Progress in oxygen carrier development of methane-based chemical-looping reforming: a review

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Abstract

This work comprehensively reviews the recent advances for chemical-looping reforming of CH₄ (CLR) technology, which breaks down the traditional CH₄ reforming process (including steam and dry reforming) into two separate half-steps, namely CH₄ oxidation and replenishment of oxygen carrier (OC) with appropriate oxidizing agents. In order to steer the conversion of CH₄ toward partial oxidation (POM) for synthesis gas (H₂+CO) production rather than total oxidation for producing CO₂ and H₂O, the appropriate selection of OC becomes a critical issue. Moreover, instead of the commonly used air to re-oxidize the oxygen-depleted OC after reaction with CH₄, steam and CO₂ have been proposed as two alternatives, opening up the opportunities to produce extra H₂ and CO. However, owing to much weaker oxidization ability of steam and CO₂ than air, the low oxidation degree and slow oxidation rate seem to remain as challenges. Furthermore, the resistance of OC to attrition, agglomeration and carbon deposition is also of great importance. In these regards, the latest major milestones are compiled.

Keywords:

Chemical-looping reforming; CO₂ capture; Partial oxidation of CH₄; Oxygen carrier; Syngas production

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Abbreviations

AR: Air reactor

CFB: Circulating fluidized bed

CLC: Chemical-looping combustion

CL-DRM: Chemical-looping dry reforming of methane
CLOU: Chemical-looping oxygen uncoupling
CL-POM: Chemical-looping partial oxidation of methane
CLR: Chemical-looping reforming
CL-SRM: Chemical-looping steam reforming of methane
COG: Coke oven gas
CSR: Carbon dioxide splitting reaction
DRM: Dry reforming of methane
FR: Fuel reactor
GTL: Gas-to-liquid
OC: Oxygen carrier
OSC: Oxygen storage capacity
POM: Partial oxidation of methane
SRM: Steam reforming of methane
TGA: Thermo-gravimetric analyzer
TPR: Temperature-programmed reduction
WGS: Water-gas shift
WSR: Water splitting reaction
YSZ: Yttrium-stabilized zirconia

1. Introduction

Sustainable energy supply has become a necessity for the advancement of modern society. Although both renewable energy and nuclear power may lead the growing energy sources globally, each increasing by 2.5% per year, almost 80% supply of world energy consumption through 2040 is projected to strongly depend on fossil fuels (coal, petroleum and natural gas) [1]. However, the combustion of fossil fuels is widely considered as a leading cause for CO₂ emissions, which is the main contributor to global warming effect [2–5]. Among current and emerging technologies for CO₂ capture, chemical-looping combustion (CLC) is a particularly promising approach [6,7]. The first step of CLC involves the reduction of metal oxide (also named as oxygen carrier, OC), MO, in contact with a fuel in one reactor (fuel reactor, FR). The reduced OC, M, is then transferred to the other reactor (air reactor, AR) for replenishment of

oxygen with an oxidizing agent which is typically air. Subsequently, the regenerated OC is conveyed back to FR, terminating the chemical loop. After the condensation of steam from the effluent of FR, a high-pressure and high-purity stream of CO₂ can be obtained without further need of expensive gas separation unit. CLC thus offers a uniquely economical and efficient route for clean, NO_x-lean, flameless combustion of fossil or renewable fuels with the efficient production of sequestration-ready CO₂ streams [8].

OC reduction with fuel in FR:

OC oxidization with air in AR:

Another advantage of CLC lies in its fuel flexibility. CLC can, in principle, work with any fuel as long as OC shows sufficient reactivity toward fuel. Up to date, CLC has been demonstrated with methane (CH₄) [9–15], synthesis gas (syngas, H₂+CO) [16,17], biofuels [18,19] and even direct coal feeds [20,21].

In this review, we focus on the chemical-looping reforming (CLR) technology, which has been developed in the effort to convert CH₄ to syngas product. In industrial implementation, the syngas product can be further processed to enrich the yield of H₂ via the water-gas shift (WGS) reaction [22].

One of the most important issues in CLC process is the selection of an appropriate OC [22,23]. Typically, OC is composed of a primary metal oxide for active lattice oxygen storage and a ceramic support for enhanced redox stability and activity. Several critical screening criteria for OC have been addressed which include oxygen storage capacity (OSC), reactivity toward both fuel and oxidizing agents, resistance to attrition, agglomeration and carbon deposition, as well as the environmental and economic impacts.

2. Choice of reactor configuration

In general, the CLC concept can be accomplished in different types of reactor configurations, respectively a) interconnected fluidized-bed reactors (named “move material”); b) alternating fixed-bed reactors (named “move feed”); c) rotating reactor (named “move reactor”) [1,25]. The schematic representations of the three reactor configurations are shown in Fig. 1.

Fig. 1 Three possible reactor configurations for CLR [1]: a) interconnected fluidized-bed reactors; b) alternating fixed-bed reactors; and c) rotating reactor adapted from Dahl et al. [25].

The most commonly visualized reactor configuration for CLC processes at the moment is composed of two interconnected fluidized-bed reactors, one of them being the FR and the other the AR. The OC particles are transported between the two reactors. In most cases this can be carried out in a circulating fluidized bed (CFB) setup having one riser reactor and one bubbling bed reactor, both of which are connected via the loop-seal devices avoiding the mixing of the feed gases. Although uniform temperature control can be achieved by adopting this configuration, potential fluidization and circulation challenges when using dense transition metal oxides have to be taken into consideration. Particularly, the particle separation is also difficult considering the required, extremely harsh reaction conditions (high pressure and elevated temperature) and the fact that even fines (resulting from inevitable particle attrition) need to be removed to protect the downstream gas turbine [26].

For the fixed-bed reactor configuration, solid OC particles are stationary and alternatively exposed to reducing and oxidizing conditions by periodically switching the feed gases. The main advantages of such reactor configuration are: i) intrinsically avoid the separation of gas and particles; ii) allow much more compact reactor design; iii) optimize the utilization of the OC material (i.e., a larger difference in the degree of oxidation between the reduced and oxidized forms of the OC can be retained). Disadvantages of this configuration include the necessity to use a high temperature, high flow gas switching system. A full scale power plant using this configuration would need a sophisticated system of valves for different feeds and outlet gases that might be a problem and also the pulsed operation for the gas turbines. Moreover, the heat transfer in a fixed-bed must be carefully analyzed, since this characteristic is very important for the process [27].

In the case of rotating reactor configuration, the looping material is rotated between different gas streams which flow radially outwards through the metal oxide bed. Between the two reacting streams, one inert gas is introduced to avoid mixing of the two reacting gases. The main challenge of this reactor configuration is to avoid gas mixing between fuel and air streams, which at the moment are unavoidable [25].

