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Developing Oxygen Carriers for Chemical Looping Biomass Processing: Challenges and Opportunities

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Abstract

Amongst the various thermochemical biomass conversion pathways, chemical looping gasification (CLG) and chemical looping reforming (CLR), collectively known as chemical looping biomass processing (CLBP), offers numerous advantages, including the generation of renewable hydrogen, high exergy efficiency, inherent carbon capture, and process intensification. Like all other chemical looping applications, oxygen carriers (OCs) play key roles in determining the effectiveness and efficiency of CLBP. In addition to the requirement for high oxygen transfer capacity, the chemical activity of the lattice oxygen also needs to be modulated to steer the selectivity of CLBP towards syngas. Furthermore, it is desirable for the CLBP oxygen carriers to possess catalytic activities that accelerate the conversion of biomass-based feedstocks. However, despite the large volume of relevant research publications, the diversity in oxygen carrier formulations, biomass compositions and test conditions used leads to mixed views regarding the structural-functional relationships between oxygen carriers and their performance during CLBP. To address the above knowledge gap, this review presents a systematic, but non-exhaustive summary of the development and evaluation of oxygen carriers for CLBP applications, with an aim to elucidate the rational design principles and operation parameters towards optimal process efficiency.

Keywords: biomass chemical looping processes; oxygen carrier; gasification; reforming; syngas

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1. Introduction

1.1. Biomass as a sustainable feedstock

CO₂ emission from the combustion of fossil fuels is deemed a major contributor to global warming.¹ To limit the increase of global average temperature to within 2 °C compared to pre-industrial era,² it is necessary to rapidly reduce our reliance on fossil fuels. To this end, tremendous efforts have been put in to ramp up the capacities of renewable energy generation, including solar, wind, hydro, geothermal, tidal, *etc.*³ However, non-biological renewables are available intermittently, location-specific, and require costly infrastructures for energy storage and distribution; these characteristics constrain the economic appeal of their widespread deployment. As of 2017, the generation of modern renewables (excluding the share of traditional biomass of *ca.* 9.1%) accounted for 10.2% of global energy consumption,⁴ far behind the requirement by the 2 °C climate mitigation pathway.

Therefore, biomass, one of the oldest energy vectors, will continue to play a pivotal role in a renewable future, owing to its high energy density and its ability to fuel conventional thermal power plants to sustain the baseload of a mixed electricity grid. In addition, biomass can serve as the feedstock for synthesizing chemical products and specialty fuels.⁵ In fact, the conversion of biomass to sustainable fuels has been extensively studied in the context of reducing greenhouse gas (GHG) emission. To date, the utilization of biomass primarily comprises of biochemical routes and thermochemical routes.⁶ While biochemical methods generally have stringent requirements for feedstock purities and high water consumption,⁷ thermochemical processes are more robust in handling a wide range of biomass feedstocks, including those that cannot be converted by biochemical processes.⁸⁻¹² Key thermochemical

biomass conversion processes include gasification and reforming, both producing syngas,¹³ which can be further upgraded to multicarbon products via methanol or Fischer-Tropsch synthesis. In conventional gasification and reforming processes, a sub stoichiometric amount of air or oxygen is supplied, together with steam or CO₂, to oxidatively breakdown biomass molecules to C₁ chemical building blocks. By adjusting the ratio of oxygen to H₂O and CO₂ in the feed, the exothermicity of the reaction and the H₂:CO ratio of the syngas is controlled. However, the high oxidative power of O₂ and the low oxidative power of CO₂ could lead to practical issues such as over-oxidation to CO₂ and carbon deposition, respectively, both negatively impact the effectiveness of the thermochemical processes. As process intensification alternative, chemical looping biomass processing (CLBP) simultaneously addresses the issues of over-oxidation and carbon deposition, whilst offering the opportunity to make the overall process carbon-negative by inherently capturing CO₂ with minimal energy penalty.¹⁴

1.2. Chemical looping biomass processing

The term “chemical looping” was introduced by Ishida *et al.*¹⁵ to describe a exergy-efficient combustion process using redox active metal oxides as the reaction mediators,¹⁶ known as oxygen carriers. In a typical chemical looping system, oxygen carrier (OC) particles are circulated between two interconnected reactors, *viz.* the fuel reactor (FR) and the air reactor (AR).¹⁷ In FR, fuel is oxidized by the lattice oxygen of the oxygen carrier, which, after depletion, is regenerated in AR. Therefore, the direct contact between the fuel and air is avoided, thereby eliminating the need for product separation. In the case of combustion, fuel is completely oxidized in the FR, producing a pure stream of CO₂ and H₂O, *i.e.* carbon capture is inherently achieved without energy

efficiency penalty. Besides combustion, the chemical looping concept can also be adopted for the oxidative conversion of biomass-based feedstocks to syngas via chemical looping biomass gasification (CLBG) and chemical looping biomass reformation (CLBR). By engineering OCs with specific functionalities (*e.g.* lattice oxygen activity and catalytic activity towards breaking down biomass macromolecules), the selectivity towards complete combustion or partial oxidation (by gasification or reforming) can be controlled.

Here, we collectively denote CLBG and CLBR as chemical looping biomass conversion processing (CLBP). As shown in Fig. 1, there have been a rapid increase in the number of published studies on CLBP. Like in all other chemical looping applications, oxygen carrier formulation plays a key role in the advancement of CLBP technologies. From a practical standpoint, a commercialisable oxygen carrier should be able to undergo multiple redox cycles with minimum loss in physical integrity and chemical reactivity.¹³ Research in oxygen carrier development for CLBP application covers aspects such as chemical compositions, synthesis procedures,¹⁸⁻²¹ material characteristics and operando behavior²² of the oxygen carriers. Yet, a systematic review dedicated to the development of OCs for CLBP is not available in the literature.

Fig. 1. Number of publications on biomass based chemical looping by year. Data were obtained from Google Scholar and Web of Science on 12th Jun 2020. Keywords for searching are “chemical loop” AND “biomass”, respectively. (Note: document types of articles, meeting, others, review, abstract, unspecified, early access, editorial and book were considered for Web of Science)

1.3. Aims and objectives

Pertaining to several reviews discussing the use of biomass in of chemical looping processes, *e.g.* the papers by Zhao *et al.*¹³ and Adanez *et al.*²³, much focus has been given to the combustion of biofuels to achieve bio-energy carbon capture and storage (BECCS). We also note the recently published reviews on oxygen carrier formulation for various chemical looping applications.²⁴⁻²⁷ These reviews have comprehensively captured the recently advances in the development of oxygen carriers for the conversion of gaseous and liquid hydrocarbon fuels to heat and, or functional chemical products. However, we identify an outstanding need to complement the existing literature and to establish a comprehensive understanding of the structural-functional relationship of OCs used in CLBP. This will be done through a systematic overview of the thermochemistries involved during CLBP, followed by a systematic and critical analysis of the factors affecting the performance of oxygen carriers during CLBP cycles. We conclude the article by discussing of the key areas that merit future research focus and the outlook for CLBP technologies.

2. Chemical Looping Biomass Processing

2.1. Process overview

A generic, CLBP process is schematically illustrated in Fig. 2 (a). Taking a generic biomass with composition $C_aH_bO_c$ ($a \geq 1, b \geq 0, c \geq 0$; all other elements are considered are impurities that act as independent components) and a generic oxygen carrier composition of Me_xO_y ($x \geq 1, y \geq 1$) the reactions taking place in the various chemical looping reactors are listed in Table 1 and discussed below.

Fig. 2. Schematic depiction of biomass chemical looping processes. (a) Possible reactors configurations, including biomass chemical looping gasification/combustion (CLBG/C), oxygen uncoupling-biomass chemical looping combustion (OU-CLBG/C), and biomass calcium-looping gasification or combustion (BCaLG/C)). (b) Biomass conversion processes taking place in the fuel reactor, assuming biomass is bottom-fed to a fluidized bed of oxygen carriers. The yellow circles represent fluidised oxygen carrier particles.

Table 1. Summary of reactions that could possibly take place during chemical looping biomass processing.

No.	Reactions in the fuel reactor	Description
1	$C_aH_bO_c + (2a + 0.5b - c)Me_xO_y \rightarrow aCO_2 + 0.5bH_2O + (2a + 0.5b - c)Me_xO_{y-1}$	chemical looping combustion
2	$C_aH_bO_c + (a - c)Me_xO_y \rightarrow aCO + 0.5bH_2 + (a - c)Me_xO_{y-1}$	<i>In situ</i> biomass gasification
3	$aCO + 0.5bH_2 + (a - c)Me_xO_{y-1} \rightarrow aCO_2 + 0.5bH_2O + (2a + 0.5b - c)Me_xO_{y-2}$	Combustion of the gasified biomass by oxygen carrier
4	$Me_xO_y \rightarrow Me_xO_{y-1} + O_2$	Oxygen uncoupling (CLOU)
5	$C_aH_bO_c + (a + 0.25b - 0.5c)O_2 \rightarrow aCO_2 + 0.5bH_2O$	Combustion of biomass in uncoupled oxygen
6	$C_aH_bO_c + (0.5a - 0.5c)O_2 \rightarrow aCO + 0.5bH_2$	Biomass partial oxidation
7	$CO + H_2O \rightleftharpoons CO_2 + H_2$	Water-gas-shift reaction
8	$CaO + CO_2 \rightleftharpoons CaCO_3$	CO ₂ uptake by CaO-based sorbent
Reactions in the steam reactor		
9	$Me_xO_{y-1} + H_2O \rightleftharpoons Me_xO_y + H_2$	Thermochemical water splitting
10	$Me_xO_{y-1} + CO_2 \rightleftharpoons Me_xO_y + CO$	Thermochemical CO ₂ splitting
Reaction in the air reactor		
11	$Me_xO_{y-1} + 0.5O_2 \rightarrow Me_xO_y$	Oxidation of oxygen carrier in air
Reaction in the regenerator		
12	$CaCO_3 \rightleftharpoons CaO + CO_2$	Regeneration of CaO based sorbent

In the fuel reactor (FR), the oxidative conversion of the biomass takes place (R1-R7), as depicted in Fig. 2(b). As the biomass enters FR, its temperature rapidly increases and undergoes devolatilization and pyrolysis to form hydrocarbon molecules (viz. volatiles and tar) in the gas phase and biochar. Both fractions, when allowed sufficient residence time in FR (typically operating above 800 °C), will be completely oxidized by the lattice oxygen of the OCs to produce H₂O and CO₂ (R1), *i.e.* chemical looping biomass combustion (CLBC). When the lattice oxygen is insufficiently reactive, or is the limiting reagent, the biomass will be partially oxidized to produce syngas (R2), *i.e.* chemical looping biomass gasification (CLBG). Further oxidation of the syngas by lattice oxygen will produce CO₂ and H₂O (R3). R2 and R3 are collectively known as *in situ* gasification-chemical looping biomass combustion (*iG*-CLBC). If the oxygen carrier is unstable at high temperatures (*e.g.* CuO, Co₃O₄, Mn₂O₃ and certain types of perovskites), it will decompose and release gaseous oxygen (R4), which is capable of rapidly oxidizing the biomass (R5). R3 and R4 are collectively known as chemical

looping oxygen uncoupling (CLOU).²⁸⁻³¹ For the combustion of solid biomass, iG-CLBC (R2+R3) and CLOU (R4+R5) are faster than R1, because the formers consist of fast, gas-solid reaction steps, whereas the latter is a solid-solid reaction with sluggish kinetics.

