Chemical Science



REVIEW

View Article Online
View Journal | View Issue



Cite this: Chem. Sci., 2025, 16, 4971

Metal ferrite derivative chemical looping systems: a review towards a multiscale approach for technology readiness enabling clean energy conversion and carbon neutrality

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Chemical looping technologies offer a promising pathway for clean energy production, addressing the urgent need for decarbonization in light of escalating global energy demands and climate change concerns. This review explores the metal ferrite oxygen carriers in chemical looping applications, emphasizing their versatility in handling diverse feedstocks—from gases like methane to solids like plastics—and their robust performance in terms of stability and efficiency. The ferrite derivative chemical looping reactions involve the transfer of lattice oxygen from the metal ferrites to the fuel, enhancing fuel conversion without direct emission of pollutants. The structural and functional advantages of ferrites, including their ability to regenerate and sustain repeated redox cycles, are highlighted. Innovations in ferrite-based chemical looping, from small-scale laboratory setups to pilot-scale installations, demonstrate significant advancements in achieving high energy—exergy efficiencies with minimal ecological impact. The review also identifies ongoing challenges, such as the stability and effectiveness of metal ferrite oxygen carriers, suggesting improvements through material engineering and process optimization. This work aims to deepen understanding of ferrite oxygen carriers and propel forward their application in scalable, commercially viable clean energy solutions.

Received 31st August 2024 Accepted 25th February 2025

DOI: 10.1039/d4sc05865h

rsc.li/chemical-science

1 Introduction

The unprecedented increase in energy demand coupled with a growing concern for climate change has created an impetus for clean energy production.1 Although a great emphasis is observed on harnessing energy from renewable sources, the U.S. Energy Information Administration has projected that more than 50% of the world's energy demand will be dependent upon fossil-based energy sources by 2050.2 The growing industrial sector consumes \sim 33% of the total energy produced in the U.S., which amounts to nearly 26.7 quadrillion British thermal units (BTU).3 The production of commodity chemicals like syngas, hydrogen (H2), methanol (CH3OH), ethanol (C₂H₅OH), ammonia (NH₃), etc., via state-of-the-art technologies like auto-thermal reforming (ATR), steam methane reforming (SMR), Haber–Bosch process, etc. consumes \sim 35% of total industrial energy.4 Although these technologies have been established for decades and have proven to be economical at larger scales of operation, they are challenged by carbon deposition and poor catalyst stability, leading to the formation of undesirable side products.¹ This results in huge capital investment and high operating costs to comply with environmental protection policies. International treaties like the Paris Agreement aim to limit atmospheric CO₂ concentration below 430 ppm by 2030, necessitating the de-carbonization of industrial processes.⁵,6

Chemical looping (CL) is an emerging versatile alternative to produce commodity chemicals with inherent emission control.7-10 This technology involves splitting the reaction scheme into a series of steps, facilitating complete fuel conversion, inherent product separation, and higher energyexergy efficiencies. 11-15 Splitting of the reaction scheme is facilitated by a metal oxide carrier circulating within interconnected reactors and undergoing subsequent reduction and regeneration cycles.16,17 During the reduction reaction, the metal oxide carrier donates its lattice oxygen to the fuel, resulting in the complete conversion of the fuel to the desired products (carbon dioxide - CO₂, steam - H₂O, or carbon monoxide - CO, H₂). This lattice oxygen is then replenished using oxidizing gases like air, steam, or CO2, thus completing the redox loop. The overall reaction scheme remains the same as combustion or reforming.18,19

Breaking down the reaction scheme in this manner enables the isolation of the pure products without the need for

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a separation unit after the reactor.²⁰ While breaking the reaction into several steps helps to optimize each individual step to obtain near thermodynamic yields, the absence of direct contact of fuel and oxidizing gases at high temperatures mitigates the formation of pollutants like dioxins and nitrous oxides (NO_r).²¹⁻²³ The high-grade heat produced during the regeneration step can cater to the low-grade heat requirement in the reducer reactor, thus eliminating any external heat requirement.²³ Moreover, advancements in efficient heating solutions offering near-unity conversion of renewable energy to heat negate the possible hindrance to the implementation of CL technologies requiring additional thermal input.24

The choice of the metal oxide carrier plays a pivotal role in determining the technical feasibility and the economic viability of this technology. 5,25 Transition metal oxides are highly favored for the CL process due to the high number of valence shell electrons, which facilitate ionic diffusion, providing a large number of active sites and correspondingly high reactivity.26 Several transition metal oxides, including but not limited to nickel oxide (NiO), copper oxide (CuO), iron oxide (Fe₂O₃), chromium oxide (Cr₂O₃), vanadium oxide (V₂O₅), manganese oxide (Mn₂O₃), cobalt oxide (Co₃O₄), ceria (CeO₂), etc., have been tested as probable candidates for the different CL schemes.27-35 Iron-based oxygen carriers (OC) have garnered increased attention due to their favorable thermodynamics towards many CL applications, environmentally friendly nature, abundance, and low cost.28 However, iron oxide faces several drawbacks, such as poor cyclic stability, poor kinetics, and high sintering.30,36,37 In order to eliminate the challenges associated with iron oxide carriers, additional active metal oxides, dopants, promoters, binders, and inert supports are incorporated, creating a class of OC that can be classified as ferrite-based

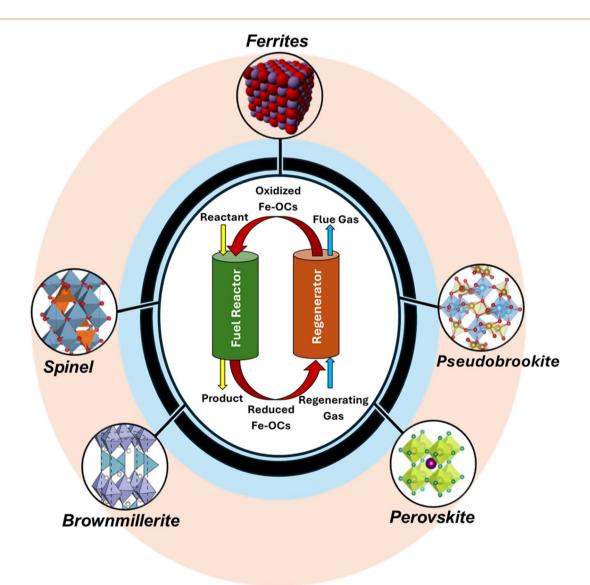


Fig. 1 Prominence of metal ferrite derivatives in chemical looping. Brownmillerite structure adapted with permission from ref. 39. Copyright 2009 Springer Nature. Pseudobrookite structure adapted with permission from ref. 40. Copyright 2023 Elsevier. Perovskite structure adapted from a 2022 article published by MDPI (ref. 41) under a Creative Commons (CC BY) License. Spinel structure adapted from a 2020 article published by Springer Nature (ref. 42) under a Creative Commons Attribution 4.0 International (CC BY 4.0) License.

oxygen carriers (Fe-OC).³⁸ As illustrated in Fig. 1, the development of various Fe-OC composites with different crystal structures like spinel, brownmillerite, perovskite, and pseudobrookite has been of central importance to various CL applications.

