Chemical looping beyond combustion – a perspective

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As a promising approach for carbon dioxide capture, chemical looping combustion has been extensively investigated for more than two decades. However, the chemical looping strategy can be and has been extended well beyond carbon capture. In fact, significant impacts on emission reduction, energy conservation, and value-creation can be anticipated from chemical looping beyond combustion (CLBC). This article aims to demonstrate the versatility and transformational benefits of CLBC. Specifically, we focus on the use of oxygen carriers or redox catalysts for chemical production – a $4$ trillion industry that consumes $40.9$ quadrillion BTU of energy. Compared to state-of-the-art chemical production technologies, we illustrate that chemical looping offers significant opportunities for process intensification and exergy loss minimization. In many cases, an order of magnitude reduction in energy consumption and CO\textsubscript{2} emission can be realized without the needs for carbon dioxide capture. In addition to providing various CLBC examples, this article elaborates on generalized design principles for CLBC, potential benefits and pitfalls, as well as redox catalyst selection, design, optimization, and redox reaction mechanism.

1. Introduction

Although the term “chemical looping” was first minted by Richter and Knoche in 1983 in the context of reducing exergy loss in fossil fuel combustion,\textsuperscript{1} the concept of chemical looping (CL), i.e. decomposition of a chemical reaction into multiple sub-reactions facilitated by solid reaction intermediates, was investigated long before that.\textsuperscript{2,3} Owing to the pressing demand for carbon emissions reduction,\textsuperscript{4,5} chemical looping combustion (CLC) has been studied extensively over the past three decades as a new technology for power generation with integrated CO\textsubscript{2} capture,\textsuperscript{6–22} as evidenced by more than 2400 peer-reviewed publications to date (based on the chemical abstracts service). In comparison, research related to chemical looping strategies prior to 1983 was scattered and often dealt with concepts other than power generation and CO\textsubscript{2} capture.\textsuperscript{2,23–25} A good example is the commercially implemented steam-iron process for hydrogen production, which was later replaced by methane reforming in the 1930s.\textsuperscript{23} However, besides the limitations from the lack of global policies on fighting global warming via carbon capture and storage (CCS)-related technologies, the lack of fundamental...
understanding and absence of effective strategies to design and optimize the reaction intermediates, also known as (oxygen) carriers, have largely hindered the research progress in the “pre-CLC” era. We note that the extensive investigation of the CLC technology has built up significant background knowledge and fundamental insights for potential breakthroughs in chemical looping applications well beyond combustion and power generation. It is, therefore, not too surprising to see that the extension of the chemical looping strategy has drawn significant attention over the past decade. In fact, journal articles covering such topics increased by nearly 10-fold over this period.

Although there have been quite a few excellent reviews and books covering the topic of chemical looping, they tend to focus on CLC and, in some cases, chemical looping reforming (CLR) both with and without being integrated with CO₂ or H₂O splitting. A recent review by Zeng et al. provided comprehensive discussions of the various aspects of chemical looping including chemical looping for the production of chemicals. However, CLC and CLR related topics were still the primary focus, and many chemical production cases, as summarized in Table 1, have not been covered. Another review by Bayham et al. gave an overview of CLC for power production with CO₂ capture and CLR for hydrogen or syngas production with carbon capture. It mainly focused on the potential process configurations (reaction systems and reactor design) and applications. As a highly versatile and effective process intensification strategy, the chemical looping concept can be applied to many applications beyond CO₂ capture and reforming with significant merits in efficiency improvements, emission reduction, and potential cost savings. This article aims to offer a perspective on various potential applications of chemical looping beyond combustion (CLBC) and the generalized design principles for oxygen carrier or redox catalysts in chemical looping processes.

2. The case for chemical looping beyond combustion

2.1. Chemical looping – the general principle

As illustrated in Table 1, chemical looping can take various forms for numerous applications. Generalized schematics and representative reactions of different chemical looping processes are summarized in Fig. 1 and Table 1, respectively. As can be seen, reactive separation facilitated by solid (oxygen, nitrogen, and hydrogen) carrier particles represents an important underlying feature of all chemical looping reactions and processes. In chemical looping processes, oxygen carrier, usually composed of metal oxides, acts as an oxygen reservoir for oxygen donation and regeneration. Nitrogen carrier composed of nitride or nitride-hydride mixed compounds enables the storage and release of N₂ and H in the redox cycle for chemical looping ammonia synthesis. In a similar manner, hydride based hydrogen carrier allows the storage and release of hydrogen to participate in chemical reactions or shift the reaction equilibrium. Although recent research on nitrogen, and hydrogen carriers offer significant new opportunities, the vast majority of the carriers investigated to date are oxygen carrying agents. In order to maintain coherency, we elected to focus exclusively on chemical looping approaches for chemical production using oxygen carriers, also known as redox catalysts. Table 1 summarizes both the key CLBC schemes reported to date and promising CLBC schemes for future investigations. To further illustrate the thermodynamic favorability of the various potential reaction pathways, Fig. 2 summarizes potential reaction pathways and Gibbs free energy changes among various carbon-containing feedstock and products. To maintain consistency, 1 bar oxygen partial pressure (P₀₂) was assumed in all cases. Fig. 2 is intended to be used as a screen tool to determine the thermodynamically favorable reactants, products, and CLBC schemes. It is also important to note that while one can anticipate similar trends in relative ease of product formation irrespective to the oxygen carrier used in CLBC, the equilibrium P₀₂ of oxygen carriers, which is dependent upon both the composition/phase of the redox pair and the reaction temperature, can span more than 20 orders of magnitudes. This large degree of freedom in P₀₂ and the ability of chemical looping to decouple a single overall reaction into multiple redox steps, provides unique flexibility in “manipulating” the extent and feasibility of certain chemical reactions, as will be illustrated in Section 2.2. Besides redox based CLBC schemes, this article also covers the use of CO₂ sorbents (i.e. calcium looping) to enhance the oxygen carrier-based chemical looping approaches, as will be elaborated in Section 4.4.

A typical chemical looping process involving oxygen-carrying agents is composed of two or more reduction and oxidation steps that form a redox loop. In its simplest form, an oxygen carrier or redox catalyst first donates its lattice oxygen under a low oxygen partial pressure environment. The reduced oxygen carrier is subsequently exposed to an oxidant for the replenishment of its lattice oxygen, thereby completing a two-step redox loop. As illustrated in Table 1, the use of oxygen carrier offers significant flexibility and opportunity for process intensification by breaking an overall reaction into sub-reactions because: (i) besides acting as a reactant, the oxygen carrier also acts as a mass separation agent since the looping reactions prevent the mixing among the products from each sub-step; (ii) the carrier’s oxygen donation properties can be tailored for improved thermal management of the overall process; and (iii) the reduction or oxidation steps can be further broken into multiple sub-steps. When designed properly, an oxygen carrier can be compatible with various oxidizing and reducing agents to facilitate the generation of multiple value-added products with minimal separation requirements.