3. Partial oxidation of CH₄

Nowadays, industrial production of syngas from CH₄ is almost exclusively from the mature steam reforming of CH₄ (SRM) technology. However, SRM is an energy intensive process due to the endothermic nature of this reaction as well as the necessary downstream refinement required to yield a syngas ratio (H₂/CO) of 2, which is favored for the subsequent gas-to-liquid (GTL) processes [28,29]. As a promising alternative, catalytic partial oxidation of CH₄ (POM) has attracted great attention over the past decades [30–33]. Through a simple and one-step reaction, CH₄ can be directly converted with oxygen to produce syngas typically over a noble metal (such as Pt, Pd, Rh and Ru) based catalyst. Overall, POM offers several advantages over SRM: i) possess mild exothermicity, allowing for auto-thermal operation at temperatures exceeding 1000 °C; ii) avoid external heat supply which is unnecessary; iii) reduce the carbon footprint of traditional syngas production; iv) provide rapid reaction rates that allow the configuration of compact reactors with high space-time yields. Nevertheless, three issues have

been addressed which hamper the industrial implementation of POM, including: safety concern regarding the upper flammability limit for CH_4 and oxygen when both gas components are in close contact at elevated temperatures; the additional cost for air separation to produce undiluted syngas; and the use of expensive noble metal based materials.

Applying the CLC concept to POM enables an opportunity to resolve the first two issues by spatially separating CH_4 conversion into two half-steps, which absolutely avoids the direct contact between CH_4 and oxygen and intrinsically eliminate the presence of N_2 from the effluent. Fig. 2 displays the scheme for chemical-looping partial oxidation of methane (CL-POM) process.

Fig. 2 Schematic representation of CL-POM

During the CH₄ oxidation step in FR, depending on the nature of OC and the ratio of the available oxygen to carbon, the total oxidation, partial oxidation and pyrolysis of CH₄ can occur in sequence as the OC is progressively reduced. Meanwhile, the surface of OC would gradually become fuel-rich. In order to effectively utilize OC for selective POM, it is thus crucial to figure out the product spectrum at different stages of OC reduction. This is more important in a fixed-bed process, in which the gradient in the oxidation state of the OC along the bed axis can result in the onset of coking on the over-reduced OC at the bed inlet, while the OC in the other part of the bed remains only partially reduced [30].

The most studied non-noble metal catalyst for POM, nickel (Ni), is well-known for its high C-H scission activity, thereby achieving high CH₄ conversion [34–36]. However, Ni-based OCs are essentially unselective for POM. Even the presence of a relatively small amount of NiO can completely control the selectivity of the reaction and drive it toward the total oxidation of CH₄ [30].

In contrast to Ni, another extensively studied non-noble metal, iron (Fe), which has a series of oxidation states, can indeed be used quite efficiently in selectively converting CH₄ into different oxidation products. Bhavsar and Vaser [30] subjected 0.1 g Fe₂O₃-CeO₂ in a fixed-bed reactor for extended reduction with CH₄ (16.7 vol.%, 1 ml/min) at 900 °C. Fig. 3 shows the selectivity traces toward various products as a function of reduction of the OC, in which as indicated that 0% reduction refers to Fe₂O₃-CeO₂ whereas 100% reduction corresponds to Fe-CeO₂. Upon contacting fully oxidized Fe (Fe₂O₃) with CH₄, a large supply of oxygen or a high ratio of available oxygen to carbon allows the total oxidation of CH₄ to proceed with a high selectivity. Meanwhile, the first reduction stage of OC (Fe₂O₃ to Fe₃O₄) provides high selectivity toward CH₄ combustion. The second reduction stage of OC (Fe₃O₄ to FeO) behaves as a step-wise transition from the unselective total oxidation to the predominantly selective partial oxidation. Further reduction of OC (beyond FeO to metallic Fe) gives a broad plateau where partial oxidation to syngas with selectivity above 70% dominates. Virtually, identical selectivity for H₂ and CO which is normalized by the stoichiometric coefficient for POM suggests a H₂/CO ratio roughly maintained at 2. Since a quarter of the amount of oxygen (per mole of CH₄) is stoichiometrically required for POM in comparison to total oxidation, with gradual depletion of the oxygen reservoir of OC or decreasing ratio of available oxygen to carbon, the conversion of

CH₄ becomes more preferential toward syngas generation. Eventually, as the OC gets completely reduced, CH₄ pyrolysis becomes favored over the oxygen-free metal, being in accordance with the marginal increase in H₂ selectivity and the receding CO selectivity, as well as the occurrence and subsequently intensive rise of carbon deposition.

Total oxidation of CH₄:

Partial oxidation of CH₄:

CH₄ pyrolysis:

Fig. 3 Selectivity toward various reaction products as a function of reduction of 0.1 g Fe₂O₃-CeO₂ with CH₄ (16.7 vol.%, 1 ml/min) at 900 °C in a fixed-bed reactor [30].

Now that Fe shows high selectivity toward POM with poor CH₄ conversion, while Ni is unselective for producing syngas but has good CH₄ conversion, Bhavsar and Vesar [30] hypothesized that an appropriate combination of these two transition metals could help to

eliminate the two characteristics undesirable for efficient POM. The mixed $\text{Ni}_x\text{Fe}_{1-x}$ oxides with a broad range of compositions over CeO_2 support were synthesized, and their reactivity and selectivity for POM were evaluated by extended reduction of the OCs with CH_4 . It was found that a minor addition of Ni strongly enhanced the reactivity of Fe-based OCs at no distinct interference for the selectivity to syngas. However, a higher Ni loading above 12 wt.% significantly decreased the syngas selectivity, which could be rationalized by the presence of isolated Ni centers that can initiate rapid C-H bond breakage, while the surrounding Fe oxide surface catalyzes POM to produce syngas. With increasing Ni loading, sufficient amount of Ni oxide clusters can be formed within OC, which catalyzes the scission of C-H bonds and the occurrence of unselective oxidation of CH_4 on NiO, thereby resulting in a rapid and continuous drop in syngas selectivity.

4. Oxidation of oxygen carriers

Air is the most commonly used oxidant, since the replenishment of OCs using air is exothermic. The heat released from the reaction can be first utilized to compensate any heat duty from the reducer, and then the excess heat can be subjected to producing electricity and meeting the parasitic energy demand. However, the oxidation of OCs using air is generally carried out in a dilute bed regime, making the conversion of oxidant less important [6,7]. In addition to air, steam and CO_2 have been widely considered as oxidants although the oxidation kinetics of both steam and CO_2 are significantly slower than air [37].