Fe-OCs have demonstrated thermodynamic superiority, capacity to handle versatile feedstocks ranging from gases like methane (CH₄) to solids like waste plastics, stable cyclic performance for an extended period of operation, and have proven to be suitable for several CL applications, including chemical looping combustion (CLC), gasification (CLG), partial oxidation (CLPO), reforming (CLR), and hydrogen generation (CLHG).43-54 The commercialization potential of the CL technology has been realized through successful demonstrations at bench-scale, sub-pilot scale, and pilot-scale testing using Fe-OCs. These developments highlight the multiscale approach for implementing Fe-OC for multiphase reaction engineering.⁵⁵ While the superiority of Fe-OC has been established for a long time, a comprehensive review for understanding the role of each component incorporated in various ferrites is missing in the literature. This insight is crucial to achieving harmony between the chemical and physical properties of the OC and fine-tuning the OC composition for specific commercial applications. This review aims to understand the influence of different components on thermodynamics, the underlying mechanisms, the overall performance of ferrite OCs, and the feasibility of specific CL applications. This knowledge would be critical in tailoring and optimizing the OC composition, which is essential for the economic viability of the commercial process.

2 Fundamental insights into Fe-OC for performance enhancement

Understanding the fundamentals of ferrites as versatile OC is vital for their applications in CL systems. This section provides an in-depth exploration of the key fundamental aspects of Fe-OCs, focusing on how ionic diffusion influences its morphology, volume expansion, and structural integrity. It also examines the role of oxygen vacancies in enhancing lattice oxygen transport and overall reactivity. Additionally, the formation of core–shell structures and their advantages for improving stability and preventing sintering are discussed.

2.1. Role of ionic diffusion in Fe-OC

The morphology of Fe-OC is pivotal in influencing its surface area, reaction kinetics, and structural integrity, thereby directly affecting its overall performance. It is closely tied to ionic diffusion and changes in molar volume. The ionic diffusion during Fe-OC oxidation results in a net outward transport of Fe ions from the core to the surface, where they are oxidized to form Fe_2O_3 . This results in an inward progressing Fe_2O_3 layer, leading to the complete oxidation of Fe-OC particle. Simultaneously, the oxidation reaction leads to volume expansion of Fe-OC, as observed from macroscopic studies on Fe-Ti OC by Li et al. and microscopic investigations on Fe_2O_3 OC by Cheng

et al. 56,57 The volume increases from 31.7 to 54.4 cm³ mol⁻¹ in the case of FeTiO₃ converting to Fe₂TiO₅ and from 7.1 to 30.5 cm³ mol⁻¹ in the case of Fe converting to Fe₂O₃, both of which exhibit larger volume changes compared to many other transition metal oxides like NiO and CuO investigated in the literature. 57 The high molar volumes of Fe-OC enhance the transport of Fe ions from the core to the surface and provide greater surface area for redox reactions, making Fe-OCs an attractive choice for CL applications. 58 Therefore, understanding these ionic diffusion processes and the resulting changes in molar volume is essential for predicting and controlling the morphological transformations that occur during the reduction and oxidation cycles of Fe-OCs.

The performance and macroscopic behavior of metal oxides are heavily influenced by their nanoscale morphology, which is shaped by solid-state ionic diffusion. This morphology can vary significantly from single-metal systems to bimetallic ones. Lang et al. discuss the evolution of nanoscale morphology in such contexts. During the oxidation of Fe particles, the growth of nanostructures, such as nanowires and nanopores, depends significantly on the surface curvature of the grains. This process is governed by a stress-driven mass transport mechanism, where the curvature of Fe2O3 grains determines the type of nanostructure that forms. Positive surface curvature leads to the outward diffusion of Fe atoms, resulting in perpendicular nanowire growth, while negative surface curvature promotes oxide growth, leading to the formation of nanopores within the grain, as shown in Fig. 2(a) and (b), respectively.58 Lang et al. further extended the scope of their research to include bimetallic Fe-Ti particles. The difference in the diffusion rate of Fe ions compared to Ti ions resulted in the formation of nanobelts on the surface. Repeated redox cycles make these structures highly porous with improved morphological stability, as depicted in Fig. 2(c).59 These studies highlight the critical role of ionic diffusion in the design and performance of Fe-OCs.

2.2. Effect of oxygen vacancy in Fe-OCs

During the reduction step of CL applications, the lattice oxygen from the Fe-OC, whether from the surface or bulk, is transferred to the hydrocarbon fuel, resulting in partial, selective, or complete oxidation. This process leads to phase transition and creates oxygen vacancies on the Fe-OC, which can significantly alter its morphology, chemical properties, and electronic structures. It also facilitates the transport of lattice O atoms from the bulk of the Fe-OC to the surface. Cheng et al. conducted DFT simulations to study the effect of oxygen vacancy on CH₄ combustion using Fe₂O₃ as an OC. They stated that the presence of oxygen vacancies significantly increases the CH₄ activation on the Fe-OC by lowering the dissociation barrier for the C-H bond of the CH₄ molecule.⁶⁰ During the oxidation reaction of Fe-OC in the absence of oxygen vacancies, the interstitial diffusion energy barrier for O moving inward is higher than the outward diffusion energy barrier of Fe, as shown in Fig. 3(a). This leads to a rapid formation of a Fe₂O₃ layer on the outer surface of the Fe-OC particle due to the reaction between outward diffusing Fe ions and oxidant.

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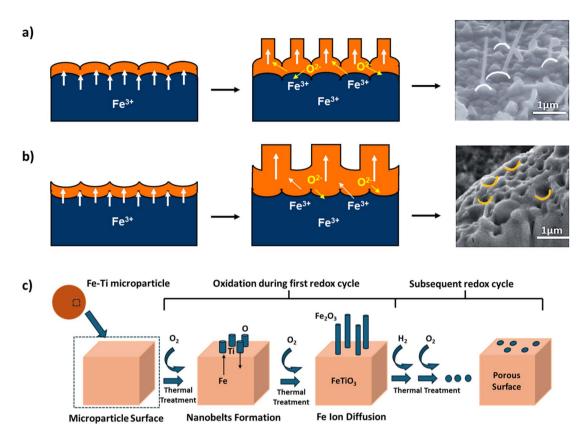


Fig. 2 Nanoscale morphological transformations showing growth mechanisms for (a) nanowires, (b) nanopores of ferrite material, and (c) iron oxide nanobelt formation in Fe–Ti composite. White curves in (a) indicate a positive curvature, while yellow curves in part (b) highlight the negative curvature on the surface. (a) and (b) Adapted with permission from ref. 58. Copyright 2014 Royal Society of Chemistry. (c) Adapted with permission from ref. 59. Copyright 2015 Royal Society of Chemistry.