From a thermodynamic standpoint, the oxygen donation ability of oxygen carriers/redox catalysts can be evaluated by the equilibrium oxygen partial pressure (P₀₂) of the reaction MeOₓ → MeOₓ₋₁ + 1/2O₂. Redox pairs with high P₀₂S, which are suitable for chemical looping air separation (CLAS), chemical looping with oxygen uncoupling (CLOU), or CLR, can only be regenerated with air. As applications summarized in Table 1, CLBC can take advantage of redox pairs with a significantly wider range of P₀₂S. As such, valuable products can be produced
Table 1  Representative redox schemes for chemical looping beyond combustion. The redox reactions are named from (R1) to (R41)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Products</th>
<th>Product generation</th>
<th>Balance of the loop</th>
<th>Name of the process&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Sample oxygen/nitrogen carriers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>Air separation</td>
<td>(R1) MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(R2) MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2O&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CLAS</td>
<td>CuO&lt;sub&gt;2&lt;/sub&gt;, perovskite&lt;sup&gt;54,55&lt;/sup&gt;</td>
</tr>
<tr>
<td>Methane</td>
<td>Synthesis gas</td>
<td>(R3) C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt; + MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(R4) MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2O&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CLR</td>
<td>NiO&lt;sub&gt;2&lt;/sub&gt;, FeO&lt;sub&gt;2&lt;/sub&gt;, CeO&lt;sub&gt;2&lt;/sub&gt;, perovskite&lt;sup&gt;66–68&lt;/sup&gt;, hexaaluminate&lt;sup&gt;69,70&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ethylene</td>
<td></td>
<td>(R7) C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt; + MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(R8) MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2O&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CL-OCM</td>
<td>Alkali modified Mn, Fe oxides&lt;sup&gt;71,72&lt;/sup&gt;</td>
</tr>
<tr>
<td>Methanol</td>
<td>Formaldehyde</td>
<td>(R11) CH&lt;sub&gt;3&lt;/sub&gt;O + MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt; + CH&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>(R12) MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2O&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CL-DHA</td>
<td>Mo/Zn ZSM-5 + Fe oxide&lt;sup&gt;73,74&lt;/sup&gt;, Copper-exchanged zeolites&lt;sup&gt;75,76&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ethylene</td>
<td>Ethylene oxide</td>
<td>(R15) C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt; + MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(R19) MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2O&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CL-OCM</td>
<td>FeMoO&lt;sub&gt;4&lt;/sub&gt;/Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;77&lt;/sup&gt;</td>
</tr>
<tr>
<td>Propylene</td>
<td>Propionaldehyde</td>
<td>(R17) C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt; + MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(R21) MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2O&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CL-Epoxidation</td>
<td>Ag/StrFe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;58&lt;/sup&gt;</td>
</tr>
<tr>
<td>Styrene</td>
<td></td>
<td>(R23) C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt; + MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(R26) MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2O&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CL-Selective oxidation</td>
<td>—&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Methylstyrrene</td>
<td></td>
<td>(R25) C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt; + MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(R28) MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2O&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CLR</td>
<td>Fe oxide&lt;sup&gt;44&lt;/sup&gt;</td>
</tr>
<tr>
<td>biomass</td>
<td>Synthesis gas</td>
<td>(R27) C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt; + MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(R29) MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2O&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CL-Selective oxidation</td>
<td>Vanadium phosphorous (VPO)&lt;sup&gt;90&lt;/sup&gt;</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Hydrogen</td>
<td>(R29) H&lt;sub&gt;2&lt;/sub&gt;O + MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(R30) MeO&lt;sub&gt;2&lt;/sub&gt; + 1/2O&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Thermochernical splitting</td>
<td>Perovskite&lt;sup&gt;88&lt;/sup&gt;, CeO&lt;sub&gt;2&lt;/sub&gt;, &lt;sup&gt;64&lt;/sup&gt;</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CO</td>
<td>(R32) CO&lt;sub&gt;2&lt;/sub&gt; + MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt; + CO</td>
<td>(R34) MeO&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt; + CO</td>
<td>Thermochernical splitting</td>
<td>Fe oxide&lt;sup&gt;90–92&lt;/sup&gt;</td>
</tr>
<tr>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>(R35) H&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt; + MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt; + NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>(R36) 1/2N&lt;sub&gt;2&lt;/sub&gt; + MeO&lt;sub&gt;2&lt;/sub&gt; → MeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CL-ammonia synthesis</td>
<td>Perovskite&lt;sup&gt;95&lt;/sup&gt;, Fe oxide&lt;sup&gt;96,97&lt;/sup&gt;, Transition metal nitride&lt;sup&gt;98&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> CLAS, chemical looping air separation; CL-OCM, chemical looping oxidative coupling of methane; CL-DHA, chemical looping dehydroaromatization; CL-ODH, chemical looping oxidative dehydrogenation; CL-WGS, chemical looping water–gas shift; CL-RWGS, chemical looping reverse water–gas shift.  
<sup>b</sup> Exemplary, promising CLBC schemes that has yet to be investigated.

In both the oxygen carrier reduction and re-oxidation steps, in the reduction or oxygen donation step, CLBC can valorize light alkanes, aromatics or biomass into chemicals via chemical looping partial oxidation (CLPOX). Although CO<sub>2</sub> and H<sub>2</sub>O are the most stable forms of the oxidation products (other than carbonates), many chemical products, including hydrogen, synthesis gas, alkene, aromatic, alcohol, aldehyde, epoxide, or maleic anhydride, are thermodynamically feasible as illustrated in Fig. 2b. The key challenge for high yields towards these partial oxidation products resides in the design of selective redox catalysts to minimize CO<sub>2</sub> and other byproduct formation, as will be elaborated in Section 3.2. In the regeneration step, hydrogen can be produced via water splitting or CO from CO<sub>2</sub> splitting. Selective hydrogenation reactions can also be carried out during the re-oxidation of tailored redox catalysts. Although the chemical looping cycles can be more complex...
than conventional processes in the presence of heterogeneous catalysts, they do offer multiple potential advantages from both product selectivity and process efficiency viewpoints, as will be further illustrated in the following sections.