4.1. Using steam as oxidant

Nowadays, most H_2 production in the United States is also driven by the mature SRM technology [38]. However, a large amount of heat input is required for the complicated H_2 purification. A novel two-step SRM configuration on the basis of CLC concept (CL-SRM) has been proposed and is shown in Fig. 4 [39–43].

Fig. 4 Conceptual scheme of CL-SRM

OC reduction with CH_4 in FR:

OC oxidization with steam in AR:

Overall reaction:

Although the overall reaction of CL-SRM as indicated above is identical to the traditional SRM (R4), CL-SRM spatially separates the feed of CH_4 and steam, thereby yielding a H_2 stream from AR without a need for purification while also producing syngas in FR with an appropriate ratio of 2 that is favored for GTL applications.

As previously mentioned, due to the low oxidation ability of steam in place of air, the reactivity of OC toward water splitting reaction (WSR) (R9) is a critical issue. Various metal

oxides such as Fe_3O_4 , WO_3 , SnO_2 , Ni-Fe, (Zn, Mn)-Fe, Cu-Fe and Ce-based oxides have been investigated as OC when using steam as the oxidizing agent [39]. Among these materials, Fe-based OCs were proved to be ideal for WSR. However, being thermodynamically constrained, H_2 evolution via WSR requires Fe phase to be as fully reduced as possible, while it is difficult for Fe phase to be completely oxidized beyond Fe_3O_4 by using steam [41].

4.2. Using CO_2 as oxidant

Since there is no proven technology for CO_2 sequestration with sufficient understanding of potential long-term impacts and effects, the use of CO_2 as the oxidant to replace air and steam seems to be an alternative pathway [37,44]. In this regard, chemical-looping dry (CO_2) reforming of CH_4 (CL-DRM), has been proposed as a new subset of CLC [37], and the configuration scheme of which is shown in Fig. 5.

Fig. 5 Conceptual scheme of CL-DRM

Traditional dry (CO_2) reforming of CH_4 (DRM) reaction is one of the substantially established routes in the effort to utilize CO_2 [45–47]. The main drawbacks that hinder the application of conventional DRM can be attributed to its strong endothermic nature and the

usage of expensive noble metal catalysts, as well as the concerns of catalyst deactivation due to carbon formation [44].

While the target of conventional DRM is high syngas yield, CL-DRM is optimized for CO₂ activation which results in fundamentally different stoichiometry. With an assumption of complete combustion of CH₄, the aim of CL-DRM is to maximally yield CO and no selectivity for H₂.

OC reduction with CH₄ in FR:

OC oxidation with CO₂ in AR:

Overall reaction:

One obvious challenge of this work stems from using CO₂ as the oxidant, which is well known for its fairly stable molecule structure and low free energy characteristic, leading to much slower oxidation kinetics when compared to air. Therefore, the ability of OC to maintain high activity toward the CO₂ splitting reaction (CSR) during extended redox cycles becomes the most critical issue. Najera et al. [37] evaluated the oxidation ability of various transition metals with CO₂ and found that Fe-based OCs possessed the highest OSC from CO₂ over a broad operating temperature range (700-1800 °C). However, Fe oxides tend to form dense oxide over-layers which could severely slow down the oxidation kinetics and limit accessibility of bulk Fe. In addition, high thermal stability and strong resistance to sintering is of great concern due to the elevated temperature conditions.

5. Development of oxygen carriers

The nature of solid OC is always a crucial matter in CLC applications [23]. Since CLC requires OC to be capable to undergo extended cyclic redox reactions with reproducible kinetics at elevated temperatures, materials only showing reactivity above or near their melting points should be eliminated. In addition to the reactivity of OC, its cost, toxicity, thermal stability and attrition resistance are also critical screening criteria. In the case of CLR, the reactivity of OC toward CH_4 is even more stringent, which includes not only the theoretical conversion that is dependent on the thermodynamic properties of material, but also fast reaction kinetics relying on factors such as composition, particle size, porosity, shape, structure and specific surface area. It is also widely accepted that the pore size of OC plays an important role in catalytic performance, as its special porous structure may enhance the OC reactivity over successive redox cycles especially when using steam and CO_2 as oxidants that result in much slower oxidation kinetics than air [37]. Meanwhile, the porous structure can accelerate the oxygen release from bulk to surface, leading to a good mobility of oxygen and higher reducibility of OC, and it is favorable for the diffusion of reactants, facilitating the reaction [40]. Another important factor is the reversibility of OC, which in detail is the number of cycles that OC can undergo without deactivation to convert fuel [48]. The deactivation of OC is generally caused by either carbon formation or particle agglomeration.

Among various transition metals, Ni, Cu, Fe, Mn and Co are feasible candidates to be used in CLC systems [49–51] although they possess some disadvantages: the low reactivity of Fe, Mn and Co; low melting points and high agglomeration for Cu; and toxicity concern for Ni. Fig. 6 shows the equilibrium constant K (logarithmic scale) versus $1/T$ plots for the reduction of the commonly used OCs with CH_4 being the reducing agent in FR, where a high $\log K$ value corresponds to high potential of metal oxide to react with CH_4 over a possible CLC operating temperature range (600–1200 °C). It can be observed that under the given conditions $\text{MnO}_2/\text{Mn}_2\text{O}_3$, $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$, $\text{Co}_3\text{O}_4/\text{CoO}$ and $\text{CuO}/\text{Cu}_2\text{O}$ have greater tendency to react with CH_4 as compared to $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ and NiO/Ni . Moreover, Mn- and Cu-based OCs have higher $\log K$ values at lower temperature, whereas higher $\log K$ values of Co-, Fe- and Ni-based OCs are more favored at elevated temperatures. However, at low temperatures, MnO_2 , Mn_2O_3 , Co_3O_4 and CuO may decompose into Mn_2O_3 , Mn_3O_4 , CoO and Cu_2O , respectively [8].

Fig. 6 The equilibrium constant K (logarithmic scale) versus $1/T$ plots for the reduction of common materials with CH_4 [8].

The carbon formation for CLR mainly originates from either CH_4 decomposition or CO disproportionation reactions. Ni-based OCs are the most systematically studied material as both reactions can be naturally catalyzed by metallic Ni. It was found that carbon formation on Ni-based OCs strongly depends on the availability of oxygen. In detail, the degree of carbon deposition on Ni-based OCs becomes more prominent at the end of the reduction period when more than 80% of the available oxygen is consumed [52]. Hence, carbon formation on Ni-based OCs speeds up as soon as the combustion of CH_4 is hindered due to the lack of available oxygen. A similar phenomenon was observed over Cu-based OCs with metal oxide conversions higher than 75%. In contrast to both Ni- and Cu-based OCs, Fe-based OCs have no or negligible carbon formation, even when the conversion of CH_4 is at a fairly low level.