Should the amount of gaseous oxygen released in R4 be less than that required for complete oxidation, the biomass will be partially oxidized to produce syngas (R6). For CLBP, one of the goals is to maximise syngas production (R2 and R6). The selectivity of biomass oxidation in the FR strongly depends on the activity of the lattice oxygen. In other words, tuning the lattice oxygen activity is an effective way to manage the production distribution of CLBP. In addition, the rate of biomass gasification in FR may be accelerated by any catalytically active components present in the OC.

The gas mixture in FR typically contains H₂O, H₂, CO, CO₂ and inert components. The composition of the product gas is further modulated by the water-gas-shift reaction (WGS, R7) or its reverse reaction (RWGS). Some researchers also propose to enhance the hydrogen yield during CLBP by removing CO₂ using a CaO-based sorbent (R8) to achieve sorbent-enhanced WGS.^{1, 13, 32, 33} The carbonated sorbent is then regenerated (R12) in the separate regenerator (RG).

When the oxygen carrier is deeply reduced in the FR, it will possess enough reducing potential to thermochemically split H₂O or CO₂. If this is the case, the reduced oxygen carriers can be sent to a steam reactor (SR) to produce additional hydrogen and, or CO from H₂O and, or CO₂ (R9 and R10, respectively). Thus, CLBP with additional hydrogen generation can be performed by either circulating OC between a FR and a SR,

or using a three-reactor system consisting of a FR, SR and an AR. The inclusion of an air reactor (AR) allows the OC to be fully regenerated via an exothermic reaction (R11), which also provides additional heat to the system. In other cases, a CLBP system may only consist of a FR and an AR. If solid biomass is used as the feedstock, the unreacted biochar particles leaving the FR will have to be separated from the reduced OC particles by a carbon stripper (CS). The performance of CLBP is largely determined by the thermochemical reactions that convert biomass in the FR. Accordingly, the behavior of the oxygen carriers in the FR will also be the focus of the present review.

2.2. Effect of operation parameters

The performance of the CLBP is strongly influenced by the operating conditions, such as temperature and OC-to-fuel ratio.¹⁶ Understanding the correlation between the operating conditions and the performance of the CLBP allows us to better interpret, compare and predict the behavior of oxygen carriers under different test conditions.

2.2.1. Feed composition

The feed compositions, including the composition of the biomass and that of the co-fed gases, critically affect the operation of the FR and the composition of the product gas leaving it.

Fig. 3 plots the gas yields (*viz.* the total volume of gaseous product produced per unit mass of fuel consumed) reported by the various studies in the literature with comparable operating conditions as functions of fixed carbon content, volatile content and moisture content. In general, biomass with more fixed carbon, lower volatile content and less moisture yields more gaseous products. Amongst the various types of biomass, rice

straw and toluene generates the least amount of gases per unit mass of feed. The gas yield also depends on a number of other factors, including the composition of the OCs, the nature of the biomass, and other operation conditions such as steam/CO₂ to biomass ratio. For instance, chemical looping reforming of toluene in a bed of NiFe₂O₄ produces 13 times more hydrogen than a bed of NiO under otherwise identical conditions.³⁴ Fig. 4 plots the product gas composition by CLBP of various biomass at different temperatures.

Fig. 3. Gas yields as a function of fixed carbon (FC, %), volatile (%), and moisture (%) contents of CLBP using different OCs and different fuels under comparable operational conditions. Gas yield corresponds to the production CO, CH₄, H₂, and CO₂, unless otherwise stated. Data were reproduced from ³⁴⁻⁵⁷. In case when multiple values are reported for the same fuel and same OC, maximum gas yields are plotted. Correlation coefficients, ρ , between the gas yield and the attributes of the biomass compositions are also shown in each plot.

For the CLBP of rice husk, rice straw and vegetable oil, H₂ is the dominate product in the syngas, even though the feedstocks contain more carbon than hydrogen^{35, 37, 43, 44, 52-54}. This is attributed to the fact that these experiments were performed with steam co-

feeding, which triggers the WGS reaction to generate more H_2 . However, in the case of chemical looping gasification of sewage sludge with steam co-feeding, CO_2 is the dominant product, regardless of the type of OC used; this can be explained by the high oxygen content of the sewage sludge and its high intrinsic activity^{56, 57}. Therefore, CLBP of sewage sludge should be performed in a bed of highly selective OCs in order to maximize the productivity of H_2 and CO. In the absence of steam co-feeding (*i.e.* in the case of pine sawdust and bio oil in Figs. 4 m, 4n and 4o), CO is the dominate component in the syngas.

When solid fuels are used, only small amount of CH_4 can be found in the product; this is in line with the fact that CH_4 is thermodynamically unfavourable under the reaction conditions used.^{58, 59} In contract, the CLBP of liquid fuels result in high methane yield(e.g. 13.1 – 29.7 mol.%) , due to the fact that liquid fuels have relatively low residence time in the FR, *i.e.* the pyrolysis products, *e.g.* CH_4 and H_2 have insufficient time for further oxidation to CO_x ^{60, 61}. The trends discussed above exemplify the importance of understanding the effect of feed composition on the syngas production by CLBP.

Fig. 4. The effects of temperature on gas content (%) with different OCs and chemical looping systems. F, N, FC and FN in the legend denotes the use of iron-based, nickel-based, calcium ferrite-based and nickel ferrite-based oxygen carriers. Details of the biomass, OCs, chemical looping systems and key operational parameters can be found in Table S3. Data were reproduced from ref. ^{35, 38, 43-45, 49, 52, 54, 56, 60-65}.

2.2.2. Effect of temperature

Despite the large diversity in product gas composition as a function of OC and feed composition, some general trends with respect to temperature can be observed in Fig. 4. Most noticeably, the CO_2 content tend to decrease with increasing temperature, whereas CO follows the opposite trend, as highlighted by the linear regressions shown in Fig. 5a, which plots gas contents as functions of temperature when rice husk, wheat husk or straws was used as the fuel. The change in CO/CO_2 ratio with operation temperature can be explained by a thermodynamics. Fig. 5b plots the equilibrium gas

mole fraction of C, CO, CO₂, CH₄, H₂, H₂O and O₂ during steam gasification at 1 atm total pressure. Indeed, it can be seen that, the production of CO and H₂ are more favored at higher temperatures, whereas CO₂ is less favoured.

Fig. 5. (a) A statistical analysis of the compositions of the gas products from selected studies (%) (The straight lines represent the line of best fit. Data were adapted from refs. 35, 38, 43, 44, 52, 54, 62), (b) Equilibrium product mole fraction during steam gasification of carbon at 1 atm total pressure; the black line represents the fraction of solid carbon at equilibrium.

2.2.3. Effect of OC/fuel ratio

The OC/fuel ratio may also affect the conversion and selectivity of CLBP. Accordingly, we examine the studies in the literature that report the effect of the OC/fuel ratio on the performance of BCLP. In addition to the gas mole fraction of the various components in the product, the performance of CLBP is also characterized by combustion efficiency (wt.%), carbon conversion efficiency (%) and gas yield (Nm³ kg⁻¹), which are plotted in Fig. 6. The specific definitions of combustion efficiency (wt.%), carbon conversion efficiency (%) and gas yield (Nm³ kg⁻¹) can be found in S.I.

From Fig. 6, it can be seen that, high OC/fuel ratios generally correspond to high carbon conversion efficiency, whereas the trends in product selectivity differ and can be categorized into three scenarios. In the first scenario (Figs. 6 a-d), the combinations of oxygen carriers and biomass favour complete combustion, therefore increasing OC/fuel ratio leads to higher CO₂ yield and lower syngas yield. In the second scenario (Figs. 6 e-h), the OC-biomass interaction is chemoselective towards syngas, therefore more syngas and more CO₂ are produced at higher OC/fuel ratios, whilst the selectivities remain roughly unchanged. In the third scenario (Figs. 6 i - k), the OCs contain mixtures of highly reactive and moderately reactive lattice oxygen towards the biomass, therefore showing mixed selectivity towards CO and CO₂. However, the biomass reacts preferentially with the more active lattice oxygen to generate CO₂. Therefore, increasing the OC/fuel ratio results in high CO₂ yield and high CO₂ selectivity. In all cases, the yield of CH₄ is low and does not seem to vary significantly with OC/Fuel ratio.

From the discussion above, it is apparent that the OC/fuel ratio in CLBP is fundamentally different from the air/fuel ratio in conventional thermochemical processes. Unlike the chemical activity of gaseous O₂, which scales with its partial pressure, the chemical activity of the lattice oxygen is a strong function of the type of oxygen carrier used, rather than the amount of OCs. Therefore, the most effective way to control the product selectivity of CLBP is to tune the oxygen carrier formulation.

Fig. 6. The effect of OC/fuel ratios on gas production during CLBP. (Details of the biomass, OCs, chemical looping systems and key operational parameters can be found in Table S4. Data were reproduced from refs. ^{35, 38, 40, 46, 49, 50, 54, 56, 66-68})

3. Overview of oxygen carriers

3.1. Oxygen carrier characteristics

As mentioned above, the performance of the oxygen carriers is a determining factor to the effectiveness of CLBP. Oxygen carriers that are suitable for CLBP should meet a number of criteria, some of which are examined *operando*, e.g. redox kinetics, reversibility of phase changes, resistance to carbon deposition and resistance to contaminants, whereas others are characterized *ex situ*, e.g. oxygen transfer capacity (OTC), surface area and mechanical strength against attrition.⁶⁹ The properties of the oxygen carriers that can be characterized *ex situ* allow us to quickly analyze the oxygen carriers prior to chemical looping testing. In this section we overview the measurements of this type of properties (oxygen carrier characteristics) and discuss how they are linked to the performance of the OCs during CLBP.

