactor. For commonly used fixed bed reactors, deactivated catalysts are usually regenerated ex situ with removal only possible after completion of one cycle of reaction. This is typically suitable for slow deactivating catalysts. In situ regeneration is necessary for fast deactivating catalyst and are operated in a system such that DRM proceeds at the same time with catalyst oxidation with CO_2 . In so doing, carbon formation, deposition and gasification occur simultaneously. Carbon gasification is strongly exothermic thus, leads to increment in catalyst bed temperature [169].

10. Crystalline oxides catalysts

Crystalline oxides nanoparticles have been rarely applied as support for DRM reactions due to the inertness of their bulk structure. Nevertheless, their crystalline well-defined structure can be utilized to

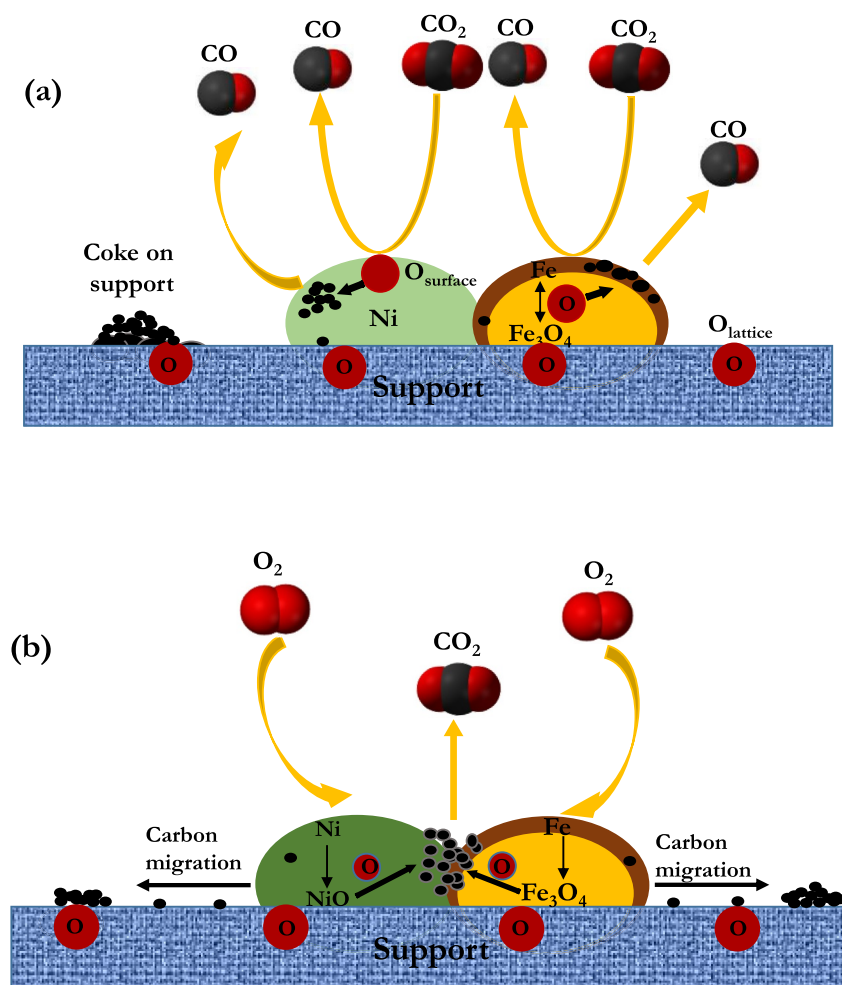


Fig. 7. Schematic representation of deposited carbon removal with (a) CO_2 , (b) O_2 as the gasifying agents over $MgAl_2O_4$ supported Fe-Ni catalyst. Modified from Ref. Theofanidis et al. [169].