The defluidization or agglomeration of particles is another significant problem that needs to be avoided in CLC with the configuration of two interconnected fluidized beds since it can cause solid circulation disturbances and channeling of the gas stream through the bed. Furthermore, the channeling could obstruct the contact between gas and looping particles, reducing the efficiency of reactant conversions [1]. It was found that the agglomeration can be

relieved by varying the combinations of metal content, type of support and preparation method. In the case of Ni-based OCs, particle sintering was absent when the reaction was carried out in the batch and continuous configurations even at 950 °C which is a typical CLC operation temperature [53,54]. The use of support for NiO such as Al₂O₃, NiAl₂O₄ and ZrO₂ in fluidized bed configuration also showed no tendency to sintering. For Mn-based OCs, the agglomeration occurred when using ZrO₂ as support modified with Ca, Mg and Ce in a batch fluidized bed [51]. Among the three supporting materials, MgO modified ZrO₂ showed no further indication of defluidization after 70 h successive operation. In addition to the supporting material, the agglomeration of Mn-based OCs can be affected by both the metal content and calcination temperature. When using Fe-based OCs, the defluidization may occur in the oxidation period after extended reduction operation, during which the hard agglomerates would generate as a result of deep reduction of Fe₃O₄ to FeO [18]. Hence, the conversion of OC would be inevitably suppressed by agglomeration along the course of successive CLC operation. In the situation for Cu-based OCs, the tendency to agglomeration presents to be fairly high due to the low melting temperature of Cu (1085 °C) [55]. It was found that the preparation of Cu-based OCs using common mechanical mixing and wet impregnation methods would result in poor dispersion of CuO over the support, inducing severe agglomeration. Therefore, the preparation methods of OC can have an impact on agglomeration as well. Some of the commercially feasible methods, in an increasing order of cost, are mechanical mixing, spray drying, impregnation, co-precipitation [1]. Although promising methods such as sol-gel synthesis and solution combustion can be applied to large-scale implementation, a large capital cost has to be taken into consideration [56].

5.1. Ni-based oxygen carriers

As mentioned earlier, Ni-based OCs are the most extensively studied material for CH₄ reforming [53,57–60] mainly on account of their high reactivity and stability at harsh operation temperatures (900–1100 °C). Although an almost complete CH₄ conversion is achievable over Ni-based OCs during the CLR process, their selectivity toward POM for syngas production is poor [10]. Furthermore, the high cost and toxic nature of Ni hinders its commercial application. Another major barrier for Ni-based OCs is the rapid catalyst deactivation caused by carbon deposition and metal sintering problems. The use of supporting material has been investigated as an approach to improve the stability of Ni-based OCs. Various materials such as La₂O₃ [61],

CeO₂ [31] and Al₂O₃ [22,34,62] have been extensively studied as they may affect the dispersion of NiO, thereby alleviating the sintering problem. Besides, the presence of support can give the OC surface the basic property that would be helpful in inhibiting the carbon deposition. Moreover, using various supports can affect the oxygen mobility and interaction with Ni to different degrees, both of which can have effects on the reducibility of OC and essentially catalytic behavior.

Indeed, in addition to the use of a specific support, the effect of preparation method cannot be neglected. Pantaleo et al. [31] prepared two series of 6 wt.% Ni catalysts supported by La₂O₃, CeO₂ and mixed CeO₂-La₂O₃ (50 wt.% Ce and 50 wt.% La) via co-precipitation and wet-impregnation methods. In the case of Ni/La₂O₃ prepared by either wet impregnation or co-precipitation procedure, the strong interaction between Ni and La could yield a variety of Ni-La mixed oxides ranging from LaNiO₃ to La₃Ni₁₂O₇. In contrast, when CeO₂ was used as support, the weak chemical interaction between Ni and Ce determined a procedure dependent surface distribution of Ni with a remarkably larger Ni/Ce atomic ratio for the impregnated sample than the precipitated one. Nevertheless, the co-precipitation of Ni and Ce ions was found to produce smaller NiO and CeO₂ crystallites which are favored for POM at lower reaction temperatures (rapid deactivation is expected over a long-term operation at 800 °C). As it is shown in Fig. 7, Ni/La₂O₃ prepared via wet impregnation exhibited higher activity than the co-precipitated one at lower temperatures. On the contrary, the co-precipitated Ni/CeO₂ possessed better activity than the impregnated one. It was then worthwhile to simultaneously use CeO₂ and La₂O₃ as the support for Ni. In such case, a stable phase Ce_xLa_{1-x}O_a was formed, in which Ce⁴⁺ was partially replaced with the trivalent La³⁺ ions. This phase could enhance the oxygen mobility of composite oxide material, which in detail favors the oxygen transfer to the supported Ni, facilitating the removal of surface carbon and meanwhile inhibiting the carbon formation.

Fig. 7 CH₄ conversion and selectivity to CO and CO₂ as a function of temperature in POM over Ni/La₂O₃, Ni/CeO₂-La₂O₃ and Ni/CeO₂ prepared via co-precipitation (CP) and wet impregnation (WI) [31].

NiO/Al₂O₃ exhibited excellent reactivity toward different gaseous fuels, negligible agglomeration problems, low attrition rates and strong resistance toward carbon deposition during CLC operation between the fluidized beds [63]. However, the reduction of NiO/Al₂O₃ is impeded by the partial transformation of NiO into a spinel compound, NiAl₂O₄, which has poor reactivity [62]. Although the formation of NiAl₂O₄ may be inhibited adopting mechanical mixing for OC preparation, the resulting OC material could have low crushing strength which is also an undesired property for CLC application. In this regard, excess NiO needs to be added and found as free NiO within the OC particles, giving it a high reactivity during continuous CLC operation. It was found that a 60 wt.% loading of free NiO over the Al₂O₃ (total Ni content present within the particle is up to 80 wt.%) would lead to the highest reactivity [64].