3.1.1. Oxygen transfer capacity

The oxygen transfer capacity (OTC) is the amount of lattice oxygen that can be removed from the oxygen carrier under chemical looping conditions. Amongst the various OC characteristics, OTC is often the first screening criteria. High OTC means small bed inventory and low solid circulation rate, which translate to low capital cost and low parasitic energy penalty associated with solid circulation, respectively. Theoretically, OTC can be estimated based on the mass fraction of the reducible lattice oxygen present in the OC. Fig. 7 shows the theoretical OTCs of the most commonly

used OCs, viz. oxides of 3d transition metals. Given the similarity in the atomic mass of the metal elements, the theoretical maximum OTC values are correlated to the valency of the oxides, *i.e.* $\text{Fe}_2\text{O}_3/\text{Fe}$ has the highest theoretical OTC, followed by $\text{Co}_3\text{O}_4/\text{Co}$ and MnO_2/MnO . In practice, the OTC accessible during chemical looping cycles also depends on the thermodynamic properties of the oxides. For example, MnO_2 decomposes in air above 535 °C and is inaccessible for high temperature applications. Similarly, the deep reduction of iron oxides to metallic Fe is a kinetically slow process requiring strong reducing environments,^{70, 71} often not feasible in a continuous process. Given these thermodynamic constraints, unsupported NiO/Ni and CuO/Cu are the oxygen carriers with the highest accessible OTCs.

Owing to requirements for stable operation, *e.g.* resistance to sintering and attrition, the redox-active metal oxides are typically supported on largely inert refractory materials. Consequently, practical OTCs are often considerably lower than the theoretical maxima shown in Fig. 7. The OTCs may be further compromised as a result of chemical interactions between the redox active oxides and the support to form chemically unreactive mixed oxides, which are also discussed in section 4.6.⁷²⁻⁷⁵

Experimentally, OTC is often measured by thermogravimetric analysis (TGA). Typical reducing gases used by TGA include H_2 , CO or methane, diluted in a balancing inert gas.⁷⁶⁻⁷⁸ In specific cases, biochars have been used as the reducing agents in TGA.⁷⁹ As shown in Fig. 5, OTCs measured by TGA vary from 1 wt.% (*e.g.* in the case of iron oxide-based LD slag) to 12 wt.% (*e.g.* in the case of 60 wt.% NiO supported on MgAl_2O_4). Under chemical looping operations, other rate limiting factors such as intraparticle mass transfer resistance and product layer diffusional resistance could

further reduces the practically available OTC,^{22, 80-82} unless the issues above can be adequately addressed through improved OC designs.

Fig. 7. Oxygen transfer capacity of Cu-, Fe-, Mn-, Ni, and Co-based OCs vs. their respective theoretical capacities. Most experimental OTCs were obtained by TGA measurements with gaseous reactants,^{39, 41, 55, 69, 82-90} except the case of “oxidized LD slag”, whose OTC was calculated from the conversion of syngas in the batch reactor.⁸⁴

3.1.2. Lattice oxygen activity

As mentioned above, lattice oxygen activity, which can be tuned by adjusting the OC formulations, plays a key role in determining the product selectivity. High lattice oxygen activity give rise to fast oxygen release kinetics, which in turn accelerates the oxygen transfer rates (OTR) during redox reactions.⁹¹ For instance, the iron rich residue from the Bayer’s process carries more redox active lattice oxygen and exhibits higher OTR and higher fuel conversion than ilmenite,⁸⁶ owing to the formation of highly reactive NiFe_2O_4 .⁹² Wang *et al.* ranked the lattice oxygen activity of MFe_2O_4 ($\text{M} = \text{Cu}$, Ni and Co) by the OTR measured in a TGA: CuFe_2O_4 (maximum weight loss rate =

0.529 wt.% min⁻¹) > CoFe₂O₄ (max. weight loss rate = 0.314 wt.% min⁻¹) > NiFe₂O₄ (max. weight loss rate = 0.307 wt.% min⁻¹).⁹³ They attributed the high activity of the CuFe₂O₄ to the highly reducible Cu²⁺ species, which facilitates fast oxygen release kinetics and synergistically promotes the reducibility of Fe³⁺ species.^{94, 95}

Very often, temperature programmed reduction (TPR) experiments, performed either in a TGA or in a micro-tubular reactor, are used to distinguish the different types of redox active lattice oxygen. On a TPR curve, low temperature peaks (below 500 °C) are typically ascribed to lattice oxygen favoring complete oxidation to CO₂, whereas high temperature peaks correspond to lattice oxygen that are more selective towards syngas generation. Furthermore, lattice oxygen showing reduction peaks above 900 °C are considered kinetically unfavorable for fast chemical looping cycles. For example, H₂-TPR of NiO/Al₂O₃ oxygen carriers shows three reduction peaks, which are ascribed to the reduction of surface NiO, bulk NiO and NiAl₂O₄. The lattice oxygen associated with the first two peaks favour chemical looping combustion whereas the lattice oxygen associated with the last peak is more selective towards syngas production.⁷⁶ Similarly, during the TGA reduction of iron ores in CO/N₂, the three distinct derivative thermogravimetry (DTG) curves can be exactly assigned to the sequential phase transitions of Fe₂O₃→Fe₃O₄→FeO→Fe.^{60, 61, 96}

The use of different reductants during TPR measurements could give very different TPR curves and allows one to probe different properties of the oxygen carriers. For example, the TPR of NiFe₂O₄ in 5 vol.% CO (N₂ balance) shows two reduction peaks around 800 °C, which are assigned to the reduction of NiFe₂O₄ spinel and FeO, respectively.⁷⁸ In contrast, TPR conducted on the same material in 10 vol.% CO (Ar

balance) revealed several more DTG peaks,⁹⁷ suggesting the reduction pathway of: $\text{NiFe}_2\text{O}_4 \rightarrow \text{Ni-Fe}_2\text{O}_3 \rightarrow \text{Ni-Fe}_3\text{O}_4 \rightarrow \text{Ni-FeO} \rightarrow \text{Ni-Fe}$.⁹⁸ Similarly, TPR of ilmenite in low and high CO partial pressures result in one and two DTG reduction peaks, respectively, further signifying the importance of using appropriate reducing gases for TPR.^{61, 80} Wei *et al.* studied Fe-Al-Ni OCs using a combined TGA-XRD approach, which directly established the correlation between the DTG peaks during TPR and the specific phase transformations.⁷⁹ Their results shows that the two DTG peaks could be assigned to the reduction of $\text{Fe}_{0.99}\text{Ni}_{0.6}\text{Al}_{1.1}\text{O}_4$ to Fe_{1-x}O and the subsequent reduction to metallic Fe.

Besides temperature changes, reduction experiments involving pressure changes can also be used to distinguish different types of lattice oxygen. Moldenhauer *et al.*⁵⁹ investigated a series of Mn-Fe-based OCs under CLOU conditions and observed a phase transformation from $(\text{Mn}_x\text{Fe}_{1-x})_2\text{O}_3$ bixbyite to $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$ spinel under high oxygen partial pressure; this phase transition corresponds to the loss of lattice oxygen that is relevant to CLOU. A further phase reduction to $(\text{Mn}_x\text{Fe}_{1-x})\text{O}$ (mangano-wüstite) is observed under low oxygen partial pressure, which is corresponds to the loss of lattice oxygen relevant to chemical looping reforming or gasification.

When using TGA to investigate mixed oxide samples consisting of components that decompose at high temperatures (*e.g.* CuO to Cu₂O at 850-950 °C, Co₃O₄ to CoO at 750-860 °C, and Mn₂O₃ to Mn₃O₄ at 700-850 °C),⁹⁹ the OC's weight loss in the absence of O₂ can be used to deduce the amount of Cu, Mn and, or Co present in the OCs, whereas the weight loss in a more reducing as (*e.g.* H₂) can be used to quantify the content of other redox active components (*e.g.* NiO and Fe₂O₃) present.⁹¹

3.1.3. Surface area

Fig. 8a summarizes the specific surface area of the various OCs, categorized according to the active metal component, *viz.* Mn, Cu, Ni, Co and Fe. In all cases, the surface areas are estimated by the Brunauer-Emmett-Teller (BET) analysis of the nitrogen adsorption-desorption isotherms. From Fig. 8a, it can be seen that, the specific surface area of the different OCs ranges from 0.1 to above 100 m² g⁻¹, primarily because of the difference in the type of supporting material used and the synthesis methods. On average, Ni-based OCs exhibit higher surface areas than the other OCs, probably owing to the fact that NiO is often loaded on high surface area supports.^{23, 100} For Mn, Fe and Cu based oxygen carriers, there is a tendency to use low porosity Mn,⁶⁹ Fe^{101, 102} and Cu^{39, 103} containing natural ores and minerals as the oxygen carriers for CLBP applications. Nevertheless, Mn, Fe and Cu-based OCs with high surface area comparable to that of Ni-based OCs can also be obtained through material synthesis.¹⁰⁰ In the most extreme case, nanostructured oxygen carriers give access to high surface areas up to ~100 m² g⁻¹. The various methods of preparing synthetic oxygen carriers are discussed in details in section 3.2.

Fig. 8. Key characteristics of OCs, including (a) surface area of OCs (The hollow bars represent the range between 25% and 75% quartiles. Data extracted from ^{31, 36-39, 41, 45,}

47, 69, 82-85, 87, 93, 101-111), and (b) crushing strength. (data from ^{21, 29-31, 36, 39, 40, 59, 69, 83, 85-87, 102, 103, 110, 112-115})

Although the external surfaces of the OCs act as the reaction fronts during CLBP reactions, the surface area does not necessarily corresponds to high performance, which also depends on a number of other rate limiting factors, *e.g.* external mass transfer resistance, intraparticle diffusion and product layer diffusion. In addition, structural changes owing to phase changes and sintering could drastically reduce the surface area of the freshly prepared oxygen carriers and alter the reaction kinetics over repeated redox cycles. Therefore, care must be taken when attempting to correlate surface area to the CLBP performance of the OCs.