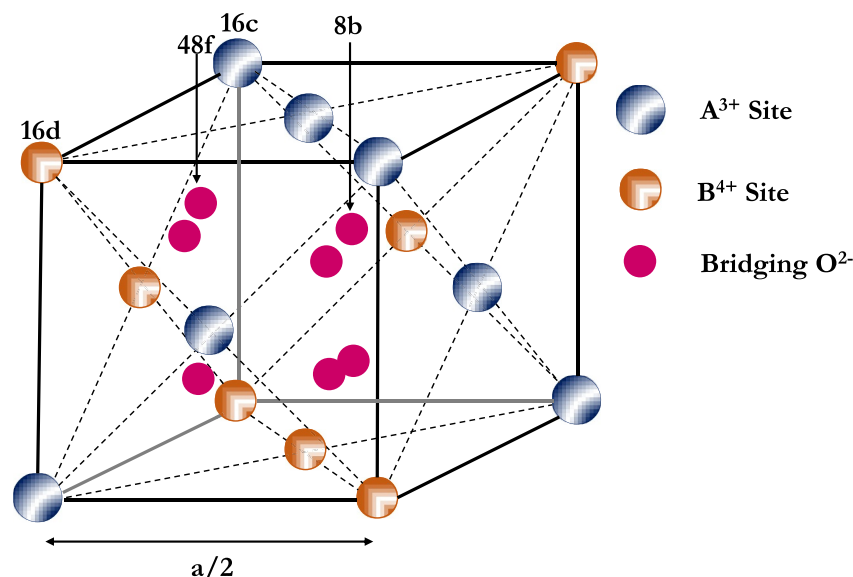


Fig. 8. Pictorial diagram of pyrochlore structure ($A_2B_2X_7$) depicting positions of A, B and O sites in the lattice. Modified from Ref. Perriot and Uberuaga [205].

accommodate catalytically active metals to produce DRM catalysts with high thermal stability and metal dispersion. Metals on these types of supports are bound within the support structure and their subjection to a reduced environment triggers migration of metal atoms to the surface of crystalline oxide precursors [173,174]. These oxides are known to mostly have oxygen vacant sites developed from inherent oxygen mobility which is a strong inhibitor for carbon deposition. The available oxygen vacancies are favoured by substitution of metal atoms and their subsequent migration to the surface [31]. Examples of crystalline oxides that have so far been employed as supports for active metals in DRM catalysts are pyrochlores, perovskites, spinels, fluorites and hexaaluminates. Besides producing a coke-resistant catalyst, combination of elements from mixed metal oxides promotes stability of dispersed active metal phases as a result of partial substitution of incorporated cations.

Pyrochlores are enthralling group of ternary crystalline oxide minerals with a 3-D structure comprising of a rare-earth or transition metal species connected by oxygen atoms (Fig. 8). They are generally represented in the form of $A_2B_2X_7$, where A and B represents sites occupied by transition or rare-earth metal while X is the bridging oxygen atoms [175]. The anion deficient, cation ordered pyrochlores with high thermal resistance and a lattice framework comprising of La and Zr in the 'A' and 'B' metal sites ($La_2Zr_2O_7$) have displayed long-term stability over a wide range of fuel conversion reaction conditions [176,177]. The propensity of these minerals to allow partial substitution of their 'A' and/or 'B' sites in the lattice with different metals have been exploited in tailoring their structure for catalytic application [175,178]. As a result, these materials have received significant attention in DRM for providing the much sought-after stability at high temperatures. Two important properties possessed by these minerals making them suitable for this reaction are: (1) characteristic oxygen ion conductivity with resultant oxygen vacancies developed during synthesis. Oxygen atoms migration inhibits coke deposition during CH_4 activation, (2) isomorphic substitution potential of catalytically active metals into the 'B' site thus, preventing their sintering at high DRM temperatures [47]. The substitution of metals in the A/B site reduces the bond energy for A–O and B–O lattice bond causing release of oxygen from the lattice.