However, the high energy barrier for O diffusion decreases the rate of oxidation within the particle bulk. In the presence of oxygen vacancies, the inward diffusion barrier of O is reduced. It is slightly lower than the outward diffusion barrier for Fe, as observed from Fig. 3(b), thus facilitating the formation of iron oxide product at the $\rm Fe_2O_3$ –Fe interface. This results in a rapidly progressing $\rm Fe_2O_3$ layer towards the center of the Fe-OC, enabling faster reaction rates for complete oxidation.⁵⁷

Numerous atomistic studies on Fe-OCs have explored how dopants and support modifications can lower oxygen vacancy formation energy ($\Delta E_{\rm vac}$) to enhance lattice oxygen transport and redox activity. Modifying Fe₂O₃ with TiO₂ support decreases $\Delta E_{\rm vac}$, enhancing the oxygen atom diffusion and substantially increasing the recyclability of the Fe-Ti composite OC.60 The addition of 5% Ni dopant to $Ca_2Fe_2O_5$ lowers ΔE_{vac} by 58%, resulting in a substantial improvement of nearly 1149% in the Fe-OC's redox activity.61 In another study, it was observed that doping Fe₂O₃ with 1% Cu and 2% Co reduces ΔE_{vac} by 29% and 31%, respectively. 62,63 Composite Fe-OCs have also been utilized in CLC applications. For example, adding CeO2 to Fe2O3 OC significantly reduces $\Delta E_{\rm vac}$ from 9.56 eV (in pure Fe₂O₃) to 3.95 eV (in the CeO₂/Fe₂O₃ composite OC). This facilitated the increase in the formation of surface oxygen vacancies, improving the composite material's performance compared to pure Fe₂O₃.64

2.3. Structural design for enhanced Fe-OC performance

The reactivity and stability of Fe-OCs can be significantly enhanced by modifying their structural design, with core-shell structures showing promise in CL applications. Core-shell structures often form during redox cycles through solid-solid reactions between the active material and an inert support. During these cycles, cations diffuse outward, transporting the active material from the core to the surface, forming a protective shell around the core. The sol-gel method is one of the major preparation techniques that enable the synthesis of core-shell OCs with controlled composition and structure, making them well-suited for CL applications.⁶⁵⁻⁶⁷

Core–shell structures often outperform homogeneous composite materials. Ma *et al.* found that Fe₂O₃@CeO₂ coreshell OC exhibited significantly higher redox reactivity and stability compared to Fe₂O₃/CeO₂ homogeneous composite FeOC in CLHG applications. This improvement was due to the core–shell structure's strong resistance to sintering, which prevents Fe cations from migrating to the particle surface, thus maintaining the OC's stability and performance. In contrast, the homogeneous composite OC suffers from significant sintering, with Fe cations accumulating on the surface, leading to reduced performance.⁶⁸ The careful design of both core and shell materials is essential for superior CL performance.

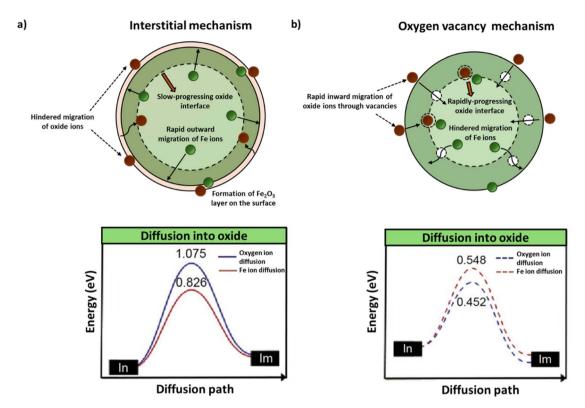


Fig. 3 Ionic diffusion and corresponding activation energy diagram for Fe₂O₃ OC under (a) interstitial mechanism. (b) Vacancy mechanism. Green and white spheres indicate Fe ions and oxide ions, respectively, while white spheres depict oxygen vacancies. Energy diagrams adapted from a 2018 article published by Elsevier (ref. 57) under a CC BY-NC-ND 4.0 License.

Blaschke et al. studied the impact of shell composition on the performance of OCs by using Fe₂O₃ as the core and preparing two samples with different shell compositions: yttriumstabilized zirconium oxide with 8 mol% Y2O3 (YSZ8-CS) and yttria-stabilized zirconium oxide with over 10 mol% Y₂O₃ (YSZ10-CS). The ratio of weights of Fe₂O₃ and the support YSZ was kept constant. Both samples show increased pore volume during redox cycles, but YSZ10-CS develops poorly connected pores, reducing effective porosity and leading to sintering and agglomeration. In contrast, YSZ8-CS maintains a stable pore structure, avoiding "ink bottle" pores that trap gases, thereby preserving its effectiveness and overall performance.⁶⁹ Yin et al. investigated Fe₂O₃ nanocores covered with a CeO₂ shell. This configuration combined the superior ion conductivity of CeO₂ with the high oxygen storage capacity of Fe₂O₃. The resulting Fe-Ce core-shell OC was highly influential in selectively providing oxygen from the CeO2 shell, which improved selectivity towards syngas production and enhanced CH₄ conversion.70

Prominence of Fe-OCs in CL processes

Understanding the fundamental properties of the materials and their impact on the performance of the OC provides a strong foundation for exploring the Fe-OCs for various CL applications for carbon neutrality and clean energy production. The choice

of active component greatly dominates the feasibility of the CL process. This section dwells on the thermodynamic feasibility, experimental evaluation, and scale-up studies of Fe-OCs for different CL applications.

3.1. Thermodynamic feasibility of oxygen release and uptake by Fe-OC

Fe-OCs have enabled the application of CL technology to produce a wide range of commodity chemicals. However, the thermodynamics of the Fe-OC during the oxidation and reduction reactions dictate the feasibility of the desired CL application. CLC, CLPO, and CLHG are the prominently pursued CL applications in the literature for achieving clean and sustainable energy production.

Thermodynamic feasibility is influenced by several factors, including fuel conversion, CO2 purity, syngas purity, and product selectivity. In a commercial-scale CL process, oxygen carriers must favor complete thermodynamic fuel conversion while maintaining high selectivity toward the target product. Additionally, the kinetic activity of Fe-OCs should facilitate fuel conversion and product selectivity approaching thermodynamic limits. With the increasing emphasis on renewable feedstocks such as biomass, these properties become even more critical for achieving complete tar cracking and ensuring high product yields. The study of the Ellingham diagram presents a useful approach for determining the viability of the Fe-OC for a given CL process by evaluating the oxidation potential of the carrier.

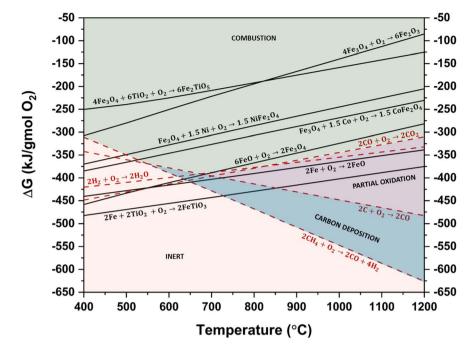


Fig. 4 Ellingham diagram for various metal ferrite OCs.