Alternatively, rather than allowing the formation of NiAl₂O₄, two modification approaches of the support, namely thermal treatment and chemical deactivation, show advantages in avoiding or minimizing the interaction of NiO with γ -Al₂O₃. In the case of thermal treatment at 1150 °C, γ -Al₂O₃ can be converted to α -Al₂O₃ via phase transformation. Although NiO/ α -Al₂O₃ prepared through impregnation method showed high reactivity, low attrition rates and negligible agglomeration, the formation of the NiAl₂O₄ phase cannot be completely avoided. It was also observed that the reactivity of OC as prepared was dependent on the reduction degree of OC in FR, which can be ascribed to the different contents of free NiO and NiAl₂O₄ present within the OC. The chemical deactivation approach is by definition to pre-coat the γ -Al₂O₃ support with other compounds such as MgO [22], CaO [65] and La₂O₃ [61] to increase its inert ability. The addition of MgO or CaO to Al₂O₃ could enhance the stability of support and is beneficial to the formation of a different spinel phase, MgAl₂O₄ [54] or CaAl₂O₄ [65]. Both phases were found to improve the reversibility of OC over extended redox cycles at elevated temperature conditions. The incorporation of La₂O₃ to Ni/ γ -Al₂O₃ was found to have an effect on the surface of OC so as to minimize the formation of NiAl₂O₄, and to some extent could inhibit the agglomeration of metal particles by maintaining consistent metal dispersion during the cyclic redox processes [61].

Other supporting materials such as ZrO₂, MgO, TiO₂, SiO₂, bentonite and sepiolite (Mg₄Si₆O₁₅(OH)₂·6H₂O) have also been investigated [1]. The ZrO₂ or Y₂O₃-stabilized ZrO₂ (YSZ) supported NiO showed good reactivity with poor mechanical strength. Comparably, lower

reactivity was found for NiO over bentonite as the support, especially at temperatures above 800 °C. Much slower reaction rates or absolute absence of reaction occurrence was observed when using TiO₂ or MgO as the inert material, which is due to the formation of stable phase, NiTiO₃ or Mg_{0.4}Ni_{0.6}O, except for those prepared via mechanical mixing and calcination at temperatures ranging from 1100 to 1200 °C. In addition, the use of SiO₂ and sepiolite as support for NiO gave low reactivity and weak mechanical strength, as well as the deactivation as a function of the number of cycles. Rydén et al. [66] investigated 40 wt.% NiO supported on 60 wt.% Mg-stabilized ZrO₂ prepared via freeze granulation and found that this OC possesses very high reactivity with CH₄ and low affinity for carbon formation.

5.2. Cu-based oxygen carriers

In general, Cu-based OCs demonstrate high OSC, excellent reactivity at low temperatures, the absence of carbon deposition and thermodynamic limitation for complete combustion of fuel. Moreover, Cu is much cheaper than other active transition metals such as Ni and Co, and more environmental friendly. Nevertheless, since Cu has a fairly low melting point (1085 °C), Cu-based OCs inevitably suffer from agglomeration during successive cyclic operation, especially when exposed to temperatures above 750 °C. The poor mechanical strength is another drawback of Cu-based OCs and was found to be dependent on the metal loading, sintering temperature and the option of supporting material [55,67–69]. In order to improve the thermal and mechanical stability of Cu-based OCs, their proper fluidization characteristics, and resistance to attrition and agglomeration, supporting materials such as Al₂O₃ [70], TiO₂ [69], ZrO₂ [42,67], SiO₂ [69] and MgAl₂O₄ [71,72] were investigated. In the case of using Al₂O₃, the facile interaction between CuO and Al₂O₃ may occur during the synthesis step and/or successive operation, causing a partial loss of CuO to form the spinel phases, CuAl₂O₄ and CuAlO₂. Fortunately, unlike NiAl₂O₄ spinel, the highly reducible property of CuAl₂O₄ and CuAlO₂ does not necessarily cause a problem in CLC application. It was also found that the formation of CuAl₂O₄ cross-linking CuO and γ -Al₂O₃ could contribute to the improvement of oxygen release performance and thermal stability under severe temperature conditions which are close to the melting point of Cu. With the introduction of La₂O₃ to CuO/Al₂O₃, the formation of CuAl₂O₄ would be facilitated, thereby further enhancing the reactivity of OC and its thermal stability [70].

5.3. Fe-based oxygen carriers

Fe-based OCs are considered as a promising candidate for CLC applications, mainly for the low tendency to carbon formation and strong resistance to agglomeration, both of which are the two important factors for maintaining the activity of OC over continuous redox cycles. In addition, Fe-based OCs take no risk of sulfide or sulfate formation in any sulfur-containing environment (i.e., gas concentration and operating temperature) [1]. The large natural reserves and cost effectiveness of Fe-based OCs also make them suitable for CLC implementation [73–75]. Nevertheless, Fe-based OCs have several drawbacks, which are the weak redox characteristics and relatively lower OSC, as well as the low reactivity toward gaseous fuels, especially for CH₄ [76].

As mentioned in section 3, Fe has multiple oxidation states including Fe₂O₃, Fe₃O₄, FeO and Fe. Limited to thermodynamic constraints, only the transformation from Fe₂O₃ to Fe₃O₄ is suitable for total oxidation of CH₄, while POM is more favored during the transition step from FeO to Fe [77].

The preparation methods reported for Fe-based OCs range from simple mechanical mixing to delicate freeze granulation. Other than these two methods, impregnation is also commonly used. In addition, the Fe₂O₃ loading is a critical factor which was tested over a broad range (20 to 100 wt.%). It was concluded that lower OSC is more favored when the content of Fe₂O₃ is above 60 wt.%; whereas, a small loading of Fe₂O₃ (10 wt.%) may not be suitable for CLC application due to the lack of physical strength which is required for solid circulation configuration.

Supporting materials such as Al₂O₃ [44,56,78], MgAl₂O₄ [79,80], SiO₂ [44], TiO₂ [16,81–83] and ZrO₂ [84] have been investigated for Fe-based OCs. When using Al₂O₃ or TiO₂ as the inert binder, FeAl₂O₄ or FeTiO₃ has a large tendency to be formed, respectively. Both FeAl₂O₄ and FeTiO₃ correspond to Fe²⁺ species that would assist in fully converting CH₄ into CO₂ and H₂O. Comparably, Fe₂O₃/Al₂O₃ has better CH₄ conversion than Fe₂O₃/TiO₂, which can be rationalized because Al₂O₃ provides more porous structure and higher surface area than TiO₂ [81]. Although the formation of FeAl₂O₄ may have a positive effect on the OSC property, it would slow down the reduction rate when Fe oxides are reduced beyond Fe₃O₄. It was found that the addition of Mg (the atomic ratio of Al to Mg equals 2) could successfully mitigate the

formation of FeAl_2O_4 [78]. In the case of SiO_2 as inert binder, the formation of unreactive Fe_2SiO_4 species and partial loss of core-shell structure could drastically decrease the OC selectivity toward syngas production [44]. MgAl_2O_4 is favorable for its high thermal and chemical stability as well as the specific heat capacity [85]. When MgAl_2O_4 is used to support Fe_2O_3 in the application of CLR, the activity and stability was found to have an increase over the redox cycles [80]. This increase in activity can be attributed to the increase in specific surface area that is caused by the formation of filamentous carbon species and the fragmentation of OC [79]. Since high redox activity is especially desired in CLR applications and meanwhile the physical degradation of OC is a detrimental factor, the choice of using Ce-, Ca- and Mg-stabilized ZrO_2 as support for Fe_2O_3 has been investigated and promising improvement on stability was observed [85].