Over the past decade, Spivey and co-workers have made astonishing contributions towards exploring the potentials of pyrochlores as catalyst support DRM. Gaur et al. [178] conducted DRM on Rh, Ni and Ca supported on $La_2Zr_2O_7$ by partial substitution of A and B sites with the three active metals. From the results obtained, Rh substituted

pyrochlore produced the highest activity and selectivity for syngas production over Ni catalyst. This was attributed to higher carbon deposition (1.4 g/g_{cat.}) for Ni substituted catalyst ($La_2Zr_{2-x}Ni_xO_{7.8}$) over Rh substituted ($La_2Zr_{2-x}Rh_xO_{7.8}$) and Rh-Ca substituted ($La_{1.95}Ca_{0.05}Zr_{2-x}Rh_xO_{7.8}$) with 0.44 and 0.26 g/g_{cat.} carbon deposition respectively. Replacement of La^{3+} with Ca^{2+} was found to improve oxygen mobility. Activation energy for CO_2 and CH_4 conversion rates for substituted pyrochlore also depends largely on the nature of active metal [179]. For comparison study between Ru and Pt as substituted metals, rate of reactants conversion is lower in Ru substituted than Pt on 'B' sites of pyrochlore. Temperature-programmed oxidation (TPO) for both catalysts showed that total carbon formed decreased as the temperature of reaction increased. Stability of carbon formed however increased as the reaction temperature increased. In an effort to improve the performance of pyrochlores for DRM, the best substituted metal (Rh) catalyst was further studied for its characterizations [180]; reaction mechanisms [176]; kinetics and mechanistic studies [47].

Theoretical studies using DFT was also carried out to identify the favourable reaction sites and calculate their respective activation energies to determine the primary reaction pathway [177]. According to DFT, plane (111) is the catalytically active site for DRM and the presence of Rh reduces the activation barrier including the rate limiting steps barrier for CHO dehydrogenation and CH_2 oxygenation. This is in agreement with experimental results obtained. For validations of deductions from DFT calculations and direct measurement of some key mechanistic kinetic parameters, steady-state isotopic transient kinetic analysis (SSITKA) study was effectively used to study the kinetics of active sites which are not accessible at steady-state conditions [176]. Kinetic isotopic effects and isotope responses were analyzed with the aid of reaction mechanisms obtained from DFT studies on surface reactions.

Perovskites are a family of structured oxides with a cubic structure and having a general formula of ABO_3 , where 'A' site represent the lanthanide elements such as Pr, La, Ce and 'B' is a site for mostly transition elements such as Ni, Pt, Rh [181,182]. Larger cations located on 'A' site are mostly irreducible thus, always in their oxide forms and are responsible for providing thermal resistance to the material (Fig. 9). Cation B is however reducible and provides the activity on the catalyst [183]. Advantages of perovskites in DRM catalyst structure are: (1) high oxygen storage capacity and their mobility in the lattice owing to its well-defined bulk structure, (2) tenability of the composition of 'A' and 'B' sites by partial or total substitution with different elements but all