3.1.4. Mechanical strength

Because CLBP is often conducted in a circulating fluidized beds system, the physical integrity of the OC particles against attrition is also a key criteria to achieving cost effective CLBP. Significant attrition in fluidized beds will result in particle breakage and rapid elutriation of bed mass. To sustain the supply of lattice oxygen to the FR, large amount of fresh OCs must be replenished to the system, giving rise to additional cost, and possibly extra environmental burden.

To address the concern of mechanical strength, many studies measured the crushing strength of the OC particles and used them to characterize the OCs' resistanc against attration. Here, the crushing strengths (the compressive force required to cause a particle to fracture) of the various OCs studied are summarized in Fig. 8b; details of the test conditions can be found in Table S1. Based on the histogram analysis, the majority

(54.1%) of the OC particles tested have crushing strengths between 1 N and 3 N, for both synthetic or natural oxygen carriers. For OC particles in the size range of 180 – 250 μm , 8 out of the 61 (13.1%) measured show crushing strengths below 1 N and are regarded unfit for long-term operation in fluidized beds.^{112, 116} In contrast, OCs with crushing strength >2 N are considered suitable for applications in commercial-scale chemical looping processes.¹¹⁷

Although crushing strength is a representation of a particle's mechanical strength, it does not directly translate to attrition strength, which is the actual physical property reflecting the long-term durability of the OCs in a circulating fluidized bed. Also, crushing strength depends on the particle size, whereas attrition resistance does not. Nevertheless, given the positive correlation between crushing strength and material's resistance against attrition, it is somewhat intuitive to use crushing strength as a semi-quantitative measure to compare the attrition resistance of different OC materials under identical test conditions, when the apparatus for measuring attrition strength is unavailable.

3.2. Preparation of oxygen carriers

3.2.1. Dry synthesis

Dry synthesis methods rely on solid-state reactions between metal precursors at elevated temperatures. The consistency and uniformity of the synthesized oxygen carriers depend on the size and the chemical composition of the precursors used and the temperatures at which solid-state reactions take place. In general, dry synthesis lacks control of the surface area and the structure of the final product. For example, Liu *et*

*al.*⁹⁷ reported that the surface area of NiFe₂O₄ made by solid-state synthesis (2.365 m² g⁻¹) was lower than that made by sol-gel method (4.891 m² g⁻¹). On the other hand, dry synthesis generates little byproducts and offers excellent atom economy, which is an important consideration for sustainable production at large scales.

3.2.2. Wet synthesis

Wet synthesis methods enable more precise control of the OCs' compositions and better-defined structures than dry synthesis. Typical wet methods include coprecipitation, hydrothermal synthesis, sol-gel and wet impregnation. During coprecipitation, the pH of the metal precursors solution is raised by adding alkaline (*e.g.* NaOH, Na₂CO₃ and ammonia), resulting in the precipitation of insoluble oxides, hydroxides and, or carbonates of the metals of interest.⁷⁸ Aging of the precipitates may lead to the formation of composite metal salts with unique meso- and macro- pore structures, such as layered double hydroxides.¹¹⁸ Hydrothermal and solvothermal syntheses represent energy-intensive alternatives to coprecipitation that offers access to unique meso- and macro-porous structures, which can potentially benefit the heat and mass transfer during CLBP cycles. Wet impregnation exploits the pore structures of readily prepared catalyst supports. The permeation of metal precursor solutions into the porous supports and the subsequent drying and calcination give rise to oxide particles that are uniformly dispersed on the support material.⁵² Both methods above require stringent synthesis conditions to ensure optimal and reproducible OC structures. For example, the lack of control of the crystallization of the metal precursors would lead to low specific surface areas and poorly dispersed active metal oxides.¹¹⁹ In contrast, sol-gel chemistry offers easily reproducible recipes for preparing nano-dispersed metal oxides. Therefore, sol-gel is a preferred method for synthesizing mixed

oxides oxygen carriers, such as spinels and perovskites.¹¹¹ In addition to the above, spray drying has been widely employed by researchers who seek to obtain oxygen carrier particles with well-defined particle size distributions for applications in fluidized beds.^{29, 115, 120, 121} In a typical spray-drying preparation, a homogenized slurry of metal oxide precursors is prepared by milling, and then introduced into a spray drier. The spray-drying technique is highly cost effective and easily scalable,¹²⁰ but the final products suffer from low mechanical strength and are prone to attrition.¹²¹

3.3. Oxygen carrier formulation

3.3.1. Mono-metal oxides

3.3.1.1. Mn-based oxygen carriers

Mn-based oxygen carriers give low fuel conversion and oxidation rates. At the same time, they suffer from inferior mechanical stability and thermodynamic limitations.^{28, 122} However, these limitations may be overcome by combining manganese with other metals *viz.* Fe, Ni, Ca, Si, Co and Mg.^{20, 123} The performance of manganese based OCs can be further enhanced by preparing Mn-containing mixed oxides synthetically or use Mn-containing ores, which are discussed in sections 3.3.2 and 3.3.3.

3.3.1.2. Fe-based oxygen carriers

Fe-based OCs are attractive due to their low cost, high sintering resistance and environmentally friendliness.⁴¹ In addition, Fe-based oxygen carrier has a low tendency towards carbon deposition.¹²⁴ The reduced forms of iron oxides also have suitable thermodynamics to be used for chemical looping hydrogen generation.¹²⁵ However, Fe-based OCs generally exhibit relative slow redox kinetics, low fuel conversion, and mediocre oxygen transfer capacity under practical operating conditions of CLBP.¹⁰⁰ To

improve the reactivity and redox stability, Fe-based OC have been supported on inert materials, such as Al_2O_3 , MgAl_2O_4 , SiO_2 , TiO_2 , ZrO_2 (including ZrO_2 stabilized by yttria, MgO or CaO), bentonite and sepiolite.^{23, 126-128} Amongst the various families of OCs, Fe-based oxygen carriers have been the most studied for solid fuel applications.¹²⁹

3.3.1.3. Co-based oxygen carriers

Co-based materials are rarely studied, primarily owing to their unfavorable thermodynamics and their toxicity.^{130, 131} At typical CLBP operation temperatures of $\sim 900^\circ\text{C}$, Co_3O_4 will rapidly decompose to CoO in air, whilst the further reduction of CoO to Co requires strong reducing environment, *e.g.* 95-97 vol.% H_2 or 87-97 vol% CO at 800-1200 $^\circ\text{C}$. Additionally, the low mechanical strength of cobalt oxides further hinders their application at large-scale.⁴¹ Co-based oxides also have a strong tendency to interact with support materials including Al_2O_3 , TiO_2 and MgO , resulting in the formation of unreactive oxide compounds *e.g.* CoAl_2O_4 , CoTiO_3 and $\text{Mg}_{0.4}\text{Co}_{0.6}\text{O}$.^{132, 133} However, cobalt can serve as a very useful dopant for promoting and modulating the redox activity of other redox active metals.²³ For instance, a recent study by Liu *et al.*¹³⁴ reported that cobalt doping in $\text{Ca}_2\text{Fe}_2\text{O}_5$ brownmillerite enhanced the activity of the Fe sites. The authors found that $\text{Ca}_2\text{Fe}_{1.8}\text{Co}_{0.2}\text{O}_5$ is the most suitable for microalgae CLG, showing high H_2 yield, whereas excessive Co doping leads to unselective, complete oxidation. Similarly, Co-doped $\text{Ni}/\text{Al}_2\text{O}_3$ OC is reported to exhibit lowered activation energy for chemical looping methane reforming compared to undoped $\text{Ni}/\text{Al}_2\text{O}_3$.¹³⁵

3.3.1.4. Ni-based oxygen carriers

Ni-based OCs are well-known for their high reactivity and high oxygen release capacity across a wide range of reaction temperatures.¹³⁶ So far, Ni-based OCs are most commonly used to convert gaseous fuels, owing to their high activities towards CH₄ and light hydrocarbons. Lishil Silvester *et al.*¹³⁷ reported the feasibility of using Ni-based OCs to run chemical looping reforming of methane to hydrogen is feasible at temperatures as low as 650 °C. In addition, the reduced Ni metal is catalytically active towards CH₄ activation.¹³⁸ Complete conversion of light hydrocarbons (*viz.* C₂H₆ and C₃H₈) by Ni-based OCs at temperature above 900 °C has also been reported.¹³⁸ However, Ni-based OCs have a low resistance against sintering and a low sulfure tolerance due to the formation of NiS.¹²⁹ When Ni-based oxygen carriers are used, the sulphur content in the fuel should be less than 100 ppm in order to avoid deactivation. Supporting NiO on γ -Al₂O₃, Ca aluminates, MgAl₂O₃ or α -Al₂O₃ could improve the performance of the oxygen carriers. Major drawbacks of Ni-based OCs include the high cost and the ecotoxicity of Ni²⁺, both need to be addressed prior to large-scale application.¹³⁹

3.3.1.5. Cu-based oxygen carriers

Cu-based OCs have received much research attention owing to their high lattice oxygen activity and high oxygen transport capacity.³⁹ Meanwhile, the main disadvantages of Cu-based OCs include their low melting points and poor mechanical strength,¹⁴⁰ *i.e.* CuO must be supported on refractory-type materials, *e.g.* Al₂O₃,¹⁴¹ MgAl₂O₄,¹⁴² CuAl₂O₄,^{143, 144} ZrO₂,^{145, 146} TiO₂-Al₂O₃,^{147, 148} SiO₂,^{149, 150} diatomite,¹⁵¹ bentonite,¹⁵²⁻¹⁵⁴ sepiolite,¹⁵⁵ and olivine,¹⁰³ in order to render resistance against sintering, agglomeration and attrition. CuO's ability to release gaseous oxygen at temperatures

above 800 °C makes it suitable for chemical looping oxygen uncoupling (CLOU). Some supports react with CuO to form less reactive compounds, *e.g.* CuAl₂O₄,^{155,156} whereas others, *e.g.* ZrO₂, are completely inert and can render excellent stability during CLOU of petroleum cokes, coals and wood chars.^{21, 116, 145, 157, 158}