Fig. 4 illustrates the Ellingham diagram for some prominent FeOCs. The free energy of oxidation of the reduced counterparts of the Fe-OCs indicates the thermodynamic feasibility of Fe₂TiO₅, NiFe₂O₄, CoFe₂O₄, Fe₂O₃, and Fe₃O₄ for CLC application, while FeO and FeTiO₃ can establish equilibrium with syngas during CLPO application.^{43,71,72} While this theoretical assessment indicates if a particular process is thermodynamically favored, an experimental examination is necessary to assess the kinetics and oxygen transport capacity (OTC) of the Fe-OC material. Therefore, the experimental evaluations are studied in Section 3.2 to investigate the practical application of Fe-OC for CL processes.

3.2. Experimental evaluation of Fe-OC for diverse CL processes

In order to enable complete carbon capture during the CLC process, it is essential to utilize materials with high oxygen transport capacity, similar to Fe₂O₃, which has a theoretical OTC of 30.06%. As observed in Section 3.1, Fe-OCs, such as CoFe₂O₄, exhibit a high oxidation potential and demonstrate a high theoretical OTC of 27.28%. With the OTC being similar to Fe₂O₃ and thermodynamics favoring complete combustion, CoFe₂O₄ has been extensively examined for CLC application. Evaluation conducted by Fan and co-workers to synthesize OC with high OTC using Cu, Fe, and Mn as constituent metals revealed the notable performance of CuFeMnO4 Fe-OC for CLC, owing to the theoretical OTC of 20.04%, synergistic effect of the trimetallic system, and distinct reaction profile.73,74 Composite OC like NiFe2O4 also exhibits a high theoretical OTC of 27.31%, allowing complete carbon capture and improved tar cracking properties arising from the high

catalytic activity of the metallic Ni formed in the reduced phase and unique spinel structure.^{72,75}

As opposed to CLC, where a higher OTC is favored, materials with a lower oxidation potential and lower OTC than Fe₂O₃ are promising for CLPO. Ca₂Fe₂O₅, having a low theoretical OTC of 17.66%, has revealed high conversions and remarkably high syngas selectivity, as showcased by Shah et al.61 More than 99% CH₄ conversion with >98% syngas selectivity obtained can be ascribed to the brownmillerite type structure and favorable thermodynamics of oxygen transfer for partial oxidation. Moreover, the ability of Ca₂Fe₂O₅ to regenerate using CO₂/H₂O increases the overall syngas yield.76 Other probable candidates for CLPO applications, such as Li₅FeO₄, SrFe₁₂O₁₉, etc., with a maximum OTC of 12.13% and 23.73%, respectively, possess bifunctional properties with both catalytic and oxygen transfer properties. 77,78 The Fe-Ti-based synthetic OC developed by Ohio State University (OSU) has shown excellent syngas yield due to its oxygen migration control, achieving syngas purities as high as 90%.43,47 While theoretical OTC helps identify the potential CL application for Fe-OC, it is important to note that the thermodynamics and kinetic activity of the Fe-OC play a crucial role in determining actual OTC and the product selectivity, as seen in the case of $SrFe_{12}O_{19}$.

CLHG processes are commonly combined with CLC or CLPO, where the oxidizer produces H₂ by steam oxidation of the OC. The favorable thermodynamics of OC for steam regeneration are an essential prerequisite for its use in CLHG. The H₂ yield from the material highly depends on the degree of reduction of Fe-OC, which is higher in CLC than in CLPO. Thus, to maximize the yield of H₂, CLC followed by the CLHG process was studied using metal ferrites like CaFe₂O₄, Co_{0.85}Fe_{2.15}O₃, NiLa_{0.2}Fe_{1.8}O₄, *etc.*, which display higher redox stability over

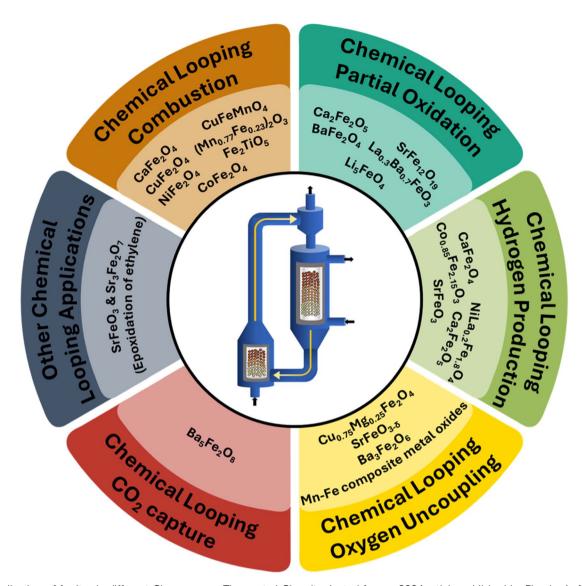


Fig. 5 Application of ferrites in different CL processes. The central CL unit adapted from a 2024 article published by Elsevier (ref. 20) under a Creative Commons Attribution 4.0 International (CC BY 4.0) License.

Fe₂O₃.⁷⁹⁻⁸² At the same time, the ability of Ca₂Fe₂O₅ to regenerate completely using steam has made it a promising candidate for syngas-H2 co-generation.

Apart from the conventional applications of the CL processes, several OCs have been developed for applications such as CLOU, oxidative dehydrogenation, preferential oxidation, selective dehydrogenation, etc., as summarized in Fig. 5. SrFeO₃ and Sr₃Fe₂O₇ in a 1:1 ratio have been utilized for chemical looping ethylene epoxidation and have shown significantly higher yields of ethylene oxide as compared to conventional processes.83-85 Controlled oxidation enables a four times higher yield than conventional processes due to its property of controlled oxidation. Similarly, a mixture of Ba₅Fe₂O₈ and Ba₃Fe₂O₆ can be utilized for CLOU with inherent CO₂ capture at high temperatures, leveraging the superior capture performance of the former and higher oxygen uncoupling of the latter. Table 1 summarizes details on the structure, method of preparation, and applications of some Fe-OCs.

3.3. Performance evaluation of Fe-OC for scaled-up CL applications

With a realization of the scale-up potential of various Fe-OCs, various demonstrations on bench-scale, sub-pilot scale, and pilot scale have been conducted, highlighting the capability of chemical looping technology for clean energy production and achieving carbon neutrality. This section draws attention to the scale-up attempts of CL spanning from kWth to MWth scale using synthetic and natural Fe-OCs for diverse feedstocks.99

Southeast University has experimentally investigated CLC in continuous fluidized bed reactors ranging from a scale of 1-50 kW_{th} for a wide range of solid fuels using synthetic Fe-OC. 100-103 These tests proved the potential of Fe-OC as a low-cost carrier for commercial coal-fueled CLC units. OSU demonstrated a 25 kWth followed by a 250 kWth high-pressure moving bed reactor configuration for syngas utilization using Fe-Ti OC to enable H2 production with 100% CO₂ capture. 46 Another 250 kW_{th}

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Table 1 Classification of Fe-OC based on phases and the effects observed on CL processes due to different preparation methods and experimental conditions