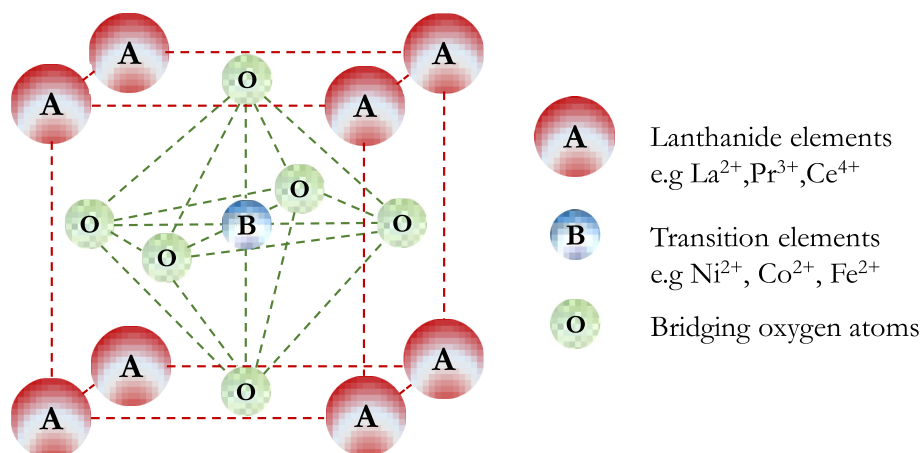


Fig. 9. Pictorial diagram of a partial unit cell of perovskite with ABO₃ arrangement in the lattice. Modified from Ref. Gupta et al. [206].

with the same basic structure, (3) exceptional redox properties, (4) good thermal stability with control over their valency, vacancy and stoichiometry [184]. Due to their relatively lower cost and high thermal resistance, structured perovskite oxides have particularly proven attractive as precursors for DRM catalysts. Among numerous perovskite materials available, LaNiO₃ and similar compounds have received appreciable attention as a result of their notable stability and activity during harsh DRM reaction [117].

High dispersion of active metals is expected on perovskite oxides even when subjected to arduous redox reactions at high temperatures. Strong resistance to coking and sintering is attributed to the placement of active metal phase within the perovskite lattice. This help in raising the reduction temperature closer to the DRM temperature. On reduction, some atoms of the homogeneously dispersed active metals migrate to the surface from the bulk crystalline lattice [30]. Thus, a highly dispersed metal phase with minimal coke formation, increased metal-support interaction and thermally stable catalyst is obtained. Kühl et al. [183] produced Ni/La₂O₃ catalyst from LaNiO₃ precursor for high temperature DRM. Addition of Ru results to Ni-Ru alloy formation and enhanced stability of the perovskite structure. This prevents the decomposition of catalyst into NiO and Ruddleden-Popper mixed oxides (La_{n+1}Ni_nO_{3n+1}) as obtained for the Ru-free catalyst. Ru introduced also reduced the proneness to coke formation. When subjected to a reducing environment, the precursor was partially reduced to an intermediate of the form LaNiO_{2.5} and the La₂O₃ supported Ni metal reduction was found independent of Ru content in the catalyst. Substitution of LaNiO₃ with Ce high in OSC produces higher oxygen vacant sites in the lattice needed for C–H bond activation. This improved the H₂ selectivity from 57 to 61% at 600 °C [185]. Basicity of perovskite catalyst improved significantly by addition of promoters through partial substitution of its ‘A’ site as obtained from the work of Yang et al. [186]. They investigated the influence of partial substitution of La by Ca or Sr and Ni by Fe in the ‘B’ site. They found that La_{0.9}Ca_{0.1}Ni_{0.5}Fe_{0.5}O₃ catalyst exhibits superior catalytic performance and stability over the unsubstituted and other prepared perovskite catalysts. Promoters added improved considerably the catalyst basicity which facilitates CO₂ adsorption, activation and desorption on catalyst surface. This is responsible for the increased conversion on promoted catalysts. Partial substitution of Ni by Zn in LaNiO₃ was found to increase the reduction peak temperature [187]. This led to a perovskite structure with improved stability than LaNiO₃. From TGA results obtained, LaNi_{0.8}Zn_{0.2}O₃ developed better resistance to coke formation than LaNiO₃ after 75 h time on stream.

Besides their usage as supports for active metals, perovskites have also been supported on highly porous materials to improve their characteristic low surface areas which is the bottleneck of their application in the field of catalysis. Wang et al. [117] conducted comparative

studies on LaNiO₃ loaded on different silica source (SBA-15, MCM-41 and SiO₂). They were synthesized by filling the pores of silica support with citrate complex precursors of Ni and La, with further treatments leading to formation of LaNiO₃ in the pores and channels of the various silica materials. LaNiO₃ supported on MCM-41 produced the highest catalytic performance having the best dispersion of Ni. In terms of stability, SBA-15 supported LaNiO₃ outperforms LaNiO₃/MCM-41 which is attributed to more stable silica matrix preventing Ni crystallite sintering.