3.3.1.6. CeO₂-based oxygen carriers

CeO₂ is an excellent redox catalyst for the selective oxidation of CH₄ to CO and H₂¹⁶ though the Ce⁴⁺/Ce³⁺ redox couple.¹²⁷ However, CeO₂ alone does not have sufficient amount of redox active lattice oxygen to sustain high rate of fuel conversion and resistance to carbon deposition.¹⁵⁹ On the other hand, CeO₂ can be used as a support material, which is capable of promoting the activity of Fe and Ni-based oxygen carriers, whilst maintain a stable performance over repeated redox cycles.^{100, 134, 160, 161} For example, the comparable lattice parameter between CeO₂ (0.835 nm) and NiFe₂O₄ (0.834 nm) makes CeO₂ an excellent support for NiFe₂O₄, whereas NiFe₂O₄ supported on alumina formed metal aluminates quickly loss activity over redox cycles.¹⁰⁰ Fe₂O₃/CeO₂ shows high catalytic activity, high syngas selectivity, and structural stability,^{127, 162} which are attributed to the enhanced oxygen mobility of the Ce-Fe mixed oxide solid solution.¹³⁹ The role of Ce in promoting lattice oxygen activity has also been exploited by Abou Rached, who found that doping Ce to NiO/Mg-Al-O lowered the temperature of 50% toluene conversion from 407 °C (in the case of undoped NiO/Mg-Al-O OC) to 365 °C.¹⁶⁰

3.3.2. Mixed oxides

As discussed in section 3.3.1 above, each type of mono-metal oxide OC has its unique advantages and drawbacks. To combine the advantages and circumvent the limitations,

researchers turned to mixed oxides containing more than one type of functional oxides. Indeed, many of the mixed oxide OCs show outstanding performance. For example, bimetallic Cu-Fe oxides prepared by sol-gel combustion synthesis (SGCS) are found to be a good candidate OC for CLBP, showing high gas yield, carbon conversion, gasification efficiency, and resistance to tar formation.^{40, 163} The synergy between Cu and Fe oxides is mainly attributed to the formation of new phases, such as CuFe_2O_4 spinel^{40, 164, 165} and perovskites,^{35, 90, 163, 166} Similarly, Wang *et al.*³¹ reported synergy between manganese ore and CuO for biochar conversion. Also, a $\text{Mn}_3\text{O}_4\text{-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ OC showed strong resistance to agglomerating as well as propensity to absorb ash components.¹¹⁵ Two of the most common types of mixed oxides studied in the literature are spinels and perovskites.

3.3.2.1. Spinel

Many mixed oxides OCs contain spinel phases, *e.g.* NiFe_2O_4 , CuFe_2O_4 and CoFeAlO_x ,¹³⁴ Since different redox-active metals specialize in reacting with different types of fuels, multi-metallic spinel OCs can potentially facilitate synergy between metals with different functionalities. Such oxygen carrier formulation is ideal for CLBP, which requires the simultaneous conversion of different hydrocarbon components in the biomass (*e.g.* pyrolysis gas, tar and char) in FR. For example, Ni-Fe spinels show excellent activity in C-C cleavage, C-H cleavage, tar removal and H_2 production.^{34, 97, 167, 168} Additionally, the compositional flexibility of spinel's AB_2O_4 structure makes it easier to further optimize the OC's performance. For example, doping Co to a NiAl_2O_4 spinel could lead to the formation of bimetallic spinels with enhanced redox activities.¹⁶⁹ Chen *et al.*⁴¹ reported the high performance of BaFe_2O_4 in producing hydrogen-rich syngas via CLBG. However, BaFe_2O_4 shows low reactivity with

pyrolysis gas. In general, spinel structured oxides show good resistance to sintering and agglomeration. However, the formation of aluminate based spinels, *e.g.* NiAl_2O_4 , CuAl_2O_4 and MnAl_2O_4 will significantly reduce lattice oxygen activities of the active metal oxides, *e.g.* NiO , CuO and Mn_3O_4 , and must therefore be inhibited.^{69, 122, 170}

3.3.2.2. Perovskites

Perovskite structured oxygen carriers have a general formula $\text{ABO}_{3-\delta}$, where the A sites are occupied by large cations (*e.g.* alkali earth metals and rare earth metals), and the B sites are occupied by smaller, often transition metal cations (*e.g.* Mn , Co , Fe , *etc.*).¹²⁰

Perovskite structured oxides have received increasing attentions as oxygen carriers because of their outstanding redox activities. In particular, the rapid oxygen ion diffusion in the perovskite crystal lattice is facilitated by high concentrations of lattice oxygen vacancies,¹⁷¹ whereas the alkalinity of the A-site cations are good promoters for tar destruction during CLBP.^{172, 173} For example, CaMnO_3 -based perovskites, *viz.* $\text{CaMn}_{0.875}\text{Ti}_{0.125}\text{O}_3$, $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$, and $\text{CaMn}_{0.775}\text{Ti}_{0.125}\text{Mg}_{0.1}\text{O}_{3-\delta}$ have been employed extensively for chemical looping combustion, over a wide range of operational scales, *viz.* from 300 Wth up to 1 MWth.^{120, 174-181} A lifetime of several thousand hours was recorded, together with a small mass loss due to attrition and elutriation.¹⁷⁷ For $\text{LaNi}_x\text{Fe}_{1-x}\text{O}_3$ perovskite oxygen carriers, tuning the Fe to Ni could result in optimal CLBP performance over repeated redox cycles.^{182, 183} When using perovskite OCs, special attentions must be paid to the reversibility of phase changes over long-term redox cycling. For example, deep reduction of CaMnO_3 could result in the irreversible accumulation of CaMn_2O_4 , which is less reactive than CaMnO_3 .¹⁸⁴ A noticeable drawback of using perovskite OCs is their low specific surface areas,¹⁸⁵ which may lead to slower overall surface kinetics.¹⁷¹ Also, practical issues associated

with the use of biomass, including (i) the interaction between the OC and the biomass ashes and (ii) chemical deactivation by sulfur contamination when using fuels with high sulfur contents, must be addressed.¹⁸⁴ Pachler *et al.*¹⁸⁰ reported the formation of crystalline MgS and significant deactivation of the $\text{CaMn}_{0.775}\text{Mg}_{0.1}\text{Ti}_{0.125}\text{O}_{3-\delta}$ OC, when H_2S impurity was present in the fuel. Phosphorus-containing compounds in the biomass are also found to be detrimental to the performance of brownmillerite OCs (a type of perovskite), owing to the OC-ash interaction and the formation of calcium phosphate ($\text{Ca}_5\text{HO}_{13}\text{P}_3$).⁶³ In a different CLBG study conducted using Thai rice straw, the $\text{Ca}_2\text{Fe}_2\text{O}_5$ was reportedly deactivated by the high silica content in the biomass ash, forming CaSiO_3 and Fe_2O_3 after just 3 cycles, accompanied by a drop in hydrogen yield.⁵²

3.3.2.3. Core-shell structured oxygen carriers

Nanostructured oxygen carriers offer functionalities that are inaccessible by conventional mixed oxides.¹⁸⁶ In some oxygen carriers, core-shell structures form spontaneously as a result of phase segregation. For example, the redox cycling of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ results in the diffusion of iron cations from the interior of the OC particle to the surface to form an Fe_2O_3 shell and an Al_2O_3 core.¹⁶ In this case, the core-shell structure formed will facilitate rapid sintering and is undesirable. However, rational design of core-shell structures can potentially maximize synergistic effects between different functional components. For instance, a redox active core and a thermally stable shell can maximize the resistance to sintering, as the shell creates a physical barrier that prevents the core materials from migration. Indeed, a core-shell structured $\text{CaO-CuO/MgO@Al}_2\text{O}_3$ material (CCMA), prepared by a self-assembly template synthesis (SATS) technique, showed a high resistance to agglomeration (CaO and CuO)

over 30 chemical looping.¹ As a result, CCMA shows 10% higher oxygen donation capacity than its compositional equivalent prepared by wet-mixing. The same core-shell structure also offered stable CO₂ uptake capacity of around 0.55 g-CO₂/g-CaO over 30 chemical looping cycles.

3.3.3. Natural ores, minerals and waste residues

The use of natural ores, minerals and their derivatives as oxygen carriers is preferred by large-scale chemical looping processes because of the availability of the natural materials and simple production processes compared to synthetic OCs.⁶⁶ Fig. 9 summarizes the compositions, in wt.% of functional oxides, of selected natural material-derived OCs.

Fig. 9. The bulk compositions of selected natural OC materials. (*: black close circles represent carbon conversion efficiency, while open circles represent carbon capture efficiency) (Details of the fuels, OCs, chemical looping systems and their key operation parameters are provided in Table S2. Data are reproduced from ^{37, 46, 54, 57, 60, 61, 68, 87, 113, 187-}

From Fig. 9, it can be seen that, amongst the various natural material derived OCs, hematite ores contain the most redox active metal oxides (78.1 - 95.4 wt.%), whereas Cu ores and Mn ores contain 21.0 - 54.3 wt.% CuO and 3.1 - 43.4 wt.% MnO, respectively. Manganese ores have gained much research attention recently owing to their high reactivity towards char.⁶⁹ In particular, the deposition of alkali metals (Na, K) from the Mn ores to the char particles is considered responsible for the high rate of char gasification¹⁹⁰ However, this promotional affect wore off soon after the depletion of Na and K in the Mn ores. Screening the manganese ores of different origins revealed that the ores from brazil, Australia and Gabon exhibit high reactivities and good fluidization properties.¹⁹¹ These advantages, however, are compromised by the high attrition rates¹⁹² and the low durability.¹⁹³ Depending on operation conditions, the lifetimes of Mn ores are estimated to be *ca.* 100 - 400 h.¹¹³ It is also reported that the chemical interaction with ash will severely deteriorate the performance of manganese ores.¹⁹⁴

Natural copper ores have also been investigated for CLBP, considering their low cost and high natural abundance.³⁹ For example, a natural Cu-Fe based ore has shown good resistance against sintering, agglomeration, and attrition over 10 hours of CLOU operation using anthracite as the fuel.⁶⁸

Another commonly used natural oxygen carrier is ilmenite, which is a special class of iron ore. Under chemical looping comditions, ilmenite undergoes reverse phase segregation, forming iron oxide on the particles' surface and TiO₂ in the cores. Potassium fixation may be achieved simultaneously through the formation of KTi₈O₁₆.¹⁹⁵ Comparing to other types of iron ores, ilmenite can access a higher OTC

via its two-step reduction: $\text{FeTiO}_5 \rightarrow \text{FeTiO}_3 \rightarrow \text{Fe/TiO}_2$ under strong reducing conditions.⁶¹ Concurrently, ilmenite exhibits high activities towards syngas conversion and tar reforming in the fuel reactor,^{196, 197} whilst demonstrating high resistance against carbon deposition and Fe_3C formation.¹⁹⁸