Rare earth metal oxides such as CeO_2 have also been investigated as supporting material for Fe_2O_3 . CeO_2 has a fluorite structure, with each Ce^{4+} cation surrounded by eight equivalents, nearest O^{2-} that form the corners of a cube and coordinated to four Ce^{4+} ions. When the Ce^{4+} ions are replaced by lower valence cations, oxygen vacancies would be created. In addition, when two Ce^{4+} ions are replaced by trivalent ones, for instance, by two Ce^{3+} ions, an oxygen vacancy, or lattice defect, can be created which is considered to be the most reactive site. Both surface and bulk oxygen vacancies tend to form within CeO_2 and are suitable for adsorption purposes. The addition of CeO_2 was found to enhance the reducibility of Fe_2O_3 by taking the advantage of the Ce-Fe interaction [86]. The interaction can be established through the formation of cubic CeO_2 solid solution where Fe^{3+} cations dissolve in the ceria structure. Since Fe^{3+} cation (0.64 Å) and Ce^{4+} cation (1.01 Å) have different ionic sizes, any cationic substitution can result in the contraction of the unit cell and corresponding decrease in the lattice parameter [87]. The evolution of the Ce-Fe structure as a function of composition is shown in Fig. 8.

Fig. 8 Schematic illustration of the evolution of Ce-Fe structure as a function of composition [87].

Although the reduction reaction at the surface of $\text{CeO}_2\text{-Fe}_2\text{O}_3$ is independent of whether CeO_2 is present or not, after consuming the available surface oxygen for CH_4 oxidation use, the oxygen can be transferred from bulk to surface more rapidly over $\text{CeO}_2\text{-Fe}_2\text{O}_3$ than the one without CeO_2 modification. It was postulated that the CeO_2 additive could enable the creation of oxygen vacancies in a solid solution. These vacancies are able to transfer oxygen from the bulk of Fe_2O_3 quickly to the surface of OC through vacancy diffusion or even oxygen tunnels formed by vacancies. Therefore, the formation of Ce-Fe solid solution provides a prerequisite for these short-range interactions [23].

The enhanced reducibility through the interaction between Ce and Fe can thus improve the reactivity of Fe_2O_3 toward selective CH_4 oxidation. Fig. 9 shows the results of temperature-programmed reduction of CH_4 ($\text{CH}_4\text{-TPR}$) for $\text{Ce}_{1-x}\text{Fe}_x\text{O}_{2-\delta}$ with various compositions ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$ and 1) [39]. According to the profiles for both CeO_2 and Ce-Fe-O samples, the removal of the most reactive oxygen mainly occurred at lower temperatures, giving deep oxidation product of CO_2 ; while CO was the principle product at higher temperature conditions. Pure CeO_2 showed a high CH_4 oxidation activity at a lower temperature around 650°C due to the rapid consumption rate of surface lattice oxygen. In comparison to the profile of CeO_2 , $\text{Ce}_{0.9}\text{Fe}_{0.1}\text{O}_{2-\delta}$ showed a dramatic decrease in producing CO_2 but correspondingly an increase in CO selectivity, which is due to the depression of lattice oxygen activity. With the increasing content of Fe, the volumetric concentration of CO_2 and CO gradually increased until the Fe loading reached beyond 0.5 in the temperature range of $800\text{-}900^\circ\text{C}$. The Ce-Fe mixed oxides

with Fe content above 0.5 failed to increase the conversion of CH₄ and showed a decline in CO selectivity, which is due to the increasing amount of pure Fe giving deep oxidation products. Therefore, an equal weight loading of Fe and Ce can maximally promote the reactivity of the redox reactions [39].

Fig. 9 CH₄-TPR profile of Ce_{1-x}Fe_xO_{2-δ} oxygen carriers (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 1) [39].

A further reduction of $\text{Fe}_2\text{O}_3\text{-CeO}_2$ mixed oxides can be achieved by the introduction of Ni. In this case, the evolution of CO during the OC regeneration with CO_2 was estimated to be roughly 10 times higher than the OC that was free of Ni. It was also found that the reduction of NiO started from 327 °C and the interaction between Ni with Fe could lead to the formation of Ni_3Fe alloy above 527 °C. This Ni-Fe alloy remained stable during OC oxidation with CO_2 at 650 °C, above which the alloy could completely decompose into Ni and Fe_3O_4 . Moreover, the removal of the accumulated carbon on the surface of OC would give rise to a higher yield of CO, comparing to the theoretical CO generation over Ni/Ce-Fe material [88].

5.4. *Mn-based oxygen carriers*

Similar to Fe, Mn can also have several oxidation states [51]: MnO_2 , the highest oxidation state of Mn which can be used as OCs, tends to start decomposition in air at about 500 °C; Mn_2O_3 is thermodynamically stable in air at temperatures below 900 °C; and Mn_3O_4 is the only Mn species that shows its presence at temperatures above 800 °C. Hence, only the redox transformation between Mn_3O_4 and MnO is feasible for CLC applications. Some merits of Mn-based OCs which have been highlighted are their toxic-free nature, low cost and higher OSC.

The use of looping particles composed of only pure Mn oxides was found to possess low reactivity toward CH_4 . Inert materials for Mn-based OCs such as SiO_2 , TiO_2 , Al_2O_3 , ZrO_2 and MgAl_2O_4 were investigated only to find none of these are satisfying choices due to the formation of highly irreversible and unreactive phases [24]. Moreover, the use of sepiolite as support for Mn-based OCs showed low mechanical strength and thereby is not an appropriate option either. When using ZrO_2 as support, the composite OC showed good reactivity and stability over consecutive redox cycles. However, cracks were formed within the OC structure as a consequence of phase transformation between Mn species and ZrO_2 during thermal treatment and redox reaction [51]. The agglomeration of particles was also observed and most of the particles were found to stick to the reactor wall. In an effort to avoid these problems, MgO, CaO, or CeO_2 was introduced as the stabilizing agent for ZrO_2 . All the stabilized ZrO_2 support can not only increase the reactivity of Mn oxides, but also inhibit the structure-wise changes and particle agglomeration during cyclic operations. Furthermore, the redox response of $\text{CeO}_2\text{-ZrO}_2$ mixed

oxides is quite sensitive to the thermal aging conditions, being considered as a characteristic and challenging feature [89].