The potentials of other perovskites have been recently tested for DRM with various degrees of improvement in activity and stability of catalysts recorded [188,189].

11. Prospects

Recent progresses have this far been recorded as a revolutionary development of DRM catalysts through controlled synthesis route, comprehensive material characterization at atomic and molecular levels using real-time reaction conditions and state-of-the-art theoretical modelling and simulation with the aid of computer software systems. These advances converge on development of a new paradigm for robust DRM catalysts research based on novel insights into relationships between catalyst structure with activity, selectivity and stability of active sites as highlighted in Table 3. Concerted efforts have been made towards understanding of interactions among active metals, supports, reactant gases and reaction conditions for discovery of better catalysts. This era of catalysis in DRM reaction is stimulated by progresses recorded so far in theoretical and experimental methods.

In recent times, remarkable breakthroughs have been recorded by changes in active metals loading via atomic layer deposition [195,199] and in situ exsolution [200,201]. Loading metals by ALD in the field of DRM especially for Ni-based provides a protective layer of support shield on metal surface thus preventing susceptibility to agglomeration and carbon deposition. Unlike ALD technique, ex-solved active metal particles are socketed into the parent support structure thereby providing the much-needed resistance to coking and sintering. Exsolution has recently been used to synthesize catalysts with exceptionally high metal-support interaction by solid-phase crystallization on ordered crystalline oxide precursors. These methods have produced better stability over conventional techniques with superficial interaction between metal and support. The improved resistance to coking and sintering does not in any way compromise catalytic activity. To improve metal dispersion, basicity, oxygen mobility, oxygen vacant sites, mass transfer and porosity which are supportive to enhanced catalytic activity, morphology of support have been increasingly tailored. Mesoporous support such as MSN [202], SBA [114], KCC-1 [203] and MCM [30] produced improved performance due to their enhanced

Table 3
Highlights of recent advancements in catalyst development for DRM.