Many of the natural materials are mixed oxides themselves. Therefore, when developing natural material-based OCs, the interaction between the redox active components (*i.e.* transition metal oxides) and the “impurities” could lead to different consequences. For example, copper ores/slugs containing a large fraction (23.9-70.1 wt.%) of CuFe_2O_4 show activity comparable to that of CuO .¹⁶⁵ Liu *et al.*¹⁶⁶ also reported that CuFe_2O_4 spinel is a promising oxygen carrying material, owing to its high reactivity during CLBPs. The presence of iron oxide (12.9-53.6 wt.%) and CuFe_2O_4 spinel in manganese ores and copper ores/slugs helps to promote the redox activities, thermal stability and mechanical strength of the low-cost OCs.¹⁹⁹ Similarly, Deng *et al.*⁵⁷ reported a relatively high (70.2%) carbon conversion during CLBP of sewage sludge (SS), when copper slag with high Fe_2O_3 content was used as the oxygen carrier, with no chemical interaction between the copper slag and the SS ash. Other “impurities” in natural minerals could also lead to synergistic effects. For instance, the presence of CaO renders the possibility to achieve sorbent-enhanced fuel conversion,^{33, 43} whereas CaO in iron ores gives rise to the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$ brownmillerite, which is a suitable oxygen carrier for CLBG.²⁰⁰ The presence of MgO in the natural minerals leads to the preferential formation of MgAl_2O_4 , inhibiting the formation of unreactive spinel compounds between redox active metal oxides and Al_2O_3 .¹ Furthermore, the alkalinity of MgO makes it an excellent coking inhibitor.¹³⁹ In contrast, although SiO_2 is ubiquitously found in most natural minerals, chemical interaction between transition

metal oxides and SiO_2 leads to accelerated sintering and deactivation, owing to the low melting points of silicate eutectics.⁶ Given the significance of interactions between active metal oxides and impurities, the functionalities of the other impurities commonly present in natural mores and minerals, *e.g.* P_2O_5 , ZnO , V_2O_5 , should also be carefully studied and fully understood in future investigations.

4. Operando characteristics of oxygen carriers

This section evaluates and compares the performance of different OCs under similar working conditions. The results of comparison are graphically presented in Figs. 10 and 11. To elucidate the structural-functional relationships of the OCs formulations, we attempt to analyze the oxygen carriers performance based on a few key indicators, as discussed below.

4.1. Biomass conversion

The OCs' ability to convert biomass to gaseous products is characterized by carbon conversion, as plotted in Fig. 10. Generally speaking, carbon conversion increases with increasing gasification temperature and also strongly depends on the type of OC used. For example, 60 wt.% CuO supported on calcium aluminate cement has 30% higher carbon conversion than 60 wt.% Fe_2O_3 on calcium aluminate cement.³⁵ Carbon conversion is also indicative of the compatibility between the OC and the biomass. For instance, only 40% carbon conversion is achieved by natural hematite during chemical looping waste cooking oil reforming,³⁷ meaning that Fe-based OCs are not ideal for oil reforming, which requires catalytic activity towards hydrocarbon cracking, and is better performed by Ni-based OCs.^{18, 76} Overall, a number of generalizations can be made. First, the presence of calcium significantly enhances the H_2 yield by taking up CO_2 and

shifting the equilibrium to syngas production.³⁶ Secondly, natural ores of different origins, *e.g.* hematite from Australia ($\text{Fe}_2\text{O}_3_{\text{AU}}$) vs. hematite from China ($\text{Fe}_2\text{O}_3_{\text{CH}}$) could have drastically different performance in CLBP.³⁷ Thirdly, bimetallic oxides present synergistic improvements in biomass conversion, as exemplified by the case of Fe-Cu-O mixed oxides.³⁵ The synergy between different redox active metal oxides is further discussed in sections 3.3.2 and 4.5.

Fig. 10. Comparison of carbon conversion efficiency and gas yield (including CO, CH₄, H₂, and CO₂ unless otherwise stated) by different OCs under comparable operational conditions. (Details of biomass, OC, chemical looping system and their key operational parameters are provided Table S5. Data were reproduced from³⁴⁻⁴¹)

4.2. Selectivity

H₂, CO, CH₄ and CO₂ are the major gaseous products of CLBP. The gas mole fraction of each species, plotted in Fig. 11, reflects the characteristics of both the biomass and the OCs. By comparing the product gas compositions of CLBP using the same biomass, the correlation between the OC formulation and product selectivities can be elucidated. In general, Cu-based OCs favor complete oxidation to produce CO₂ (Fig. 11a). Co-doped brownmillerite oxides (Ca₂Fe_{2-x}Co_xO₅, $x = 0 - 1$) show high CO₂ selectivity during the CLBP of microalgae (Fig. 11h). The addition of CaO to the Fe-based OCs suppressed CO₂ concentration during coal gasification, as depicted in Fig. 11i, owing to the reaction between CaO and CO₂ (R8, Table 1). However, the practical availability of CaO to remove CO₂ also depends on the operating conditions. Below 800 °C, the reduction of calcium ferrite is kinetically sluggish, thereby inhibiting the precipitation of CaO from the iron ferrite and the subsequent CO₂ uptake, resulting in little change in product gas composition with increasing CaO content (Fig. 11c).⁵² During chemical looping oil reforming, bi-metallic ferrites (MFe₂O₄, M = Ni, Co, Cu, Ba) yields significantly more hydrogen (Fig. 11e) and less methane than monometallic NiO-based OCs or iron ores (Figs. 11d and 11g), whereas a bed of inert Al₂O₃ only produced large quantities of CH₄ and H₂ via pyrolysis. These findings highlight the catalytic activity of spinel ferrites during methane reforming, while toluene cracking takes place in the gas phase.³⁴

Fig. 11. Comparison of product gas composition (vol. %) by different OCs under comparable operation conditions. (Details of biomass/fuel, OC, chemical looping system and key operating parameters can be found in Table S5. Data were reproduced from ^{34-41, 52})

4.3. Interaction between OCs and ash

One unique feature of CLBP is the high ash contents, which typically comprise of Ca, K, Si, Mn, Al, S, Fe, P, Cl, Na and other trace elements.^{66, 194} Fine ash particles can be removed from the chemical looping system using specifically designed cyclones. However, it is practically impossible to completely separate the ash from the OC particles. Also, sufficiently long residence time of the ashes in the chemical looping system will result in chemical reactions between the oxygen carriers and the ashes.¹⁸⁴

On one hand, the reaction between alkali metals and silica produces glassy alkali silicates with low melting points, which can induce rapid particle agglomeration and eventually defluidization.^{201, 202} For example, severe agglomeration of Cu-based OCs occurred when biomass was used as the fuel, owing to the formation of low melting point eutectics between the OC and the biomass ash. On the other hand, the high alkali metal content of biomass ashes (*cf.* coal ash) can catalyze char gasification. For instance, biomass with a high ash content, *e.g.* 20 wt.% was used to promote the redox activity of Fe-based OCs. This promotion effect is ascribed to the formation of ilmenite-type mixed oxides.²⁰³ Gu *et al.*²⁰⁴ used a biomass ash to decorate iron ore for chemical looping hydrogen production and found enhanced redox activity due to the formation of K-Fe-O species. However, the high ash content (>10 wt.%) also negatively impacted on the H₂ yield, whereas the Si-rich biomass ash resulted in the formation of K-Si-O species, which accelerated sintering and OC deactivation. In a separate study by Shen *et al.*,²⁰⁵ no interaction between pine sawdust ash and the iron ore was observed after 78 h of continuous operation. Based on the different results, it can be seen that the extent of ash-OC interaction depends on both the nature of the OCs and the type of biomass used.

In recent years, investigations into ash- OC interaction have led to deeper insights. The development of ash layers over the surface of OC particles can be described by one of the three modes:²⁰⁶ (a) inert bed materials act as ash carriers, which transport new ashes and deposit them on the exterior surfaces of the OC particles, (b) the chemical reaction between the OC and the ash elements drives a net migration of ash components to the interior of the OC particles, and (c) a combination of (a) and (b). Experimental observations suggest that (c) is the most encountered mode of ash-OC interaction.^{189,}

²⁰⁷ For example, Corcoran *et al.*¹⁸⁸ reported the migration of potassium and calcium from the ash layer into the ilmenite particle, forming $\text{KTi}_8\text{O}_{16.5}$ and CaTiO_3 , respectively. At the same time, a calcium layer mixed with other ash components (*e.g.* Si and P) gradually developed over the surface of the ilmenite particles.

4.4. Carbon deposition

The formation of solid carbon (*i.e.* coking) deactivates the OCs by covering the redox active sites.³⁴ The extent of carbon deposition depends on a number of parameters, including temperature, pressure, type of fuel used, the gas phase environment, the availability of redox active lattice oxygen on the surface of oxygen carriers and the presence of active sites that catalyze coking.²⁰⁴ In general, coking is favored on oxygen carriers whose concentration of redox-active lattice oxygen is low.²⁰⁴ For instance, carbon deposition is absent during the reduction of highly redox active NiFe_2O_4 by CO ,⁷⁸ whereas an early onset of carbon deposition was observed when methane was used as the fuel during the reduction of $\text{Ca}_2\text{Fe}_2\text{O}_5$.¹⁰⁶ Carbon deposition also depends on the metal's ability to catalyze C-C bond cleavage. Amongst the 3d transition metals, Ni is the best cracking catalyst and is also the most prone to carbon deposition, followed by Co, Fe, Mn and Cu.⁴¹ In cases when heat management, hydrogen balance and oxygen balance are not primary concerns, carbon deposition can be effectively suppressed by injecting small amount of water into the fuel reactor.²⁰⁸ However, to fundamentally solve the problem of carbon deposition, coking-resistant oxygen carriers should be used.²⁰⁹ To this end, OCs containing alkali or alkaline earth metal elements, *e.g.* calcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$), emerge as promising formulations for suppressing coke deposition.²¹⁰ Supporting Ni on rare earth oxides, *e.g.* CeO_2 and La_2O_3 , which contains active lattice oxygen, is also an effective means to mitigate carbon deposition.²¹¹

4.5. Bifunctionality

During CLBP, mixed oxides oxygen carriers often show synergistic effects arising from (1) and the formation of new phases with superior redox activity and, or (2) bifunctionality of oxygen carriers containing more than one functional components. The first type of synergy is discussed in detail in section 3.3.2, whereas the second type of synergy has also been mentioned in numerous occasions above.