5.5. Co-based oxygen carriers

Although Co is relatively expensive and has environmental concerns, it can be considered as a good OC candidate owing to its high OSC [1]. During the redox operation, Co can have a few oxidation states, namely Co_3O_4 , CoO and Co, among which Co_3O_4 is unstable above 900 °C and easily converted into CoO. Regarding this, the phase transformation between CoO and Co should be taken into consideration and only a few works were conducted for Co-based OCs in the CLC applications. The commonly used supporting materials such as Al_2O_3 , TiO_2 and MgO suffer from a strong interaction with CoO forming unreactive compounds, CoAl_2O_4 , CoTiO_3 and $\text{Mg}_{0.4}\text{Co}_{0.6}\text{O}$, respectively. In contrast, good reactivity and low tendency to carbon deposition was found by using YSZ as support.

5.6. Mixed oxides as oxygen carriers

It is well accepted that complex metal oxides may sometimes have better properties than single ones. The main objectives desired from this viewpoint aim to increase the reactivity and stability of OC, improve the mechanical strength of particles, minimize carbon deposition and avoid using toxic and expensive ingredients.

Wang et al. [90] evaluated Fe_2O_3 -CuO supported on MgAl_2O_4 using coke oven gas (COG) as fuel in a thermo-gravimetric analyzer (TGA) and a laboratory pressurized CFB system. It was found that the agglomeration problem of Cu-based OCs was relieved, which could be attributed to the high melting point of both Fe_2O_3 and MgAl_2O_4 . The incorporation of Cu and Fe into a spinel structure was achieved by using different methods, and the resulting composites were also subjected to experiments over TGA and a batch fluidized-bed reactor. The best working spinel formulation was found to be $\text{Cu}_{0.95}\text{Fe}_{1.05}\text{AlO}_4$, which showed high OSC and oxidation rate but a relatively low reduction rate. The addition of NiO could further increase the OSC and give a rise in the reactivity. Lee et al. [42] used YSZ supported Cu-Fe mixed oxides for H_2 and syngas production via stepwise CH_4 reforming and WSR processes. Co-precipitation and impregnation were used in this case. When using Cu-Fe/YSZ prepared through impregnation, CH_4 conversion

retained at a high level of 85% while the H_2/CO ratio was maintained close to 2. Contrarily, Cu-Fe/YSZ prepared via co-precipitation possessed a lower CH_4 conversion of 30%. Moreover, negligible carbon deposition and aggregation of Cu-Fe/YSZ prepared by impregnation was detected over a 10-cycle operation.

Materials containing Ni and Fe with a spinel structure were tested using a TGA apparatus simulating the oxidation and reduction periods in CLC [91]. It was found that the presence of NiO increased both the OSC and reactivity of the resulting OC. Furthermore, the effect of Ni addition over a Fe-based OC was evaluated and compared using two different strategies: the chemical and physical mixing. In the case of chemically mixed Fe-Ni OC, negative effect on the combustion efficiency for CH_4 was observed compared to the results obtained with the unmixed Fe-based OC, which can be ascribed to the reduced catalytic effect of Ni addition by the formation of Fe-Ni compounds [92]. In contrast, the physically mixed Fe-Ni OC with 2 wt.% NiO addition significantly improved the combustion efficiency at low temperatures.

The thermodynamic constraints for Mn-based OCs regarding oxygen release could be overcome by incorporating Mn with other active and/or inert materials, producing Mn-containing spinels with thermodynamic properties dissimilar to pure oxides [93–95]. The ternary system of Mn-Fe-O compound has an exceptionally interesting property, namely the capability to release considerable amounts of gas phase oxygen during the reaction. Rydén et al. [96] synthesized a range of different materials including $(Mn_yFe_{1-y})O_x$, $(Mn_ySi_{1-y})O_x$, $CaMnO_{3-\delta}$, $(Ni_yMn_{1-y})O_x$, $(Mn_yCu_{1-y})O_x$ and $(Mn_yMg_{1-y})O_x$, among which $(Mn_{0.8}Fe_{0.2})O_x$ showed the highest oxygen releasing rate at 850 °C (0.001 kg/s oxygen per kg OC). Azimi et al. [97] prepared Mn-Fe composite (Mn:Fe molar ratio of 3) together with $MgAl_2O_4$, CeO_2 , ZrO_2 and $Y_2O_3-ZrO_2$ as support for the feasibility investigation of chemical-looping oxygen uncoupling (CLOU). With the exception of the material binded with $MgAl_2O_4$, the oxygen uncoupling or oxygen transfer properties of the active combined oxides was largely kept intact using the added supporting materials. In addition, the combined oxide supported by ZrO_2 showed poor resistance to attrition and fragmentation after calcination at 950 °C.

Fan and Siriwardane [50] synthesized Group II metal ferrites ($MgFe_2O_4$, $CaFe_2O_4$, $SrFe_2O_4$ and $BaFe_2O_4$) and transition-metal ferrites ($NiFe_2O_4$, $CuFe_2O_4$, $MnFeO_3$ and $CoFe_2O_4$) by both the microwave precipitation method and the direct decomposition method and evaluated

their catalytic performance for coal-based CLC application. It was found that Group II metal ferrites showed better reduction and oxidation rates than Fe_2O_3 . Among all the novel metal ferrites, BaFe_2O_4 showed the highest reduction and oxidation rates; its reduction rate is comparable to CuO but can be operated at higher temperatures up to $1000\text{ }^\circ\text{C}$ without agglomeration. Moreover, BaFe_2O_4 had stable reduction rates and improved oxidation rates along the course of cyclic operation.

Although YSZ supported Co-Ni oxides showed slightly lower reduction and oxidation reaction rates than the unsupported one, which could be due to the formation of solid solution NiCoO_2 , the bimetallic oxides exhibited higher catalytic performance including good reactivity, complete avoidance of carbon deposition and promising regenerability [98]. It was found that the addition of Co could inhibit the agglomeration of particles and also enhance the reducibility of OC by the abatement of the formation of NiAl_2O_4 .

The incorporation of NiO to the $\text{CuO}/\text{Al}_2\text{O}_3$ can stabilize the CuO phase [99]. In contrast, K or La modified Cu-Ni oxides did not show any improvement on the catalytic performance for CLC. The $\gamma\text{-Al}_2\text{O}_3$ supported Cu-Ni oxides (13 wt.% CuO and 3 wt.% NiO) showed complete CH_4 oxidation and retained low attrition rate over 67 h operation at high temperature conditions ($900\text{ }^\circ\text{C}$ for FR and $950\text{ }^\circ\text{C}$ for AR).