Catalyst	Preparation method	Reactor type	Key findings	Ref
$\text{CaZr}_{0.8}\text{Ni}_{0.2}\text{O}_{3-8}$	In situ exsolution by citrate gel perovskite method	Packed bed tubular reactor	Ca substituted perovskite catalyst synthesized shows superior catalytic performance in terms of CH_4 and CO_2 conversion, while maintaining its activity even after 500 h of reaction. This is attributed to strong metal-support interaction, basicity of support due to surface hydroxyl groups, oxygen defects and formation of amorphous carbon with insignificant effect on stability.	[188]
Ru/SrTiO_3	In situ exsolution by microwave-assisted hydrothermal	Microwave reactor system	Ruthenium-doped SrTiO_3 catalyst showed excellent dielectric properties, high and stable CO_2 and CH_4 conversion over 200 h TOS and H_2/CO ratio approximately unity at a maximum reforming temperature in the region of 940 °C.	[189]
$\text{Ni}(\text{Ru})/\text{La}_2\text{O}_3$	In situ exsolution of co-precipitated LaNiO_3 by Ru doping	Continuous flow fixed-bed tubular quartz reactor	Doping of LaNiO_3 with Ru stabilized of the perovskite structure and hinders its decomposition into NiO and Ruddlesden-Popper mixed oxides $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$, which was observed for the Ru-free sample upon calcination at 1000 °C. Ru introduced led to the formation of Ni-Ru alloy with higher dispersion of metallic phase and reduced propensity for carbon deposition.	[183]
$\text{La}_2\text{Zr}_{1.888}\text{Rh}_{0.112}\text{O}_7$	isomorphic substitution of Rh on La-Zr pyrochlore	Fixed bed reactor	The catalyst exhibited long-term stability and resistance to deactivation. The work is geared towards further catalyst improvement using surface reaction kinetics using steady-state isotopic transient kinetic analysis (SITKA) experiments to explain carbon species migration to product formation.	[176]
$\text{Fe}/\text{Zr}@/\text{Zr}-\text{Ni}@/\text{Zr}$	Incipient wetness impregnation on the as-prepared ZrO_2 support	Chemical looping autothermal quartz tube micro-reactor	Combination of core-shell structured $\text{Fe}/\text{Zr}@/\text{Zr}-\text{Ni}@/\text{Zr}$ bifunctional catalyst possesses excellent catalytic activity and stability for CH_4 conversion in the reduction half-cycle due to small Ni particle size (< 3 nm), high resistance to coking and thermal stability due to its eccentric core-shell structure. Double-zone bed with the catalyst provides high highest oxygen storage capacity for CO_2 utilization, offering a promising reactor technology.	[190]
Ni/CeO_2	Wetness impregnation of the Ni on precipitated CeO_2	Chemical looping fixed-bed quartz reactor	Strong interaction between Ni^{2+} and Ce cations was observed even after exposure to CH_4 while part of the Ni is reduced and remain in metallic state during the looping process. However, both Ni species play important roles on reactants activation and oxygen supply by the solid.	[147]
$\text{Ni}-\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$	Sol-gel	Chemical looping fixed-bed reactor	Active phase of Ni aluminate in the Ni-reinforced oxygen carrier facilitated dry reforming at a suppressed CH_4 decomposition, high CO selectivity of 96.76% and at minimal carbon deposition. The Ni-reinforced oxygen carrier also showed stability in its redox activity during repetitive reduction and oxidation cycles.	[191]
$\text{CeO}_2/\text{LaFeO}_3$	Gas-bubble-assisted loading of hard-templated perovskite	Chemical looping tubular fixed-bed reactor	Formation of Ce^{3+} and Fe^{2+} from strong $\text{CeO}_2\text{-LaFeO}_3$ interaction enhanced the reducibility, oxygen mobility and activity for CH_4 oxidation. These factors are significant in slowing down the rate of carbon deposition.	[192]
$\text{Mn}-\text{ZrO}_2/\text{Al}_2\text{O}_3$	Wet impregnation of co-precipitated $\text{ZrO}_2/\text{Al}_2\text{O}_3$	Chemical looping in a fixed bed reactor	ZrO_2 loading in the support structure inhibited significantly the deposition of carbon on the oxygen carrier surface and produced CH_4 and CO_2 conversion, H_2 yield and H_2/CO molar ratio of about 99.0%, 96.6%, 65.2% and 2.55 were achieved at 650 °C using the optimized oxygen carrier.	[193]
Fibrous $\text{Ni}/\text{Al}_2\text{O}_3$	Electrospinning	Fixed bed quartz tube reactor	Fibrous $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst exhibit high structural stability because the fibrous morphology gives it higher resistance to sintering compared to conventional supported catalysts. However, higher calcination temperature results to larger Ni particles due to large NiAl_2O_4 crystal formation which requires a higher reduction temperature. As a result, activity of the DRM catalyst decreased with calcination temperature while the high reduction temperature promotes uniform dispersion of Ni via nucleation.	[194]
$\text{Ni}/\text{porous } \gamma\text{-Al}_2\text{O}_3$	Atomic layer deposition	Fixed bed quartz tube reactor	The catalyst showed high catalytic activity and long-term stability over 300 h DRM reaction at temperatures range from 700 °C to 850 °C. Its long-term stability is attributed to the formation of NiAl_2O_4 spinel and excellent activity is due to effective and uniform dispersion of Ni crystallites by atomic layer deposition.	[195]
$\text{Ni}/\text{AISBA-15}$	Impregnation using ethylene glycol	Fixed-bed micro-reactor	From HAADF-STEM results, Ni nanoparticles were successfully encapsulated in the hexagonal mesopores of AISBA-15 having a perfect peasecod-like structure. Ni/AISBA-15 showed improved activity and stability over the conventional Ni/SBA-15 catalyst. Its superior hydrothermal stability over Ni/SBA-15 makes it more suitable for harsh hydrothermal reaction condition such as RWGS.	[196]
$\text{Ni}-\text{SiO}_2@\text{CeO}_2$	Centrifuging	Quartz tube reactor	Novel Ni catalyst sandwiched between ceria and silica forming a core-shell structure displayed excellent coking resistance with no carbon formation detected after a 72 h TOS. Encapsulation effect of the sandwiched structure and its resultant shift from mono-functional Ni/SiO ₂ to bifunctional pathway of DRM are the primary reasons for the excellent coke resistance of the Ni-SiO ₂ @CeO ₂ catalyst.	[197]
$\text{Ni}-\text{Sn}/\text{CeO}_2\text{-Al}_2\text{O}_3$	Sequential impregnation	Tubular quartz reactor	Addition of tin and ceria improves significantly the weak stability inherent to Ni/ Al_2O_3 catalyst for both bi- and dry reforming processes producing an equilibrium H_2/CO ratio in the process. Tin loading causes occupation of Sn atoms at the C nucleation sites in proximity to Ni crystallites thereby slowing down coke formation process. Presence of ceria also improves coking resistance due to its high OSC and basicity.	[133]
$\text{Ni}-\text{Co}/\text{HAP}$	successive incipient wetness impregnation	Tubular fixed-bed ceramic reactor	Thermally stable hydroxapatite support for Ni-Co produces stable and well-formed bimetallic particles with no modification to its lattice structure. High performance and long-term stability of catalyst was obtained over 160 h reaction time with limited coke deposition and insignificant changes to metals crystallite size.	[51]