One example of bifunctionality is the use of mildly reducible supports (*e.g.* CeO_2) to enhance the redox kinetics of the active components of the OCs (*e.g.* NiFe_2O_4).¹⁰⁰ A second type of bifunctionality involves integrating surface acid/basic properties with redox activity. For example, in a OC containig iron oxide supported on attapulgite (ATP),²¹² the CaO content acts as a promoter and catalyzes the reaction kinetics of CLBP. Other types of commonly observed bifunctionalities include the enhancement of sintering resistance and mechanical strength by Al_2O_3 supports^{58, 213, 214} and the promotion of char gasification by alkali metal dopants, *e.g.* K, Na and Li.²¹⁵

4.6. Irreversible phase transformations

Reversible phase transformation is a key feature accompanying the redox cycling of oxygen carriers, whereas irreversible phase transformations are also widely reported and regarded as mode of OC deactivation. Since many OCs used in CLBP consist of mixed oxides, chemical interactions between different oxide phases to form new phases is often thermodynamically inevitable. These changes could be further accelerated by high temperatures and redox cycles. Table 2 presents selected examples of irreversible phase changes over chemical looping cycles.

We categorize the irreversible phase changes into (type-1) decomposition and phase segregation and (type -2) phase combination. In a mixed oxide oxygen carrier, both types of phase changes could take place simultaneously.

Type-1. Irreversible phase decomposition and segregation are commonly observed during chemical looping. Experimentally, irreversible phase segregation can be tracked by XRD, and is manifested by the disappearance of a multi-metallic oxide and the emergence of diffraction peakings belonging to a mixture of newly formed phases.^{42, 56} For example, Fan *et al.*¹⁶ report the formation of Fe₂O₃/TiO₂ core-shell structures due to phase segregation, which is considered undesirable to the cyclability of oxygen carriers. Ultimately, irreversible phase decomposition and phase segregation will lead to locally concentrated clusters of metal oxides, compromising the metal-support interaction that is essential to provide sintering resistance and mechanical strength.

Type-2. Phase combination refers to the chemical reaction between two- or more oxides to accumulatively form new multi-metallic oxide phases during redox cycles. This should be distinguished from the intentional synthesis of multi-metallic oxides such as spinels and perovskites, which have been readily formed prior to chemical looping cycles. For example, the unintentional formation of spinel-type bimetallic oxides has been extensively reported for active metal oxides supported on alumina.^{1, 111, 119} According to Keller *et al.*,¹⁰⁸ the use of LD stone (iron-based natural material) as OCs yielded complex iron-containing minerals, *e.g.* Ca₂Fe_{1.2}Mg_{0.4}Si_{0.4}O₅ and (Fe, Mg)SiO₃, owing to the chemical reaction between Fe₃O₄, Ca₂SiO₄, MgO, SiO₂ and Ca₃Mg(SiO₄)₃. In this case, Fe species are trapped in an inert mineral, resulting in chemical deactivation of the OCs.

Table 2. Irreversible phase changes of different OCs before and after biomass chemical looping cycles.

Oxygen carriers	Before chemical looping	After chemical looping
LD-slag ⁸⁴	Mg _{1-x} Fe _x O, Ca ₂ Fe _{3-x} B _x O ₅ , (CaO) _x SiO ₂ , <u>Ca(OH)₂</u> , <u>CaCO₃</u> , CaO	Mg _{1-x} Fe _x O, <u>Fe_{3-x}A_xO₄</u> , Ca ₂ Fe _{3-x} B _x O ₅ , (CaO) _x SiO ₂ , CaO
NiFe ₂ O ₄ ⁵⁶	NiFe ₂ O ₄	NiFe ₂ O ₄ , <u>Fe₂O₃</u> , <u>SiO₂</u> , <u>Al₂O₃</u> (after 20 cycles)
natural iron ore ⁴²	90 wt.% Fe ₂ O ₃ , 6.78 wt.% SiO ₂	Fe ₂ O ₃ , SiO ₂ , <u>MgO</u> (after 20 cycles)
CaMn _{0.775} Mg _{0.10} Ti _{0.125} O _{3-δ} ¹⁰⁸	CaMn _{0.9} Ti _{0.1} O _{0.962} , MgO	CaMn _{0.9} Ti _{0.1} O _{0.962} , MgO
CuO/MgAl ₂ O ₄ ¹⁰⁸	CuO, MgAl ₂ O ₄	MgAl ₂ O ₄ , <u>Cu₂O</u> , CuO, <u>Cu</u>
CuO/ZrO ₂ ¹⁰⁸	CuO, ZrO ₂	CuO, ZrO ₂
Fe ₂ O ₃ /α-Al ₂ O ₃ ¹⁰⁸	Fe _{1.84} Al _{0.16} O ₃ , α-Al ₂ O ₃	Fe _{1.84} Al _{0.16} O ₃ , α-Al ₂ O ₃
Fe ₂ O ₃ /MgAl ₂ O ₄ ¹⁰⁸	Fe ₃ O ₄ , Mg(Al, Fe) ₂ O ₄ , <u>MgO</u>	Fe ₂ O ₃ , Mg(Al, Fe) ₂ O ₄
La _{0.8} Sr _{0.2} FeO ₃ unsupported ¹⁰⁸	La _{0.8} Sr _{0.2} FeO ₃	La _{0.8} Sr _{0.2} FeO ₃
La _{0.8} Sr _{0.2} FeO ₃ /γ-Al ₂ O ₃ ¹⁰⁸	La _{0.8} Sr _{0.2} FeO ₃ , θ-Al ₂ O ₃ , α-Al ₂ O ₃	La _{0.8} Sr _{0.2} FeO ₃ , θ-Al ₂ O ₃ , α-Al ₂ O ₃
Mn ₃ O ₄ /ZrO ₂ ¹⁰⁸	ZrO ₂ , Mn ₃ O ₄ , <u>MnO</u>	ZrO ₂ , Mn ₃ O ₄
NiO/α-Al ₂ O ₃ ¹⁰⁸	NiO, NiAl ₂ O ₄	NiAl ₂ O ₄ , NiO, <u>Ni</u>
Bauxite ¹⁰⁸	Fe ₂ O ₃ , α-Al ₂ O ₃ , δ-Al ₂ O ₃	α-Al ₂ O ₃ , γ-Al ₂ O ₃ , Fe ₂ O ₃
Ilmenite ¹⁰⁸	Fe ₂ TiO ₅ , <u>Fe₂O₃</u> , TiO ₂	<u>Fe_{1.698}Ti_{0.228}O₃</u> , TiO ₂ , Fe ₂ TiO ₅
LD stone ¹⁰⁸	SiO ₂ , Fe ₃ O ₄ , <u>Ca₃Mg(SiO₄)₃</u> , Ca ₂ SiO ₄ , MgO	<u>Ca₂Fe_{1.2}Mg_{0.4}Si_{0.4}O₅</u> , Fe ₃ O ₄ , Ca ₂ SiO ₄ , <u>CaO</u> , <u>(Fe, Mg)SiO₃</u> , SiO ₂
Iron ore ¹⁰²	Fe ₂ O ₃ , SiO ₂ , <u>CaO</u> , <u>MgO</u>	Fe ₂ O ₃ , SiO ₂
Ni-based OC ⁶⁴	NiO, NiAlO ₄	NiO, NiAlO ₄ , <u>Al₂O₃</u> , <u>Ni</u> , <u>SiO₂</u> , <u>CaAl₂Si₂O₈</u>
Iron-containing silicate mineral ²¹⁶	<u>chrysotile and lizardite</u> , <u>magnetite</u>	<u>hematite</u> , <u>forsterite</u>
CuO/olivine OC ³¹	Mg _{1.826} Fe _{0.159} Ni _{0.015} SiO ₄ , <u>MgCu₂O₃</u> , MgSiO ₃ , CuO	Mg _{1.826} Fe _{0.159} Ni _{0.015} SiO ₄ , MgSiO ₃ , CuO, <u>MgO</u>
CMO (CuO + manganese ore) ³¹	CuMn ₂ O ₄ , SiO ₂ , <u>Fe₂O₃</u> , CuO	CuMn ₂ O ₄ , SiO ₂ , CuO
Copper ore ⁶⁸	CuO, CuFe ₂ O ₄ , <u>SiO₂</u> , <u>CaSO₄</u>	CuO, CuFe ₂ O ₄
Cu-Fe OC ¹⁰⁴	Fe ₂ O ₃ , <u>CuFe₂O₄</u> , <u>CuO</u>	Fe ₂ O ₃ , <u>CuFeO₂</u> , <u>Fe₃O₄</u>
Manganese ore (Morro da Mina) ¹⁹²	(Mn,Fe) ₃ O ₄ , Fe ₃ O ₄ , Mn ₇ SiO ₁₂ , <u>SiO₂</u> , unidentified	Fe ₃ O ₄ , Mn ₇ SiO ₁₂ , unidentified
Manganese ore (Tshipi) ¹⁹²	(Mn, Fe) ₃ O ₄ , <u>Mn₇SiO₁₂</u> , <u>SiO₂</u> , CaO, unidentified	(Mn, Fe)O/CaO, Fe ₂ O ₃ , unidentified
Manganese ore (Guizhou) ¹⁹²	(Mn, Fe) ₂ O ₃ /Fe ₂ O ₃ , <u>Fe₃O₄/Mn₂AlO₄</u> , Mn ₇ SiO ₁₂	(Mn, Fe) ₂ O ₃ /Fe ₂ O, <u>(Fe, Si)₃O₄/Mn₂AlO₄</u> , <u>Mn₂O₃</u> , Mn ₇ SiO ₁₂ , <u>Mn₃₂Al(SiO₄)₃</u> , amorphous

Manganese ore (Braunite) ¹⁹²	<u>Mn₇SiO₁₂</u> , (Ca, Mn)O, unidentified	<u>(Mn, Fe)₂O₃/Fe₂O₃/Mn₂O₃</u> , (Ca, Mn)O
Manganese ore (Elwaleed C) ¹⁹²	(Mn, Fe) ₂ O ₃ /Fe ₂ O ₃ , (Mn, Fe) ₃ O ₄ , <u>Fe₃O₄</u> , <u>CaMn₁₄SiO₂₄</u> , amorphous, unidentified	(Mn, Fe) ₂ O ₃ /Fe ₂ O ₃ , (Mn, Fe) ₃ O ₄ , <u>SiO₂</u> , unidentified
Cu14- γ Al ⁸²	γ -Al ₂ O ₃ , CuO, CuAl ₂ O ₄	γ -Al ₂ O ₃ , <u>α-Al₂O₃</u> , CuO, CuAl ₂ O ₄
Ni18 α Al ⁸²	α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄	α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄
Ni21 γ Al ⁸²	γ -Al ₂ O ₃ , NiAl ₂ O ₄	γ -Al ₂ O ₃ , <u>NiO</u> , NiAl ₂ O ₄
Fe20 γ Al ⁸²	α -Al ₂ O ₃ , Fe ₂ O ₃	α -Al ₂ O ₃ , Fe ₂ O ₃
Iron ore (Tierga) ¹⁰²	Fe ₂ O ₃ , SiO ₂ , <u>CaO</u> , <u>MgO</u>	Fe ₂ O ₃ , SiO ₂
Metal ferrite ⁹³	MFe ₂ O ₄ (M=Fe, Ni, Co)	MFe ₂ O ₄ (M=Fe, Ni, Co)
Note: underscore “_” is applied for compounds when their mineral phases are different before and after the chemical looping processes.		