2.2. The case for chemical looping beyond combustion – a second law perspective

As discussed in Section 2.1, a common feature of chemical looping is the ability to facilitate chemical reactions with in situ product separation. With separation being the most energy-intensive step in the chemical industry, reactive separation enabled by chemical looping offers excellent opportunities for energy savings and emission reductions. The potential benefits of chemical looping, however, goes well-beyond the simplification of product separations. With strategically designed reaction scheme and intermediates, chemical looping can be intrinsically advantageous over conventional approaches from a second law of thermodynamics perspective. The potential second law (exergy) savings via chemical looping result from the following aspects:

a. Exergy savings via reactive separation. From a separation standpoint, the redox catalyst in chemical looping acts as a (reactive) mass separation agent, which facilitates feedstock and/or product separation. As such, the driving force ($\Delta G$) for the overall chemical reaction, which is broken down into two or more sub-reactions in chemical looping, can be utilized for separation in an integrated manner. This represents a distinct advantage over conventional separation, in which chemical potential gradients among the various components in a mixture are created via extensive cooling or heating (e.g. distillation, cryogenic distillation, absorption-stripping, etc.) and/or compression (e.g. membrane, adsorption, and cryogenic distillation). With tunable thermodynamic properties, the driving forces for sub-reactions (and separation) can also be adjusted in chemical looping to optimize exergy savings. This is exemplified by the partial oxidation (POx) of methane: Under the conventional scheme, synthesis gas is produced from methane in two major steps, that is, cryogenic air separation and methane partial oxidation. Air separation is a thermodynamically uphill process requiring a minimum work input of 6.2 kJ mol$^{-1}$ O$_2$ for a hypothetical and fully reversible separation process. The actual energy consumption for commercial cryogenic air separation, which requires extensive gas compression, liquefaction, and distillation, is approximately 25 kJ mol$^{-1}$ O$_2$ (at 1 bar). This corresponds to an exergetic efficiency of $\sim 25\%$. Even under an idealized scenario, conventional air separation would still lead to an exergy loss of 5.3 kJ mol$^{-1}$ O$_2$, resulting in a total energy consumption of 11.5 kJ mol$^{-1}$ O$_2$. As such, conventional methane POx, which consumes gaseous O$_2$ at a CH$_4$:O$_2$ stoichiometric ratio of 2:1, would consume at least 5.8 kJ of energy in air separation alone for each mole of methane converted. Methane POx, on the other hand, is thermodynamically highly favored with $\Delta G^\circ$ of $\sim$86.7 kJ mol$^{-1}$ of methane converted. Chemical looping POx can take advantage of the large thermodynamic driving force for methane POx and integrate it for air separation. 

![Fig. 1](imageURL) Schematic illustration of the chemical looping strategy and its potential applications.

![Fig. 2](imageURL) Normalized reaction Gibbs free energy change ($\Delta G$) per mole of carbon at 700 °C for various potential chemical products from C1–C9 hydrocarbons. Bars with different colors represent the $\Delta G$ for the partial oxidation of hydrocarbons to the corresponding products. For consistency, 1 atm gaseous oxygen is assumed to be the oxidant. To calculate $\Delta G$ with a specific redox pair as the oxidant (e.g. Mn$_3$O$_4$/MnO), one can use the corresponding equilibrium oxygen partial pressure ($P_{O_2}$) of the redox pair at the temperature to account for the oxygen chemical potential change relative to 1 atm O$_2$. 

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separation. Using Mn$_3$O$_4$ as an example, the two chemical looping sub-reactions are each favored thermodynamically:

Sub-reaction 1: CH$_4$ + 3Mn$_3$O$_4$ → CO + 2H$_2$ + 2Mn$_3$O$_4$

$$
\Delta G^0 = -9.8 \text{ kJ mol}^{-1}
$$

Sub-reaction 2: 2Mn$_3$O$_4$ + 1/2O$_2$ → 3Mn$_2$O$_3$

$$
\Delta G^0 = -76.9 \text{ kJ mol}^{-1}
$$

Overall reaction: CH$_4$ + 1/2O$_2$ → CO + 2H$_2$

$$
\Delta G^0 = -86.7 \text{ kJ mol}^{-1}
$$

As can be seen, the thermodynamic driving force required for air separation is embedded in the chemical looping reactions, thereby eliminating the associated energy consumptions and exergy loss. It is further noted that, even when the chemical looping scheme is used for air separation only, it can be significantly less energy-intensive than cryogenic air separation.$^{54,55}$

b. Exergy savings via in situ conversion of byproducts. The production of value-added chemicals can be intensified by chemical looping, via selectively oxidizing the reaction byproducts. As exemplified in Table 1, this principle has been applied to olefin production via oxidative coupling of methane, oxidative dehydrogenation, and naphtha cracking. From a second law standpoint, chemical looping can lead to exergy savings in the following two ways. On one hand, the in situ oxidation of byproducts such as hydrogen can compensate for the thermal energy required by endothermic reactions, e.g. the non-oxidative coupling of methane or ethane cracking/dehydrogenation. Compared to conventional approaches where hydrocarbon fuels are combusted to neutralize the reaction endothermicity via indirect heat transfer through cracker furnaces, in situ combustion of hydrogen is intrinsically advantageous due to its lower exergy rate, i.e. the ratio between the exergy and enthalpy of a fuel compared to that of hydrocarbons. Fig. 3 illustrates the exergy loss for ideal steam cracking and chemical looping oxidative dehydrogenation (CL-ODH) steps,$^{111}$ assuming no heat loss in either case. When practical factors, such as the temperature difference for indirect heat transfer, are considered, a higher exergy loss can be anticipated for conventional cracking.

A second aspect of exergy savings via byproduct oxidation is through enhanced product yields. For instance, steam cracking of both ethane and naphtha are equilibrium-limited.$^{112}$ In situ combustion of the hydrogen byproduct significantly increases the olefin yield from 50% to nearly 70% in a lab-scale reactor at 850 °C while decreasing the volumetric flow rate of non-condensable product gases by ~40%.$^{81}$ The corresponding energy savings in product compression and separation alone correspond to 554 kJ mol$^{-1}$ of ethylene produced.$^{113}$ Due to these reasons, process analyses indicate that the chemical looping approach can lead to more than 80% energy savings for ethane conversion and 50% energy savings for naphtha cracking.$^{112,113}$

c. Ability to circumvent second law limitations by the redox loop. Another potential advantage of dissecting an overall reaction into sub-reactions resides in a higher degree of freedom in terms of thermodynamic characteristics for the individual sub-reactions. Moreover, the operating conditions for each sub-step, e.g. temperature and pressure, can be adjusted independently to maximize the product yields from an equilibrium standpoint. A good example of using the chemical looping strategy to circumvent second law limitations of an overall reaction is thermochemical water-splitting to produce hydrogen:

$$
\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2
$$

Spontaneous decomposition of water (equilibrium constant, \( K \geq 1 \)) only occurs at ~4100 °C or higher, making thermochemical water-splitting far from practical. This is mainly due to the high reaction enthalpy (\( \Delta H^0 = 241.5 \text{ kJ mol}^{-1} \)) and the relatively small reaction entropy (\( \Delta S^0 = 43.5 \text{ J K}^{-1} \)). Using the chemical looping principle, however, the overall reaction is broken down into two sub-reactions, as shown in Fig. 4. Take a ceria-based oxygen carrier as an example:

Sub-reaction 1: \( \text{H}_2\text{O} + \text{Ce}_2\text{O}_3 \rightarrow \text{H}_2 + 2\text{CeO}_2 \)

$$
\Delta H^0_1 = -126.6 \text{ kJ mol}^{-1}, \Delta S^0_1 = -82.3 \text{ J K}^{-1}, \Delta G^0_1 = -104.1 \text{ kJ mol}^{-1}
$$

Sub-reaction 2: \( \text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + 1/2\text{O}_2 \)

$$
\Delta H^0_2 = 368.2 \text{ kJ mol}^{-1}, \Delta S^0_2 = 125.9 \text{ J K}^{-1}, \Delta G^0_2 = 333.7 \text{ kJ mol}^{-1}
$$

Overall reaction: \( \text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2 \)

$$
\Delta H^0 = 241.5 \text{ kJ mol}^{-1}, \Delta S^0 = 43.5 \text{ J K}^{-1}, \Delta G^0 = 229.6 \text{ kJ mol}^{-1}
$$

Using ceria as the oxygen carrier, the exothermic water-splitting reaction (sub-reaction 1) is favored at lower temperatures$^{114}$ but
remains favorable up to 1300 °C (\(K_{eq} \approx 1\)). While the endothermic CeO\(_2\) decomposition reaction is equilibrium-limited at low temperatures, the large entropy term, which increases with temperature, leads to spontaneous decomposition at 2300 °C, or 1800 °C lower than the direct water-splitting temperature (\(P_{O_2} = 1\) bar). While one can argue that 2300 °C is still too high, CeO\(_2\) can be decomposed at much lower temperatures (~1200 °C) in practice by: (i) creating a low \(P_{O_2}\) environment through inert purge or vacuum,\(^{115}\) and/or (ii) inducing oxygen vacancy instead of a phase change. In this case, the chemical looping strategy, which allows “tunable” thermodynamic parameters and operating conditions for sub-reactions, enables an equilibrium-limited chemical reaction, which would otherwise be impossible under reasonable operating temperatures.\(^{116}\) Using a similar principle, other equilibrium-limited reactions such as CO\(_2\) splitting\(^{117}\) and thermochemical conversions can also be facilitated by CLBC.\(^{93,98,100,118–121}\)

**d. Tunable exo-/endothermicity of sub-reactions for improved energy integration.** Chemical looping would not alter the enthalpy or entropy changes of the overall reaction under (near) isothermal conditions. However, the distributions of the reaction enthalpy/entropy can be modified by varying the type of the oxygen carrier/redox catalyst and the chemical looping sub-reactions. As such, the heat release/demand of individual chemical looping reactors can be adjusted. This additional degree of freedom can enable significantly improved energy integration and hence reduced exergy/energy losses.\(^{122}\) With an increased understanding of \(P_{O_2}\), phase transition, and catalytic properties for the mixed oxide-based oxygen carriers, the tunabilities of oxygen carriers and hence the corresponding sub-reactions are becoming an increasingly attractive route for efficiency improvements. Fig. 5 summarizes the potential advantages of CLBC over conventional approaches.

### 2.3 Reasons for CLBC – the practical drivers

Besides the abovementioned thermodynamic “drivers”, a strong case can be made for CLBC from a practical standpoint. Commercial implementation of the CLC technology needs to address both technical challenges, in terms of scale-up, and economic challenges, resulting from the low margin of the utility industry and the relatively low economic incentive of the current carbon tax structure.\(^{22,36}\) A CLC power plant will be more complex and costlier than a standard pulverized coal combustion plant, due to large scale circulating fluidized bed operations, high solids circulation rates, and the need to continuously replenish degraded oxygen carrier particles.\(^4\) Meanwhile, low-cost and long-lifetime oxygen carrier material is required to make CLC cost effective.\(^4\) In addition, concerns over carbon sequestration, a critical downstream step for any carbon capture technology, also limits the wide spread utilization of CLC as a promising carbon capture process.\(^{123–127}\) CLBC, on the other hand, has the potential to address all the limitations identified above. In contrast to CLC whose economics is likely to be policy driven, CLBC for chemicals production is market driven because the products are of higher value than electric power. As illustrated in Fig. 6, the CLBC concept can be applied to produce chemical products that are significantly more valuable than electricity, thereby increasing the profit margin. In addition, CLBC based on partial oxidation is intrinsically more
efficient from an oxygen carrier utilization standpoint. Complete combustion of carbonaceous fuels such as methane consumes a significant amount of lattice oxygen for power generation (four [O] are required for each carbon combusted in CH₄). In comparison, the same amount of lattice oxygen can be transformed into valuable ethylene products under a CL-ODH scheme (assuming 100% ethylene selectivity whereas ~90% olefin selectivity has been reported experimentally). If oxygen carriers/redox catalysts with identical oxygen storage capacities are used, the CL-ODH plant would correspond to an eight-fold decrease in solids circulation rate compared to a CLC plant with identical feedstock processing capacity on a weight basis. In addition, at least an order of magnitude increase in reaction kinetics was observed for ethane CL-ODH when compared to methane CLC based on the experience at North Carolina State University. Considering that ethylene production could significantly increase the gross margin compared to power generation, the “breakeven” plant size for CL-ODH would likely be to one or more order of magnitude smaller than that for CLC from process economics, reaction stoichiometry, and kinetics standpoints. An even stronger case can be made for CLBC of heavier feedstock/products: applying the chemical looping strategy for butane to butadiene, if successful, would lead to a 16 times higher lattice oxygen utilization efficiency than for methane CLC. This simple case study clearly demonstrates the significant advantages of CLBC from process scale up and economic standpoints. Another interesting point to make is that many CLBC processes themselves do not offer the primary benefit of CLC, i.e. CO₂ capture, since the target products are chemicals instead of heat (Table 1). However, the process intensification and second law advantages offered by CLBC can still lead to significant CO₂ reductions by producing less CO₂ per unit amount of product generated. A recent study published by Haribal et al. indicated that CL-ODH can reduce the CO₂ emissions for ethylene production by 84% when compared to the commercial ethane cracking processes. Such integrated carbon savings without CO₂ capture (except for the removal of a small amount of CO₂ byproducts via conventional stripping) eliminates the needs for geological CO₂ sequestration, a potential technical challenge for any CO₂ capture process including CLC.