(continued on next page)

Table 3 (continued)

Catalyst	Preparation method	Reactor type	Key findings	Ref
Ni/fumed silica	Pressure dilution	Continuous flow fixed-bed quartz reactor	The novel synthesis method enhanced significantly the stability and dispersion of Ni crystallites over fumed silica in comparison to conventional impregnation. Consequently, nickel dispersion was increased from 19% to 61% as a result of 5000 psi pressure applied on nickel during synthesis which is also responsible for the increased stability.	[198]

mesoporosity.

In contemporary DRM catalyst development, there is complimentary spectra obtained from IR, X-ray absorption, Raman, NMR, UV and others produced in *operando* mode giving a clear and concise information about the sites and reaction mechanisms, integrating these techniques with other characterizations. Parallel to these, significant progress has been made in theoretical methods to validate and allow advanced interpretation of experimental results using first-principle calculations *in silico*. Theoretical computational software programs play crucial role in the search for new opportunities for catalyst discovery such that it provides a prompt and inexpensive way to screen candidate DRM catalysts. DFT is a powerful and famous tool for theoretical computations of bond energies and activation barriers of reactants, intermediate and products [204]. Other software tools have been recently used to compliment DFT such as CatApp, vienna *ab initio* simulation package (VASP), artificial neural network, B3LYP level theory and CFD calculations [26,38,40].

12. Research outlook

In the quest for industrial application and commercialization of syngas production via methane dry reforming, it is imperative to develop cheap, sustainable and robust catalysts with high performance and long-term stability. Doing requires in-depth, comprehensive and state-of-the-art understanding of synergistic interactions of all catalyst components at atomic and molecular levels using experiments and *in silico* theoretical computations. Proper tuning of these interactions is the sure way of producing catalysts with requisite selectivity, stability and conversion. Research flashlight of DRM catalysts is focused on areas as highlighted.