4.7. Physical integrity

The physical integrity of the oxygen carriers is a key to ensure the steady-state performance over prolonged cyclic operations. The changes in the OCs' physical properties, including BET surface area, OTC, crushing strength and attrition, before and after the chemical looping cycles, are plotted in Fig. 12. From Fig. 12, it can be seen that, most OCs (~75% of the data set) show reduced BET surface area over cycling, with an average fractional reduction of $40.6 \pm 20.0\%$. NiFe₂O₄ shows the most loss in surface area, *viz.* 83.7% (for NiFe₂O₄) of its initial value⁹³. The loss of OCs' surface areas is commonly attributed to sintering and agglomeration.^{67, 217} However, in specific cases, *e.g.* CuFe₂O₄,⁹³ CuO supported on olivine¹⁰³ and Fe₂O₃ supported on Al₂O₃,⁴⁵ oxygen carriers gain additional surface areas after chemical looping cycles. This phenomenon originates from the generation of additional porosity inside the OC particles over repeated redox cycles.¹⁰³

Carbon deposition does not directly contribute to sintering.²¹⁸ However, the burning of the deposited carbon in AR may result in local temperatures surges that could accelerate sintering. The measured crushing strengths follow a similar trend to BET surfaces areas,

i.e. lower crushing strengths after chemical looping cycles. Although the BET surface area, crushing strength and particle mass of oxygen carriers generally decrease over redox cycles, most studies report relatively stable oxygen transfer capacities (OTC), which do not appear affected by the physical deterioration.^{20, 117, 121} It should be noted, however, that the apparently stable OTCs may be a result of OCs being in large excess during the chemical looping experiments, and do not accurately reflect the true OTCs of individual OC particles.

Fig. 12. The variation of BET, OTC, crushing strength and attrition of OC before and after chemical looping processes. (BET data was reproduced from^{31, 36, 37, 45, 47, 82, 84, 85, 93, 101-109}. OTC data was reproduced from^{82, 84, 85, 102}. Crushing strength data was reproduced from^{31, 36, 59, 85, 102, 103}. Attrition data was reproduced from^{59, 84, 117})

5. Summary and perspective

5.1. Rational design of oxygen carriers

We summarize the historical development of oxygen carriers in several stages, as depicted in Fig. 13. During the first stage, mono-metal oxides (mostly 3d transition metal oxides) were screened experimentally for their performance under CLBP conditions. Natural material-derived OCs are often used directly after simple mechanical and thermal treatment, whereas the performance of synthetic OCs are improved by supporting them on a secondary, and usually inert oxide materials. In the second stage, experimental investigations identify practical issues leading to loss of OTC (*e.g.* including sintering, irreversible phase change, attrition and carbon deposition), and further solutions for improvements are sought. In the third stage, the lattice oxygen activities are fine-tuned by formulating mixed oxides phases such as spinels, perovskites and their solid solutions. More recently, researchers have started developing oxygen carrier formulations consisting of multiple functionalities; the effectiveness of each functionality can be further maximized by preparing nano-structured oxygen carriers.

Fig. 13. Schematic overview of the developments of OCs for CLBPs. (Note: red sectors represent the fractional OTC. Figures a-d corresponds to negative impact on OTC during CLBP, and figures e-f correspond to positive impact on OTC during CLBP)

Based on the present review, which examines how different oxygen carrier formulations perform under various CLBP applications, we propose a general strategy for designing and developing oxygen carriers for CLBP, as depicted in Fig. 14. First of all, the types of biomass and the targeted products are defined. Then, existing OC formulations that are known to be suitable for the specific applications are identified, *e.g.* CuO-based oxygen carriers for applications requiring CLOU and Ni-based oxygen carriers for applications involving long chain hydrocarbons. In the case when no suitable OC formulation can be found in the literature, new OCs are developed, following the structural-functional relationships outlined in sections 3 & 4. Specifically, attention should be paid to (1) possible phase interactions between the different oxide components, (2) tuning lattice oxygen activity based on the requirement for product selectivity, and (3) chemical interaction with impurities and biomass ashes. Candidate formulations showing favorable CLBP performance in high throughput reactors (*e.g.* TGAs and micro packed bed reactors) should be subjected to further engineering development to address practical issues such as (5) mechanical strength against attrition, (6) scaled-up synthesis, (7) further cost reduction and (8) environmental performance of the OC over its entire life cycle.

Fig. 14. Rational design principals in an upscaled CLBP application.

5.2. Scaling up

Benefiting from the advancements in the research on oxygen carriers, the development of CLBP has been encouraging. The key performance indicators, *e.g.* carbon conversion efficiency, hydrogen yield, *etc.* demonstrate the effectiveness of CLBP.²¹⁹ Despite the promising experimental results, most CLBP studied were performed at lab-scale. Therefore, more pilot scale studies are urgently needed in order to verify the feasibility CLBP at industrial scales. These studies will also enrich our understanding of the behavior of OCs under realistic operation conditions.

The chemical looping technologies have been demonstrated at pilot scales around the globe. The scale of the pilot plants vary from 10 kWth¹⁶ to 3 MWth.²²⁰ Most of the pilot plants are designed for the chemical looping combustion of coal. Alternative chemical looping technologies being demonstrated at pilot scales include chemical looping

hydrogen production (CLH, 30 kWth – 3 MWth)²²¹ and CLBP (30 – 500 kWth),⁸² both using Fe-based oxygen carriers.

The scales at which various OCs are evaluated are graphically compared in Fig. 15. From Fig. 15 (a), it can be seen that, although Ni-based OCs are the second most studied at lab scale, Mn-based OC have advanced further into large scale testing owing to the availability of highly redox-active manganese ores. Indeed, for commercial-scale deployment, both cost and environmental considerations favor the use of Fe and Mn-based ores over Ni and Cu based OCs, which merely have high theoretical OTCs.²²² While mono-metal oxide OCs dominated the early pilot scale studies, the lack of functionality of single-phase oxygen carriers limited their performance and potential for large-scale application *cf.* multiphase OCs and natural minerals (Fig. 15b). Therefore, the focus of OC development has gradually shift towards the use of low-cost natural minerals and multifunctional mixed oxide materials in the past decade.²²³

Fig. 15. Inventory of literature-reviewed different operation scales by the CLPs opted by various OC types. (Data adapted from ^{66, 221, 223-226})

5.3. Environmental aspects

Conceptually, chemical looping biomass processing is a low carbon technology that efficiently converts biomass to syngas for sustainable chemical production.²²⁷ Additionally, other environmental aspects associated with the production and supply of biomasses, the life cycle of OCs and the disposal of ash, must also be understood by scientific approaches, *e.g.* life cycle analysis (LCA).²²⁸

The LCA study by Petrescu *et al.* found that hydrogen produced from a Fe-based chemical looping process with simultaneous CO₂ capture showed significantly better environmental performance than conventional steam reforming.²²⁹ The use of non-aqueous phase bio-oil could further reduce the net fossil energy input (FEI) and net GWP to 0.597 MJ and 0.0767 kg CO₂ per MJ H₂, respectively,²³⁰ suggesting the additional environmental benefit of CLBP over fossil-fuel based chemical looping processes. However, LCA studies that take into account the lifecycle of oxygen carriers is rarely reported. Typically, the preparation of OCs impacts the environment through the energy consumption, waste water generation and emission of toxic gases and fumes²³¹. Thorne *et al.*²³² conducted a LCA study accounting for the OC's contributions to the overall environmental performance of chemical looping processes. The authors found that, if the OCs are prepared by lab-based procedures, the GWP is dominated by the energy consumption of OC processing. Only when the processing parameters are optimized and the lifetime of OC is substantially improved, the environmental performance of CLC can be more favorable than the benchmark conventional technology (*viz.* conventional combustion with post-combustion capture by amine scrubbing). Based on the findings above, OCs derived from natural minerals are likely to have better environmental performance than the synthetic ones, unless there is a

breakthrough in the development of synthetic oxygen carriers with outstanding performance and extremely long lifetimes during CLBP.

6. Conclusion

The development of oxygen carriers for chemical looping biomass processing, an emerging biomass conversion technology, has benefited from the research thrust in oxygen carriers development for a variety of chemical looping applications. The improved understanding of the behavior of oxygen carriers during chemical looping cycles enables the formulation of highly active, highly selective, multifunctional oxygen carriers with well-tuned lattice oxygen activities and good cyclic durability. In particular, spinel structured bimetallic metal oxides, *e.g.* NiFe_2O_4 and CuFe_2O_4 have shown excellent activities towards biomass conversion, whereas oxygen carriers derived from natural materials, *e.g.* iron ore and manganese ores have been employed to successfully demonstrate CLBP at pilot scales. We also note the effectiveness of incorporating surface basicity and redox activity in OC formulation to mitigate carbon deposition. The potential phase interactions between different oxide components in the mixed oxides OCs and the chemical interaction between the OCs and the biomass ashes also need to be understood in order to design oxygen carriers with stable cyclic performance. Admittedly, much of the knowledge about oxygen carrier performance are obtained from bench-top studies under idealized conditions. Therefore, there is an apparent need for more studies using realistic biomass and biofuel feedstocks to better understand the practical requirements for oxygen carriers for CLBP. For large scale deployment of CLBP, the oxygen carrier formulation must also be economically viable and environmentally justifiable.

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