3. General design strategies for CLBC

3.1 Design considerations for CLBC schemes and limitations

While chemical looping offers various potential advantages as stated in Section 2, it is subjected to a number of limitations, which occasionally are overlooked in CL process analyses. This is somewhat “understandable” considering the complexity of CL processes, which involve dynamic and intertwined gas–solid reactions, e.g. the extent of redox catalyst conversion in the reduction step(s) often affects the equilibrium conversion and practical performance of the oxidation step(s). As such, we think it is important to summarize the uniqueness of CLBC as well as its limitations and potential pitfalls in design and analysis of CLBC schemes. Compared to conventional catalytic oxidation or reduction processes, the chemical looping strategy is capable of:

(i) Providing inherently separated product streams to eliminate or alleviate the needs for separation;

(ii) Enhancing process safety by avoiding the direct mixing between a gaseous oxidant (e.g. O₂) and reductant (e.g. a hydrocarbon);

(iii) Redistributing the overall heat of reaction into two or more steps to simplify heat integration;

(iv) Breaking the “equilibrium barrier” of an overall reaction by carefully selecting redox catalysts, redox pairs and carrying out individual chemical looping steps at substantially different conditions and/or gas–solids contacting modes.

For example, the chemical equilibrium limitations in the WGS reaction under a CO–H₂O co-feed mode can be overcome using the chemical looping strategy over a non-stoichiometric mixed oxide, since such an oxide exhibits a large range of equilibrium PO₂, as a function of oxygen non-stoichiometry. Metcalfe et al. investigated such a process using a perovskite (LaₓSrₓFeO₃₋δ) as the oxygen carrier. Using a packed bed reactor operated under a countercurrent contacting mode, a significantly higher overall CO to H₂ conversion (compared to WGS equilibrium conversion) was demonstrated. The unique reactor design and oxygen carrier properties enabled the production of near pure H₂ and CO₂ as separate product streams.

(v) Potentially achieving higher product selectivity by using lattice oxygen as opposed to gaseous oxidants.

However, one must be aware of the following limitations for chemical looping when designing chemical looping schemes or performing process analyses:

(i) The sum of Gibbs free energies of the products from all the chemical looping sub-steps should be smaller than that of the feedstock;

(ii) For a two-step CL process with a single metal/metal oxide redox pair, products from an (oxide) reduction reactor 1 should not be able to oxidize products from an oxidation reactor 2. This principle would apply for both co-currently and counter-currently operated fluidized bed, fixed bed, and moving bed reactors. Using WSG/RWGS reactions as an example, one cannot produce a substantially pure stream of CO₂ or H₂O from reactor 1 while also producing a substantially pure stream of H₂ or CO from reactor 2 if a single redox pair is used. We have to make a choice between a lower CO₂/H₂O yield in reactor 1 and a decreased CO/H₂ yield from reactor 2. Note that this is different from the case illustrated by Metcalfe et al., in which a non-stoichiometric metal oxide was used as the carrier;

(iii) A three-step CL process can allow products from reactor 1 to oxidize products from reactor 2 (since the two reactors and redox pairs do not form a complete loop). However, this is only feasible with an oxidant in step 3 that, when combined with the products from step 2, exhibits a higher equilibrium oxygen partial pressure (PO₂) than do the products from step 1;

(iv) Kinetically, chemical looping reactions are generally much slower than conventional catalytic oxidation/reduction reactions. This is due to the fact that the rates of redox reactions...
are limited by the removal and replenishment of lattice oxygen from/to the bulk crystal structure of the redox catalyst. One exception is the CL-ODH operated at thermal cracking temperatures (> 700 °C). In that case, the rate of hydrogen combustion by the redox catalysts can often match or exceed the hydrogen generation rate from the cracking reactions.\(^{80,81}\)

We note that many mixed oxide-based redox catalysts, e.g. perovskites, can accommodate significant lattice defects prior to phase transition.\(^{129,130}\) As such, the redox thermodynamics of these redox catalysts are unique and cannot be categorized as redox pairs. That is, the equilibrium oxygen partial pressure of the oxide is a continuous function of the oxide’s (oxygen) vacancy concentration without incurring a distinct phase change.\(^{131}\) The unique redox properties of these mixed oxides, coupled with counter-current and/or multiple step chemical looping reactor design, can lead to interesting process configurations that are not subjected to limitations (ii) and (iii) presented above. Fig. 7 illustrates a hypothetical case where a mixed oxide redox catalyst with varying equilibrium \(P_{O_2}\) as a function of oxygen storage capacity can be used to break the RWGS equilibrium in a counter-currently operated two-step chemical looping scheme. A comparable effect can be achieved by using more than one redox pairs with different equilibrium \(P_{O_2}\). In reality, however, one must consider the complex relationships between the oxygen non-stoichiometry of the mixed oxide, which dictates the oxygen mass balance of the redox reactions, and the equilibrium \(P_{O_2}\), which determines the redox thermodynamics, in addition to kinetic and transport effects.

### 3.2 Oxygen carrier design

#### 3.2.1 Thermodynamic prerequisites and second law guided oxygen carrier selection

Although surface properties of the redox catalysts are essential for their reactivity and product selectivity in CLBC, the redox catalysts need to satisfy certain thermodynamic prerequisites. In terms of partial oxidation reactions, the oxide-based redox catalysts need to provide adequate oxygen chemical potential or equilibrium \(P_{O_2}\) to facilitate product generation. Considering the large material design space for redox catalysts, this thermodynamic prerequisite can be used as an effective tool to narrow down the candidate materials. As illustrated in the Ellingham diagram in Fig. 8, one should consider redox pairs above the equilibrium lines of the corresponding POx (selective oxidation) reaction. Taking oxidative coupling of methane (OCM) as an example, it is apparent that redox pairs such as FeO/Fe and Fe\(_2\)O\(_3/\)FeO should not be considered because they would not be sufficiently “oxidative” to facilitate chemical looping OCM at temperatures ranging from 650 °C to 950 °C. On the other hand, redox catalysts composed of MnO\(_2/\)Mn\(_3\)O\(_4\) or Mn\(_2\)O\(_3/\)Mn\(_3\)O\(_4\) redox pairs would likely need surface modifications to ensure high selectivities, since their \(P_{O_2}\)s are well above that required for OCM. Another thermodynamic consideration for redox pair selection is the upper limit for \(P_{O_2}\). For a CLBC system operated at near atmospheric pressures, practical requirement of >90% \(O_2\) conversion in the air regeneration step would impose an upper limit of 0.02 bar for equilibrium \(P_{O_2}\).