The main driving force for DRM reactions is the presence of active sites for CH₄ and CO₂ dissociation. Bi-functional active sites utilize both loaded metal and support as sites for reactant activation, common for most catalysts with basic support. In mono-functional pathway, both reactants activation take place on the active metal as is the case for most catalyst with inert support. Basicity of catalyst contributes to its activity by facilitating chemisorption, activation and subsequent decomposition of acidic CO₂ gas in the presence of active metal phase. Thus, this increases the surface coverage of CO₂ on catalyst, reduces carbon deposition from Boudouard reaction and lowers the reactant activation barriers. Oxygen vacant sites are generated from the ability of support to release oxygen atoms under reducing environment and store it under oxidizing condition. The oxygen defects also serve as sites for C–O bond cleavage for CO₂ activation which consequently generate a pool of oxygen atoms on catalysts surface. These O species provide resistance of catalyst to deactivation by oxidizing carbon initially destined for deposition. More oxygen vacant sites are expected from catalyst with high oxygen storage capacity which is a measure of surface oxide reducibility. Strong and positive interactions between metal-support, metal-promoter and other component of the catalyst is very crucial for enhanced catalytic activity and resistance towards deactivation at high DRM reaction temperature. Properties exhibited by catalysts depend strictly on the extent and manner with which its constituent components interact with one another. Strong metal-support interaction requires high temperature for metal to break-free and agglomerate with neighbouring metal crystallite thus, inhibiting metal sintering. Another approach towards the search for the most suitable catalyst for sustainable DRM application is the modification of metal-support configuration. Various configurations have successfully been retrofitted to DRM reaction with promising results, notable among them are the core and shell, CLDRM and ordered crystalline oxide configuration. Deactivation of DRM catalysts were studied with emphasis on their source, effects, development and control. In recent times, mechanistic study of deactivation pathways was carried out with the aid of experimental and theoretical studies. In an effort to further understand and explain the various interplay between active metal and support

structure, powerful tools have been employed. The most notable is the DFT calculations to validate and compliment information from experimental data.

13. Conclusion

This review entails the various advances achieved towards development of a robust DRM reaction catalyst for sustainable application in the quest for its full-fledged industrialization. It highlighted the synergistic interplays among constituting components of catalyst and their role towards enhancement of catalytic activity and stability especially for Ni and Ni-based catalysts. Salient properties and interactions of catalysts such as basicity, oxygen vacancy, active sites, metal-support interaction, redox potential, crystalline oxides, chemical looping, core-shell configuration and inherent resistance to deactivation to coking and metal sintering have been studied and tailored towards performance enhancement in the astute design of Ni catalysts. Thorough understanding of these interactions and their corresponding effects on catalyst performance have been consistently carried out with the aid of state-of-the-art experimental procedures using sophisticated equipment. There is also the need to go beyond experimental explanation of the catalyst interactions and reaction mechanisms especially at atomic level by complimenting with state-of-the-art theoretical computations such as DFT. For theoretical computations, DFT was used to compliment information obtained from experimental data by providing additional information on spectroscopic and mechanistic properties of catalyzed reactions and interactions at electronic and sub-electronic levels.

Despite the tremendous successes recorded in tuning catalyst component interactions for enhanced catalyst performance, there have always been cases of antagonistic relationship between activity and stability. Trade-offs between the two key performance parameters have been the regular decision to make during catalyst design depending on application and economy of scale. Successful development of Ni catalyst with excellent activity and sustained stability over a long period of time is the key towards industrialization and commercialization of syngas production from DRM technology. Despite the tremendous successes recorded overtime in catalysts development with excellent activity and stability results, the search for novel and economically viable catalysts with improved properties and performances is imperative for successful industrialization and commercialization of the process. Research focus are still very much on material development and tuning of relevant properties and interactions suited for the desired catalyst activity and long-term stability. However, concerted research effort is also necessary on catalyst lifespan based on recuperative and regenerative potential; comparative economics of synthesis routes and widespread application of theoretical DFT studies to cover all aspects of heterogeneous catalysis for DRM reactions.

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