		-		-	
00	Preparation method	Experimental temperature	Application	Key findings	Ref.
Spinel NiFe ₂ O ₄	Sol-gel	D ₀ 008	CLHG	Grain coalescence and surface densification lead to	98
$\mathrm{Cu}_x\mathrm{Mg}_{1-x}\mathrm{Fe}_2\mathrm{O}_4$	Mechanical mixing and calcination	900–1000°C	CIC	~98.9% conversion of waste biomass The addition of Mg improved crushing strength above	84
$M_x F e_{3-x} O_4$, $M = Cr$ and Mn	Iron ore	∂° 058	CIC	Fe-Cr-based OC demonstrates improved stability and performance due to the suinel structure	87
$\mathrm{Cu_xMn_{1-x}Fe_2O_4}$	Co-precipitation	Oo 002-009	CL-SMR	Cu _{0.6} Mn _{0.4} Fe ₂ O ₄ enabled CH ₄ conversion of ~98.7% and H ₂ yield of ~81.02%	88
$\mathrm{Cu}_{0.2}\mathrm{Co}_{0.8}\mathrm{Fe}_2\mathrm{O}_4$	Sol-gel	<750 °C	${ m CL-CO}_2$ splitting	Improved reduction facilitated by Cu and Co as co-dopants Increasing Cu doping results in the formation of impurities detrimental to the CO ₂ -splitting process	68
Perovskite La _{0.75} Sr _{0.25} FeO ₃ -encapsulated Co.ONiO	Modified Pechini	J ₀ 009	CL-RWGS	Promotes oxygen defects in the metal oxide core during	06
La _{0.5} Sr _{0.5} Fe _{0.5} Co _{0.5} O _{3-b}	Glycine-nitrate combustion and spray drying	D ₀ 006	CIC	The selectivity towards CO/H ₂ and the reactivity with CH ₄ was reduced	91
$ m La_{1-x}Sr_xFeO_3$	Sol-gel	1000 °C	CLR	Partial substitution of La ³⁺ by Sr ²⁺ causes electronic imbalance, which is compensated by oxidation of a fraction of Fe ³⁺ to Fe ⁴⁺ and/or generation of oxygen vacancies The optimum range of the degree of Sr substitution is	92
$\mathrm{LaFe}_{1-x}\mathrm{Co}_x\mathrm{O}_3$	Combustion	850 °C	CLR	x = 0.3-0.5 The surface adsorbed oxygen essential for complete oxidation of CH ₄ increases with Co substitution or The optimum degree of Co substitution is $x = 0.3$	93
$Sr(Fe_{1-x}Cu_x)O_{3-\delta}$	Calcination method	Oo 008-009	CIC	Can sustain very high temperatures (>1280 °C) with a crushing strength >39.32 MPa	94
Pseudobrookite ${\rm Fe_2TiO_5}$	Mechanical mixing followed by pulverization	875–925 °C	CLC	Improved diffusion of CH_4 through the Fe-OC led to an enhanced activity of Fe_2TiO_5 supported on Al_2O_3	95
Brownmillerite $Ca_2Ni_{0.25}Fc_{1.75}O_5$	Sol-gel	D ₀ 006	CL-SR	Ni induces structural changes to the brownmillerite lattice, increasing the distortion of the FeO ₆ octahedra. The structural changes lead to improved lattice oxygen activity.	96
$\mathrm{Ca_2Fe_2O_5}$	Sol-gel	850 °C	CL-SR	Reduction of the migration energy barrier of lattice oxygen between bulk and surface improved the reactivity	97
MgO supported $\mathrm{Ca_2Fe_2O_5}$	Solid state synthesis	1000 °C	CLR	${\rm CO_2}$ counter-oxidation enabled ${\sim}20\%$ higher ${\rm CO_2}$ utilization compared to tri-reforming	86

Table 2 A non-exhaustive list of scale-up attempts for CL processes with Fe-OC

Fe-OC	Feedstock	Hours of operation	Scale	Reactor configuration	Ref.
Synthetic iron-based					
Fe ₂ O ₃ -supported	Coal, biomass	200-600	$25-250 \text{ kW}_{\text{th}}$	Moving bed	44, 48 and 121
Fe ₂ O ₃ and Fe ₂ O ₃ /Al ₂ O ₃	Biomass	30, 60	10 kW _{th}	Fluidized bed	105 and 122
Fe-Ni and Fe-Cu on Al- and MgAl-based supports	Natural gas, biomass, coke oven gas	2-40	$10-50~\mathrm{kW_{th}}$	Fluidized bed	106, 107, 123 and 124
Natural ore based					
Iron ore	Biomass and coal	26	$100 \text{ kW}_{\text{th}}$	Fluidized bed	125
Ilmenite	Coal, petcoke, biomass, CH ₄ , CO, and H ₂	22-160	10 kW _{th} -12 MW _{th}	Fluidized bed	113-115 and 126-129
Ilmenite-iron ore	Coal and biomass	110	1 MW _{th}	Fluidized bed	119
Hematite	Coal	100	5 kW _{th}	Fluidized bed	116
Ilmenite-manganese ore	Biomass and petcoke	18	100 kW _{th}	Fluidized bed	130

demonstration highlighted the supremacy of Fe–Ti OC for near 100% conversion of direct solid fuels.⁴⁸ Over 600 hours of testing using Fe-OC for biomass gasification in a 25 kW_{th} subpilot unit exhibited excellent tar-cracking capabilities, high attrition resistance, and stable reactivity of the Fe–Ti OC for extended redox operation.⁴⁴

Incorporating additional metal oxides, such as CuO and NiO, into Fe-OCs has demonstrated the potential to enhance their reactivity while maintaining cyclic stability, positioning these OCs as promising candidates for the scale-up of CL technology. ¹⁰⁴ In a 10 kW_{th} demonstration for biomass gasification, Fe-Ni bimetallic OCs improved the gasification efficiency compared to single metal OC owing to the catalytic activity of Ni. ^{105,106} Investigations conducted in a 10 kW_{th} and 50 kW_{th} CLC unit using coke oven gas and CH₄, respectively, established the superiority of supported Cu-Fe OC for extended redox testing and for the achievement of autothermal operation. ^{107–109}

Besides synthetic Fe-OC, natural ores have gained attention for CL applications owing to their low cost and excellent sintering resistance. Experimental evaluation in 10 kWth and 100 kWth by Chalmers University using ilmenite and a mixture of ilmenite-hematite demonstrated high fuel conversion for lowvolatile solids with a projected Fe-OC lifespan of 700-800 hours.110-115 Natural mineral-based OCs, like hematite, have also been evaluated in fluidized bed CLC reactors. 116 25 kWth scale CLG investigation for coal and biomass achieved high syngas purity with high carbon conversion. 117 A CLC plant on a 1 MW_{th} scale at Technische Universität Darmstadt demonstrated autothermal operation for coal CLC using both ilmenite and hematite.118-120 These commercial-scale demonstrations show that natural iron ores could be a suitable material with good mechanical properties, low attrition, good reactivity, high OTC, and low cost. Table 2 provides a further overview of some of the scale-up attempts for CL technology reported in the literature.