Mungse et al. [100] prepared Cu-Mn oxide by co-precipitation, the resulting material of which was mainly composed of CuMn_2O_4 . This composite OC was proved to show high activity toward CH_4 combustion. In general, CuMn_2O_4 can be partially reduced to Mn_3O_4 and Cu_2O during the intermediate stages and further reduced to MnO and metallic Cu upon complete removal of reactive oxygen. As the number of redox cycles increased, the combustion efficiency of CH_4 remained unchanged and no distinct alteration in OSC was observed.

5.7. Perovskites as oxygen carriers

POM using lattice oxygen in place of gas phase oxygen offers an alternative method for syngas production, which can eliminate the air separation process and show prominent selectivity to syngas [101–103]. Other than mixed oxides with spinel structure, perovskite-type mixed oxides composed of transition metals can serve not only as lattice oxygen carriers but also catalysts for CH_4 activation [96]. As ceramic materials with well-defined structure and high

thermal stability, the ABO_3 perovskite-type complex oxides have been widely studied in some applied and fundamental areas of solid state chemistry, catalysis, advanced materials and physics [105]. While the A cation is responsible for the thermal resistance, the catalytic activity is given by the high valence cations at the B-site which is in most cases occupied with transition metals. As a consequence, the choice of B-site cations is a deterministic step for the design of perovskites and modification of their catalytic properties. In addition, both A and B cations can influence the stability of the perovskite structure as well as the reactivity and selectivity of lattice oxygen during the oxidation of CH_4 . Taking the advantage of the special structure of perovskite, the phase transformation can be avoided at typical CLC operation temperatures.

Among various perovskite materials, LaFeO_3 appears to be attractive OC candidate mainly for its high oxygen mobility in the bulk and the capability of hosting large concentrations of vacancies in the structure at elevated reaction temperatures [105–108]. Being dependent on the operation temperature conditions, the removal of oxygen and the total amount of oxygen available for CH_4 oxidation could lead to a reduction of LaFeO_3 from Fe^{3+} to Fe^{2+} , but further reduction seems to be inhibited. A kinetic study with respect to the removal of oxygen from LaFeO_3 reduction by CH_4 disclosed a step-wise kinetic control intimately relevant to the availability of surface oxygen and vacancy site. Initially, the removal of oxygen generates vacancy sites on the surface, which would help to facilitate the progressing of reaction. Subsequently, as the concentration of vacancy sites increases, the oxygen availability becomes a rate-determining step. The maximum reaction rate for LaFeO_3 was found to be at about half of the total amount of removable oxygen [105].

In addition, partial substitution of La^{3+} by Sr^{2+} causes electronic imbalance but can be compensated by the oxidation of a fraction of Fe^{3+} to Fe^{4+} and/or generation of oxygen vacancies in the perovskite lattice [107,108]. A highly variable oxygen nonstoichiometry in the perovskite structure would therefore be achieved that would easily provide removable oxygen, and the removed oxygen species can be subsequently replenished by gaseous oxygen. He et al. [108] prepared $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ perovskite-type oxides ($x = 0.1, 0.3, 0.5$ and 0.9) by combustion method. The activity of the substituted perovskites was found to show a decline as the degree of substitution x increased above 0.5 , which could be due to the inhibition of CH_4 decomposition by the Sr substitution. A maximum H_2 yield during the reduction step was obtained with

$\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ [109]. An addition of 5 wt.% NiO, by simple mechanical mixing to $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ would substantially increase reactivity to CH_4 decomposition, selectivity to syngas, and the activity to WSR for oxygen replenishment. In this case, H_2 yield up to 80% of the theoretical expectation, on the basis of complete CH_4 decomposition, can be obtained.

Further optimization with respect to the catalytic performance can be achieved by partial substitution of catalytically active B sites by aliovalent transition metal cations. This can lead to enhanced catalytic activity due to synergistic valence changes and resultant nonstoichiometric related microstructural defects into the lattice. Lori et al. [107] prepared perovskite material with the formula $\text{La}_{1-x}\text{Sr}_x\text{M}_y\text{Fe}_{1-y}\text{O}_3$ ($\text{M} = \text{Ni}, \text{Co}, \text{Cr}$ and Cu) as OC for syngas production from CLR. All the composite materials were found to be suitable for such application. The best performance, thus far, was observed over $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.05}\text{Fe}_{0.95}\text{O}_3$ mixed with 5 wt.% NiO. This perovskite material showed a H_2 yield of 90% and possessed good stability during redox operation.

Nevertheless, in reference to the demonstration of CLR application, the reduction rate of perovskite materials is in general much slower than the re-oxidation rate of the reduced perovskites. Hence, future tasks need to be focused on increasing the reduction rate of perovskites in the step of POM. Moreover, a detailed understanding of the relationship between the surface properties of the perovskites and the catalytic performance in the continuous fluidized-bed reactor configuration still needs to be explored.

Summary

CLR is a very promising technology for power plants and industrial applications with CO_2 capture. Its advantage over other competing approaches lies in the inherent CO_2 capture which avoids the energetic penalty of this process. When using CH_4 as fuel for CLR, the process can be spatially separated into two half-steps: CH_4 oxidation in FR and OC regeneration in AR. During the step of CH_4 oxidation, the selectivity of OC toward POM for syngas generation is a critical screening criterion for OC. Moreover, using steam or CO_2 to replace commonly used air for the replenishment of OC can offer the opportunities to produce extra H_2 or CO. Nevertheless, the significantly lower oxidation ability of steam and CO_2 compared to air strongly requires OC to possess higher reactivity to WSR and CSR. Among various transition metals, Ni, Cu, Fe, Mn and Co were found to be feasible OC candidates for application of CLC systems. Owing to their

different nature, approaches have been investigated to improve reactivity and resistance to attrition, agglomeration and carbon deposition, which are intimately relevant to the composition, particle size, porosity, shape, structure and specific surface area. The use of Al_2O_3 as inert binder can form spinel compound cross-linking the transition metal oxide and Al_2O_3 . It was found that in some situations the spinel compound may induce problems such as particle sintering, weak mechanical strength and reduced activity. Other than mixed oxides with spinel structure, perovskite-type materials utilizing lattice oxygen for syngas production showed prominent results. Beneficial to the unique structure of perovskite, the phase transformation can be avoided under the harsh operation conditions. The most investigated perovskite is LaFeO_3 , mainly for its high oxygen mobility in the bulk and the capability of hosting large concentrations of vacancies in the structure at elevated reaction temperatures. Further optimization was made to improve the H_2 yield and stability of LaFeO_3 by the partial substitution of La by Sr and Fe by aliovalent transition metal cations, as well as the addition of NiO . Nevertheless, the slower re-oxidation rate of perovskites needs to be taken into consideration and the relationship between their surface properties and catalytic behavior remains to be discovered.

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Graphical abstract