The thermodynamic criteria discussed above are intended for narrowing down the design space of the redox catalysts. Possessing suitable thermodynamic properties alone typically would not ensure high product selectivity. A rare exception is synthesis gas generation. As illustrated in Fig. 2b, synthesis gas is one of the thermodynamically favored oxidation product except for \(CO_2\) and water. As such, synthesis gas selectivity and yield can be optimized by tuning the \(P_{O_2}\) of redox catalysts using Gibbs free energy minimization, as illustrated in a few recent publications.\(^{89,66,67,132}\) For other POx products with higher Gibbs free energies, however, such a thermodynamically based strategy would not work since the spontaneous decomposition or oxidation of oxygenates to synthesis gas and/or \(CO_2/H_2O\) is both kinetically and thermodynamically favored at elevated temperatures.
Aside from being a redox catalyst selection tool, equilibrium $P_{O_2}s$ illustrated in the Ellingham diagram can be used to manage heat distributions among the redox steps involved in CLBC. Due to the endothermicity in the oxygen release step of redox catalysts, a large fraction of the fuel oxidation reactions with redox catalysts in CLBC are endothermic, even though oxidation of a fuel with oxygen would be exothermic. Oxides with higher $P_{O_2}$s tend to decrease the endothermicity in the fuel oxidation step while decreasing the exothermicity of the redox catalyst re-oxidation step. As such, rationally selected redox pairs can facilitate optimal distribution of the reaction heat in the redox steps to simplify heat integrations.

In CLC, a bimetallic Fe–Cu oxygen carrier composed of CuO and Fe$_2$O$_3$ was proposed to shift the endothermic reduction to exothermic or heat neutral.\textsuperscript{133,134} This $P_{O_2}$ tuning strategy has also been applied to CLBC, e.g. in ethane CL-ODH.\textsuperscript{82,83,128}

Redox thermodynamic data for monometallic oxides are readily available, as illustrated in Fig. 8. However, the number of suitable redox pairs are limited when considering the aforementioned thermodynamic criteria. Mixed oxides such as hexaaluminates, spinels, or perovskites, offer significantly increased tunability in terms of redox properties. Moreover, equilibrium $P_{O_2}s$ of many mixed oxides are often variable without incurring phase changes, as discussed in Section 3.1. As such, their multidimensional redox behavior cannot be illustrated by a simple redox reaction or a curve in the Ellingham diagram. These unique properties make mixed oxides an intriguing option for CLBC, as illustrated by a number of recent publications.\textsuperscript{61,70,135} Among the various mixed oxides, perovskite-type oxides represent a large family of materials that is particularly promising for CLBC due to their highly tunable structural, compositional, and redox properties.\textsuperscript{136–138} A recent perspective provided a comprehensive discussion on perovskites as redox catalysts for CLBC.\textsuperscript{49}

### 3.2.2 Surface modifications of redox catalysts

Similar to selective oxidation reactions facilitated by heterogeneous catalysts, a key challenge to redox catalysts in CLBC is to avoid the over-oxidation of desirable products. Recent studies have indicated that surface modifications can be an effective strategy to enhance redox catalysts' activity and/or selectivity.\textsuperscript{79–82,128,139} Generally speaking, electrophilic (surface) oxygen species such as $O_2^-$, $O_2^{2-}$ (peroxide), and $O_2^{-}$ (superoxide) are often attributed to non-selective oxidation reactions due to their high activity and electron affinity.\textsuperscript{49,140} In comparison, lattice oxygen is often believed to be the "selective" oxygen species in both CLBC and catalytic oxidation reactions involving oxide catalysts. However, such an assignment can be a rather simplistic view since the presence and relative abundance of these oxygen species is not only dependent on the type of oxide but also the reaction conditions and the degree of reduction of the oxide.

Recent experimental evidences indicate that lattice oxygen species can be dynamically converted to electrophilic oxygen under chemical looping reaction conditions.\textsuperscript{58,139} As such, the abundance of electrophilic oxygen species during the partial oxidation step can be affected by a dynamic balance between: (i) the flux of lattice oxygen from the bulk oxide lattice to the surface; and (ii) the rate of oxygen removal from the surface of the redox catalyst. More facile lattice oxygen flux to the surface would hence allow the transition or relaxation of $O_2^-$ to electrophilic oxygen especially when such oxygen is bonded with high valency transition metal cations, e.g. Fe$^{4+}$ or Mn$^{4+}$. Therefore, one would anticipate a low product selectivity resulting from the dynamic formation of the electrophilic oxygen species on the surface.

On the other hand, decreased CO$_2$ formation can be achieved by facilitating more facile surface oxygen removal compared to the lattice oxygen flux since the formation of electrophilic oxygen species can be minimized. To ensure a relatively faster surface oxygen removal rate, one can either decelerate the $O_2^-$ flux or enhance the surface activity of the redox catalyst, as illustrated in Fig. 9. Recent studies have confirmed the effectiveness of both redox catalysts.
approaches. Gao et al.\textsuperscript{79,128} investigated a La\textsubscript{5}Sr\textsubscript{8}FeO\textsubscript{12} based redox catalyst for CL-ODH of ethane to ethylene. While La\textsubscript{5}Sr\textsubscript{8}FeO\textsubscript{12} promoted the complete combustion of ethane, alkali metal oxide promoters enriched on the surface of the mixed oxide and significantly inhibited the O\textsuperscript{2\textendash}flux from the bulk. As a result, 90% ethylene selectivity was achieved. Besides alkali metal oxide promoters, alkali salt modification also play a similar role to depress O\textsuperscript{2\textendash}flux of the redox catalyst for the selective combustion of hydrogen (SHC) in CL-ODH of ethane to ethylene.\textsuperscript{81\textendash}83 Enhancement of redox catalyst’s surface activity was reported for methane partial oxidation for synthesis gas generation. Shafieeharoud et al.\textsuperscript{139} reported that impregnating Rh on a CaMnO\textsubscript{2} based redox catalyst decreased the methane activation energy on the oxide surface by more than 95%, leading to a decrease in methane conversion temperature by 300 °C and a significantly increased synthesis gas selectivity. Those practices reveal that tuning of the oxygen transfer rate from bulk of a redox catalyst to the catalytically active species on the surface is of great importance for POx. In a redox-involved context, Machida at Kumamoto University found that surface CeO\textsubscript{2} could act as a gateway for oxygen storage in and release from various oxides acting as an oxygen reservoir, such as Fe\textsubscript{2}O\textsubscript{3} or La\textsubscript{2}O\textsubscript{2}SO\textsubscript{4}.\textsuperscript{141\textendash}143

Although the abovementioned strategy for catalyst selectivity optimization has been shown to be effective, we note that it still represents a rather simplified view of the redox catalyst. It would be desirable, from both scientific and engineering standpoints, to determine the active sites and elementary reaction pathways of the chemical looping reactions, but such tasks can be daunting due to the highly dynamic nature of chemical looping reactions. In fact, both the bulk and surface of the redox catalysts can dynamically rearrange throughout the redox cycle.\textsuperscript{144} The utilization of modern catalysis and surface science techniques in a few recent studies have already started to reveal fundamental insights on the mechanisms of the redox reactions.\textsuperscript{78,128,145\textendash}151 However, significant progress still needs to be made to gain additional fundamental insights and this should be a topic of focus for redox catalyst studies within the foreseeable future.