4 Challenges and opportunities

In order to implement the potential benefits of the CL systems on a commercial scale, the ability of the Fe-OC to maintain reactivity and structural stability over an extended period of testing is crucial. This section highlights some of the key challenges encountered in the use of Fe-OCs for CL applications. Moreover, detailed insight into plausible composition modifications, which can ameliorate the barriers to the implementation of Fe-OC on a commercial scale, has been discussed.

4.1. Cyclic stability and active material dispersion of Fe-OC

Fe-OCs face a significant challenge in maintaining cyclic stability during the redox process owing to poor mechanical strength and active site dispersion on the OC, which can be improved by the incorporation of inert support material. Common supports that have demonstrated an improvement in the material stability for extended redox cycles include but are not limited to Al₂O₃, TiO₂, ZrO₂, YSZ, CaO, MgO, and CeO₂. A reactivity improvement in the order of Al₂O₃ > SiO₂ > TiO₂ > unsupported > CaO is observed in Fe₂O₃, which could be attributed to the enhanced gas diffusion through the interconnected pores in Al2O3, SiO2, and TiO2-supported OCs. Moreover, Al₂O₃ and TiO₂ also contribute to the increase in mechanical strength of the Fe-OC during the fluidized bed testing.131 Tijani et al. found that the use of ZrO2 and CeO2 supports significantly decrease the activation energy barrier by ~4 times during the oxidation step compared to Al₂O₃ and TiO₂. ¹³² In order to prevent the eventual loss of reactivity by using CeO₂ support, the Fe-Ce structure was stabilized by adding ~7 wt% of ZrO₂ in the fluorite configuration of CeO₂. This leads to the formation of oxygen vacancies and mitigates the formation of CeFeO₃, increasing the redox stability of the Fe-OC. 133

The active material dispersion and reactivity can be further enhanced using mesoporous inert supports like SBA-15 to synthesize nano-scaled carriers. Kumar *et al.* observed a remarkable 1000% improvement in reactivity using LaFeO₃-SBA-15 compared to the bulk carrier for CLC application owing to the formation of a reactive cubic phase at the nanoscale. 20 Fe₂O₃ nanoparticles synthesized by Liu and co-workers using the SBA-15 matrix for CLPO application display >99.3% selectivity toward CO formation from CH₄ and a stable performance

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for 75 redox cycles. The 70% improvement in conversion rate and ~200% higher CO concentration compared to the bulk carrier can be attributed to the lower adsorption and dissociation energies of CH₄ in the presence of nanoparticles. 134

In addition to the choice of inert support, the synthesis technique used has a profound effect on the performance of Fe-OC in chemical looping. Mechanical mixing, freeze granulation, dry and wet impregnation, co-precipitation, and sol-gel are commonly practiced methods to prepare Fe-OCs. Fe₂O₃-Al₂O₃ OCs prepared by the sol-gel process in the Fe: Al₂O₃ molar ratio of 2:1 demonstrate better reactivity and stable performance across multiple redox cycles, among other preparation methods like mechanical mixing and dipping. 135 This can be attributed to the excellent homogeneity and control over microstructure in the sol-gel method, which leads to the formation of Al₃Fe₅O₁₂.²⁸ Another study identified that the conventional wet impregnation method for preparing Fe-OCs is challenged by poor dispersion of active material on the support and insufficient penetration into the binder material. However, this challenge was resolved using the ultrasonic wet impregnation technique, characterized by a reduction in the crystalline size and better dispersion of the active material, enabling higher conversions of CH4.136

4.2. Loss of reactivity and performance degradation

The incorporation of inert support enhances the cyclic stability of the material. However, a decrease in the performance of the Fe-OC has been observed with increasing redox cycles, arising due to degradation in the OTC.137 Dopant modification is an effective technique to retain the reactive capability of the Fe-OC

over an extended number of cycles. Alkaline metals are commonly studied as dopants since they act as an electron donor and weaken the Fe-O bond. Liu et al. observed that 2.6 mol% K doped Fe-Al carrier demonstrates superior CO₂ selectivity and stable reactivity for \sim 50 redox cycles. This can be ascribed to the stiffening of the Al₂O₃ matrix in the presence of K, providing a stable path for [O] migration. ¹³⁷ Similarly, adding 5% Na using sodium salt, like NaCl, as a dopant in the Fe-Al matrix also helps increase the yield of CO2 in CLC.138 Isovalent metal oxide dopants like 1% La dramatically enhance the reactivity for the combustion of CO and regeneration by \sim 233% and 266%, respectively. This can be attributed to the lowering of the energy barrier due to La for CO bond activation. 139 Doping 2% La on Fe-CeO₂-based OC results in the Fe-La_{0.02}Ce_{0.95}O_{1.99} phase, facilitating a very high oxygen transport by altering the thermodynamic stability of CeO2. Increasing the dopant concentration beyond 10% does not contribute significantly to further enhancement owing to La phase separation to form LaFeO₃ with poor reactivity. The cyclic stability testing with 10% La doping on the CeO₂ matrix results in the formation of Fe-La_{0.1}Ce_{0.9}O_{1.95}. La-doped Fe-OC demonstrated excellent recyclability over 50 redox cycles, whereas the undoped Fe-OC lost the ability to regenerate after 11 cycles.140

4.3. Carbon and ash deposition

Carbon deposition can significantly compromise the Fe-OC stability and purity of the products, which may negate the inherent product separation advantage of CL systems. Carbon can exist in amorphous, filamentary, and crystalline graphitic

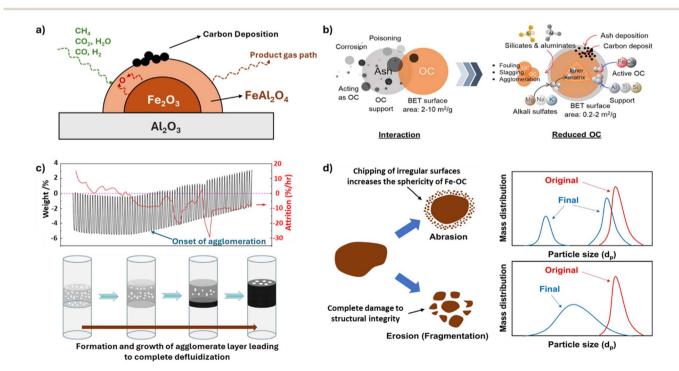


Fig. 6 Challenges encountered in CL applications while using Fe-OC. (a) Onset of carbon deposition. Adapted with permission from ref. 149. Copyright 2023 Elsevier. (b) Ash deposition. Adapted from article (ref. 150) published by Elsevier under a Creative Commons Attribution 4.0 International (CC BY 4.0) License. (c) Formation and growth of agglomerate layer. Adapted with permission from ref. 151. Copyright 2023 Elsevier. (d) Fe-OC attrition. Adapted with permission from ref. 152 and 153. Copyright 2016 and 2023 Elsevier.

forms and get deposited on the Fe-OC particles.^{141,142} Deeply reduced Fe-OCs are susceptible to carbon deposition owing to the difficulty in lattice oxygen migration through the metallic Fe and FeO phases.^{143,144} The two major strategies to prevent carbon deposition are (1) dopant and support modification to mitigate the C-H bond cleavage. (2) Synthesis of composite metal oxides to increase the lattice oxygen mobility for enhancing the oxidation of deposited carbon.