In principle, one can also combine heterogeneous catalysts or active sites with an oxygen storage material to achieve combined catalytic and chemical looping functions. For instance, as will be discussed in Section 4.2.2, Chan et al.\textsuperscript{demonstrated the CL epoxidation of ethylene over Ag/StrFo\textsubscript{3} redox catalyst where Ag acts as the epoxidation catalyst and StrFe\textsubscript{3} acts as the oxygen storage material for oxygen donation.\textsuperscript{78} Ethylene was converted to ethylene oxide (with CO\textsubscript{2} and H\textsubscript{2}O by products) in the reduction step and the reduced redox catalyst was then replenished with air. Many other CLBC systems can potentially take advantage of such a strategy. Examples include alkane ODH, methane dehydroaromatization, methane oxidative coupling, among others. These topics are discussed in Sections 4.1 and 4.2.

We note that the above discussions are intended to cover the key strategies and the underlying principles for the design of CLBC redox catalysts and reaction schemes. From a practical standpoint, the redox catalyst’s activity, available oxygen storage capacity, stability, mechanical strength,\textsuperscript{152,153} heat management,\textsuperscript{154} cost and environmental risk should all be taken into account to optimize the redox catalyst. The higher margin in the chemical industry over the utility industry can afford significantly higher redox catalyst cost in CLBC. While the raw material cost of some redox catalysts can be high (e.g. ceria-based materials), the additional value created for chemical production can potentially accommodate higher redox catalyst costs. Under CLBC schemes, redox catalysts functions similar to heterogeneous catalysts in chemical production processes.\textsuperscript{155} It is further noted that a number of CLBC redox catalysts have shown chemical productivities (in terms of weight hourly space velocity) comparable to commercial catalysts.\textsuperscript{111} The aforementioned factors should also be considered along with reactor design parameters, operating conditions as well as the reactor/process economics for CLBC process development.

4. CLPOx/CLBC process schemes

4.1 Chemical looping for C\textsubscript{1} valorization

CH\textsubscript{4} is the main constituent of natural gas and an important feedstock for the production of commodity chemicals and liquid fuels.\textsuperscript{156} It can be converted into methanol, NH\textsubscript{3} and other higher hydrocarbons either directly via a one-step process or indirectly via a synthesis gas (a mixture of CO and H\textsubscript{2}) intermediate. At present, the only cost-effective route to convert CH\textsubscript{4} into valuable chemicals is via synthesis gas.\textsuperscript{157} Synthesis gas can be obtained from CH\textsubscript{4} using the following three reactions: steam reforming (R62), dry reforming (R63) and partial oxidation (R49).\textsuperscript{158} At the industrial scale, the catalytic steam methane reforming (SMR) is used predominantly to produce synthesis gas. Although SMR is highly optimized, it is a very energy-intensive process and releases large quantities of CO\textsubscript{2} into the atmosphere.\textsuperscript{131} To reduce the energy demand of SMR, a part of CH\textsubscript{4} is combusted internally with oxygen or air. The resulting so-called autothermal reforming process enhances CH\textsubscript{4} conversion and reduces CO\textsubscript{2} emissions, but at the expense of lowered synthesis gas yields.\textsuperscript{57} Recently, dry reforming of methane (DRM) has received a lot of attention due to its potential to convert two greenhouse gases (i.e. CH\textsubscript{4} and CO\textsubscript{2}) into an equimolar mixture of CO and H\textsubscript{2} desired for Fischer–Tropsch synthesis.\textsuperscript{159,160} Although this concept has many environmental and economic incentives, there is currently no commercial process for DRM. Unlike reforming reactions, methane POx is mildly exothermic allowing for auto-thermal operation at temperatures exceeding 1000 °C. Methane POx can be performed either at elevated temperatures (> 1200 °C) without a catalyst or at lower temperatures (< 900 °C) in the presence of platinum group metal (PGM) based catalyst (e.g., Pt, Pd, Rh, Ru, etc.).\textsuperscript{161,162} Commercial methane POx processes incur a significant efficiency loss due to high operating temperatures. The catalytic route can be costly due to the high cost of the PGM and safety concerns. Both approaches also are challenged by the high cost and energy intensity of pure O\textsubscript{2}.

In 2000, Lyon and Cole\textsuperscript{163} proposed a chemical looping approach to transfer oxygen from air to a fuel using solid oxygen carriers.
for a number of applications such as pollution control, production of inert gases, delivery of heat to endothermic reactions, etc.

Since then various chemical looping cycles have been proposed to address the limitations of conventional CH₄ conversion processes (see in Table 2). Sections 4.1.1 and 4.1.2 provide a brief summary of the chemical looping approaches related to indirect and direct CH₄ conversion routes, respectively.

4.1.1 CL methane conversion to synthesis gas. Compared to conventional CH₄ reforming processes that utilize gaseous oxidants, the two-step chemical looping approach, schematized in Fig. 10, relies on the lattice oxygen of a solid oxygen carrier to partially oxidize CH₄ via (R₃).⁵³,¹⁶⁴,¹⁶⁵ A subsequent re-oxidation step then replenishes the lattice oxygen. If air is used in the regeneration step to re-oxidize the reduced oxygen carrier, via (R₄), the overall reaction is methane POx and hence the chemical looping cycle is also referred to as CL-methane POX.¹⁶⁶ Unlike the conventional methane POX reaction (R₄₉), the chemical looping route does not require pure oxygen, thereby eliminating the need of an energy- and cost-intensive air separation unit (ASU). Further, the actual CH₄ conversion step using lattice oxygen (when the oxygen carrier is reduced) is endothermic. Depending upon the thermodynamic characteristics of the oxygen carrier, it can also be re-oxidized using H₂O⁻¹⁶⁷,¹⁶⁸ see (R₅), resulting in the so-called CL-SMR.⁴¹,¹⁶⁸ Here, two separate streams of synthesis gas (with a CO:H₂ ratio of 1:2) and high-purity H₂ are produced inherently, thus intensifying the production of high-purity H₂ from CH₄. It is noted here that CL-SMR would become the CL-WGS process if CO instead of CH₄ were used to reduce the oxygen carrier.⁴²,⁹⁶,¹⁷⁰,¹⁷¹ Both CL-SMR and CL-WGS are also referred to as CL-water-splitting processes.⁴⁷,¹⁷² Recently the CL-DRM cycle, in which CO₂ is used to regenerate the oxygen carrier (via (R₆)), has been proposed to maximize the conversion of CO₂ captured from various emission sources, to CO.⁴⁶,¹⁶²,¹⁶³,¹⁷³ Most recently the modified CL-methane POx coupled with H₂O-CO₂ splitting¹⁷⁶ for the oxygen carrier regeneration allows the production of syngas with identical compositions in both the reduction and regeneration steps.¹²¹,¹⁷⁷,¹⁷⁸