Modifying the natural iron ore-based OC by adding alkali metal, Ni, and Cu-based dopants blocks the active sites for carbon accumulation and increases the mobility of lattice oxygen by alleviating the iron-oxygen interaction. MgO modification, 10% KNO₃ decoration, and co-doping of K and Cu can improve the ability to remove carbon by enhancing oxygen mobility for natural Fe-OCs. 145-148 Synthetic Fe-Al OCs face the challenge of carbon deposition owing to the increase in acidic sites, which enhances C-H bond cleavage and the formation of FeAl₂O₄ spinel with low [O] mobility, as shown in Fig. 6(a). 154,155 K₂CO₃doped Fe-Al-based OCs have demonstrated the prevention of carbon deposition by limiting the concentration of acidic sites. Y-Doped Fe-Al OCs sintered at 1200 °C form a garnet structure $Y_3Fe_xAl_{5-x}O_{12}$ (x = 1, 2, 3), demonstrating high selectivity for syngas production by avoiding carbon deposition. 156,157 Adding MgO in Fe-Al OCs gives rise to the phase of MgAl₂O₄, which mitigates the interaction between iron oxide and Al₂O₃, reducing carbon deposition.158 CeO2-Modified Al2O3 support, or Fe2O3 supported on 40% CeO2, leads to the formation of a perovskite CeFeO₃ structure that can generate channels for [O] migration, eliminating carbon accumulation on OC.52,68,159-161 Besides dopant and support modification, iron-based composites are known to enhance the reactivity and alleviate carbon deposition. Spinel structures like CuFe₂O₄, BaFe₂O₄, 4% Cu-4% Ce doped CoFe₂O₄, and 70% CeO₂-NiFe₂O₄ have demonstrated microstructural integrity over multiple redox cycles and facilitated higher [O] release to prevent carbon deposition. 104,162-168 Perovskite structures like $La_{0.5}Ce_{0.5}FeO_3$, $BaFe_{0.4}Sn_{0.6}O_{3-\delta}$, and LaSrFe_{2-x}Co_xO₆ improve the reactivity and mitigate carbon deposition owing to increased oxygen migration due to structural distortion.169 Hexaaluminates like BaFexAl12-xO19 and LaFe3Al9-O₁₉ have proved to be promising candidates for OC with low coking and high reactivity. 170,171

Solid feedstocks, including fossil fuels like coal, sustainable carbon sources like biomass, and non-conventional feedstocks like municipal waste, present a challenge of ash deposition, as illustrated in Fig. 6(b). The components in ash include SiO₂, Al₂O₃, Fe₂O₃, CaO, TiO₂, K₂O, MgO, Na₂O, and P₂O₅. While the effects of ash deposition are not completely adverse, they can cause physical damage to the Fe-OC particles by clogging the pores, resulting in loss of reactivity and inducing mechanical stresses, leading to crack formation in the particles. 172,173 Chemical interactions between fuel and low melting components like Ca and K from ash can lead to agglomeration of the particles and corrosion of the CL equipment. 150,174 While ash majorly has detrimental effects on the Fe-OC, some active components present in the ash improve the reaction rate. Cabased oxides in the ash prevent the formation of side products like Al- and Si- complexes, which are responsible for deactivating the Fe-OCs. The oxides of transition metals in the ash enhance the redox stability, and components like Fe₂O₃ and CaSO₄ promote the kinetic activity of the oxygen carrier.¹⁷⁵

In order to tackle the deteriorating effects of the ash, some techniques like washing for removing soluble salts of K, Ca, Si, P, Cl, Mg, and Na and pickling to remove water-insoluble salts by acid treatment are well-known.^{176,177} In addition to biomass pre-treatment, structural and compositional optimization to prevent the blocking of pores and improve redox activity can be beneficial in negating inhibitory effects like agglomeration and deactivation arising from ash deposition. NiFe₂O₄, MnFe₂O₄, CoFeAlO_x, CuFe₂O₄, Ca₂Fe_{1.8}Co_{0.2}O₅ are found to maintain excellent redox activity and mitigate agglomeration, which can subside the adverse effects observed due to ash deposition.¹⁷⁸⁻¹⁸⁰

4.4. Durability of Fe-OC particles over long-term redox cycling

Due to the low Tammann temperatures ($T_{\rm Tam}$) of iron oxides, Fe-OCs tend to agglomerate, causing the deactivation of the OC and a decrease in oxygen diffusion. In moving and fluidized bed CL technologies, particle agglomeration can lead to reactor bridging and defluidization, which can hinder the long-term cyclic performance of the material, as shown in Fig. 6(c).

Some bimetallic Fe-OCs like CoFe₂O₄, Fe₂TiO₅, and Ca₂Fe₂O₅ have high melting points of ~1570 °C, ~1550 °C, and ~1450 °C, respectively correspondingly increasing T_{Tam} . This helps the Fe-OCs to sustain higher operational temperatures, which can be beneficial for improving activity and thermodynamic conversions. Also, adding inert support ameliorates sintering as it increases the heat capacity of the material, thus raising the T_{Tam} of the Fe-OC. Cho et al. reported a stable performance of $Fe_2O_3-Al_2O_3$ (2:3) particles for 40 cycles without defluidization due to agglomeration.183 A bimetallic NiFe2O4 carrier supported on a SiO₂ alleviates sintering compared to unsupported NiFe₂O₄. However, after 15 redox cycles, Ni-Fe carriers demonstrate a block structure due to agglomeration, causing a decrease in reactivity. 184,185 Therefore, nanocomposites of NiFe₂O₄ impregnated on silica matrix were synthesized, which prevents particle aggregation due to enhanced dispersion of spinel NiFe2O4. Olhero and co-workers conducted a study to understand the effect of heat treatment on agglomeration using zinc-substituted Ni ferrite (Ni_{0.8}Zn_{0.2}Fe₂O₄) powders. Increasing the calcination temperature from 400 °C to 1200 °C causes a 776% increase in the average particle size and a 99.9% decrease in the specific surface area due to agglomeration. 186 Scheffe et al. synthesized $Co_{0.85}Fe_{2.15}O_4$ Fe-OC via atomic layer deposition on ZrO₂, demonstrating stable and improved reactivity and ameliorating agglomeration.80

The commercial CL process would involve Fe-OC fluidization for thousands of hours under varying temperatures and the constant swing of oxidation states. The continuous mechanical, thermal, and chemical stresses can lead to chipping, disintegration, abrasion, or fragmentation of the Fe-OC, broadly classified as attrition. As illustrated in Fig. 6(d), abrasion, characterized by the chipping of uneven surfaces of the parent Fe-OC, is majorly observed at lower particle circulation rates.

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Fragmentation, observed at higher Fe-OC circulation rates, leads to many sub-particles forming fragments. Attrition of Fe-OCs results in particle make-up cost, which is a function of attrition rate (A), solid circulation rate, and cost of Fe-OC manufacture. Therefore, attrition can greatly influence the overall operating costs of the CL plant, and hence, tremendous efforts are focused on decreasing the attrition rate and increasing the Fe-OC lifetime. Adanez and co-workers found that 20 wt% Fe₂O₃ supported on Al₂O₃ demonstrates low A of 0.09-0.14% per h, translating into a Fe-OC lifetime of 700-1150 hours at an operating temperature of ~ 900 °C. ¹⁸⁹ Pans et al. also utilized low-cost iron ore containing 76 wt% Fe₂O₃ in the CLC unit to generate syngas at 830-930 °C and observed a low A of 0.05% per h, corresponding to a lifetime of 2000 hours. 190 Mei et al. utilized four different Fe-OC compositions: 65.6% Mn₃O₄- $18.6\% \text{ Fe}_2\text{O}_3$, $67.5\% \text{ Mn}_3\text{O}_4-8.4\% \text{ Fe}_2\text{O}_3$, $71.8\% \text{ Mn}_3\text{O}_4-6\%$ Fe₂O₃, 80.7% Mn₃O₄-5.2% Fe₂O₃, dispersed over Al₂O₃ as the inert support and observed that Fe-OC composed of 65.6% Mn₃O₄ achieves the lowest A of 0.0625% per h increasing the lifetime to 1600 hours. The remaining compositions had an attrition rate in the range of 0.1-0.67% per h with an OC lifetime of 1000-150 hours.191 Chung et al. have demonstrated stable performance of Fe-OC supported on Al-based inert for over 3000 cycles. 192 It can be concluded that Al-based supports have proven to be promising in enhancing the lifetime of Fe-OC. Moreover, it has been observed for most of the synthetic Fe-OCs that the crushing strength increases with an increase in calcination temperature from 950-1600 °C but leads to a loss in the reactive capability of the material. Natural ores of ironcontaining mixed-metal oxides of SiO2, Al2O3, CaO, Na2O, K₂O, MgO, and TiO₂ show a positive effect on reducing the A. However, fewer research efforts have focused on natural Fe-OC due to their low reactivity. 153 While attrition presents a significant challenge to CL technology, the techno-economic evaluation conducted by Zhang et al. estimates that even with frequent solid make-up, the Fe-OC based CL process can be economically more attractive compared to the current state-of-the-art processes for commodity chemical production.50

Moreover, it is important to understand that the target application and the method of operation critically influence the choice of the active material and the Fe-OC composition. While the addition of a component may increase the attrition rate of the Fe-OC particles, it may prevent the deactivation of the Fe-OC due to carbon deposition. If the operational strategy of the process involves using fluidized beds, the addition of the component might be impractical since the process would require frequent solid makeup due to low OC lifetime. However, the Fe-OC can be well-suited for a fixed bed process where strength can be compromised to prevent carbon deposition for extended periods of operation. Similarly, increasing the strength and lowering the attrition rates may result in a compromise with the reactivity of the Fe-OC. In practice, the OC developed for larger scales of operation involves a delicate balance and an optimized trade-off of the extent to which each challenge is tackled by incorporating multiple components. Therefore, the precise compositions of most of the Fe-OCs that have been tested for a higher scale of operation are protected in the form of proprietary information.

5 Conclusion and perspectives

Chemical looping emerges as a highly promising technology in the pursuit of sustainable energy solutions. Metal ferrites have shown great potential as OCs for CL processes, offering a path toward reducing greenhouse gas emissions and improving the sustainability of industrial chemical production. Nevertheless, there remains a significant need to refine these materials and their associated processes to address current limitations and challenges. This review has thoroughly explored metal ferrites, highlighting their fundamental properties and critical role in advancing the efficacy of chemical looping processes. Innovation in Fe-OC is geared towards boosting OTC, increasing surface reactivity, and enhancing thermal stability. These improvements can be achieved through the development of composite metal ferrite and bimetallic systems. Employing nanoscale engineering and surface modification techniques could also markedly enhance the overall performance of Fe-OC for novel CL processes. Additionally, process optimization is vital for refining ferrite-based CL processes. This involves using sophisticated computational models and simulations to refine reactor designs and operational parameters, ensuring optimal interaction between metal ferrites and reactants and reducing energy losses. Integrating robust systems that align CL with current industrial practices could ease the adoption and implementation across various sectors. As these technologies have completed successful pilot testing and are progressing toward commercialization, enhancing lifecycle assessments to meet sustainability criteria will also be crucial. Fe-OCs-based CL processes can offer cost advantages over other transition metal oxide-based CL technologies for producing commodity chemicals. Therefore, the ongoing development of Fe-OCs and their derivative CL processes is expected to continue playing a critical role in advancing sustainable technologies, which will significantly contribute to scientific efforts and industrial practices to mitigate climate change and enhance clean energy production.

Abbreviations

British thermal units
Hydrogen
Methanol
Ethanol
Ammonia
Auto-thermal reforming
Steam methane reforming
Chemical looping
Carbon dioxide
Steam
Carbon monoxide
Nitrous oxides (NO_x)
Nickel oxide
Copper oxide
Iron oxide
Chromium oxide
Vanadium oxide

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Mn₂O₃ Manganese oxide Co₃O₄ Cobalt oxide CeO₂ Ceria OC Oxygen carriers

OC Oxygen carriers

Fe-OC Ferrite-based oxygen carriers

FeTiO₃ Iron-titanium oxide

CH₄ Methane

CLC Chemical looping combustion
CLG Chemical looping gasification
CLPO Chemical looping partial oxidation

CLR Chemical looping reforming

CLHG Chemical looping hydrogen generation;

 $\Delta E_{\rm vac}$ Vacancy formation energy

YSZ8-CS 8 mol% yttria-stabilized zirconium oxide core-

shell

YSZ10-CS 10 mol% yttria-stabilized zirconium oxide

core-shell

OTC Oxygen transport capacity
OSU Ohio State University

Na Sodium

 $\begin{array}{ll} \text{MgO} & \text{Magnesium oxide} \\ \text{K}_2\text{CO}_3 & \text{Potassium carbonate} \\ T_{\text{Tam}} & \text{Tammann temperatures} \\ \text{Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4 & \text{Zinc-substituted Ni ferrite} \end{array}$

A Attrition rate

Data availability

No primary research results, software, or code have been included, and no new data were generated or analyzed as part of this review.

Author contributions

Tanay A. Jawdekar and Ishani Karki Kudva contributed equally to this work and are co-first authors. Tanay A. Jawdekar: conceptualization, formal analysis, methodology, visualization, writing – original draft, writing – review & editing. Ishani Karki Kudva: conceptualization, methodology, visualization, writing – original draft, writing – review & editing. Sudeshna Gun: writing – original draft, visualization, writing – review & editing. Shekhar G. Shinde: writing – original draft, visualization, writing – review & editing. Ashin A. Sunny: writing – original draft, visualization, writing – review & editing. Liang-Shih Fan: resources, supervision, writing – review & editing.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced this study.

Acknowledgements

The authors greatly appreciate the helpful discussions with Dr Sonu Kumar, Dr Rushikesh K. Joshi, and Dr Anuj Joshi. Their guidance and support were extremely valuable in shaping the manuscript and improving the quality of this work.

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