The oxygen carriers used in the above-mentioned chemical looping processes are often called redox catalysts because they simultaneously act as an oxygen donor (i.e. as a reactant) and as a catalyst. NiO, Fe₂O₃, CeO₂, spinel and certain perovskite-based oxides possess suitable thermodynamic properties that permit their use as redox catalysts for chemical looping conversion of CH₄ to synthesis gas.⁴¹,¹⁷⁹-¹⁸⁴ Among various oxygen carriers, Ni-based oxygen carriers are particularly attractive for CLR owing to their high catalytic activity for CH₄ reforming.⁵⁶,¹⁸⁵-¹⁹¹ NiO possesses a low selectivity towards synthesis gas, but as NiO reduces to Ni the selectivity towards synthesis gas increases.⁵⁶ However, Ni is highly prone to deactivation via carbon deposition under low oxygen partial pressures¹⁸⁷ and the formation of sulfides in the presence of feedstock containing sulfur species.¹⁹²

<table>
<thead>
<tr>
<th>Category</th>
<th>Pathway</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal oxide redox pairs</td>
<td>Mn₃O₄ → Mn₂O₃</td>
<td>(R₄₂) 4Mn₃O₄ + O₂(g) → 6Mn₂O₃</td>
</tr>
<tr>
<td></td>
<td>MnO → Mn₂O₄</td>
<td>(R₄₃) 6MnO + O₂(g) → 2Mn₂O₄</td>
</tr>
<tr>
<td></td>
<td>FeO → Fe₂O₃</td>
<td>(R₄₄) 6FeO + O₂(g) → 2Fe₂O₃</td>
</tr>
<tr>
<td></td>
<td>CuO → Cu₂O</td>
<td>(R₄₅) 2CuO + O₂(g) → 2Cu₂O</td>
</tr>
<tr>
<td></td>
<td>Cu → CuO</td>
<td>(R₄₆) 2Cu + O₂(g) → 2CuO</td>
</tr>
<tr>
<td></td>
<td>Ni → NiO</td>
<td>(R₄₇) 2Ni + O₂(g) → 2NiO</td>
</tr>
<tr>
<td>Combustion</td>
<td>CH₄ → Power</td>
<td>(R₄₈) 1/2CH₄(g) + O₂(g) → 1/2CO₂(g) + H₂O(g)</td>
</tr>
<tr>
<td>Partial oxidation/selective oxidation</td>
<td>CH₄ → Synthesis gas</td>
<td>(R₄₉) 2CH₄(g) + O₂(g) → 2CO(g) + 4H₂(g)</td>
</tr>
<tr>
<td></td>
<td>CH₄ → CH₂O</td>
<td>(R₅₀) 2CH₄(g) + O₂(g) → 2CH₂O(g)</td>
</tr>
<tr>
<td></td>
<td>CH₄ → CO₂</td>
<td>(R₅₁) 2CH₂O(g) + O₂(g) → 2CO₂(g) + 2H₂O(g)</td>
</tr>
<tr>
<td></td>
<td>CH₄ → H₂</td>
<td>(R₅₂) C₂H₆(g) + O₂(g) → C₂H₄(g) + H₂O(g)</td>
</tr>
<tr>
<td></td>
<td>CH₄ → CH₂ ≡ CH</td>
<td>(R₅₃) 2H₂ + O₂(g) → 2H₂O(g)</td>
</tr>
<tr>
<td>Oxidative coupling</td>
<td>CH₄ → C₂H₄</td>
<td>(R₅₄) 4CH₄(g) + O₂(g) → 2C₂H₄(g) + 2H₂O(g)</td>
</tr>
<tr>
<td>Oxidative dehydroaromatization (DHA)</td>
<td>CH₄ → C₂H₄</td>
<td>(R₅₅) 4CH₄(g) + O₂(g) → 2C₂H₄(g) + 2H₂O(g)</td>
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<tr>
<td>Oxidative dehydrogenation or cracking</td>
<td>CH₄ → C₂H₂</td>
<td>(R₅₆) 6CH₄(g) + 2O₂(g) → 2C₂H₂(g) + 2H₂O(g)</td>
</tr>
<tr>
<td></td>
<td>CH₄ → C₂H₆</td>
<td>(R₅₇) 2CH₂O(g) + O₂(g) → 2C₂H₆(g) + 2H₂O(g)</td>
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<tr>
<td></td>
<td>CH₄ → H₂</td>
<td>(R₅₈) 2CH₂O(g) + O₂(g) → 2C₂H₆(g) + 2H₂O(g)</td>
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<tr>
<td>Refining</td>
<td>CH₄ → Synthesis gas</td>
<td>(R₅₉) 2CH₂O(g) + O₂(g) → 2C₂H₆(g) + 2H₂O(g)</td>
</tr>
<tr>
<td>Methane cracking</td>
<td>CH₄ → CH₂</td>
<td>(R₆₀) 2CH₂O(g) + O₂(g) → 2C₂H₆(g) + 2H₂O(g)</td>
</tr>
<tr>
<td></td>
<td>CH₄ → CH₂ ≡ CH</td>
<td>(R₆₁) 2CH₂O(g) + O₂(g) → 2C₂H₆(g) + 2H₂O(g)</td>
</tr>
<tr>
<td>Dehydroaromatization</td>
<td>CH₄ → C₂H₆</td>
<td>(R₆₂) CH₄(g) + H₂O(g) → CH₄(g) + CO(g)</td>
</tr>
<tr>
<td></td>
<td>CH₄ → C₂H₄</td>
<td>(R₆₃) CH₄(g) + CO₂(g) → 2C₂H₄(g) + 2H₂O(g)</td>
</tr>
<tr>
<td>Anaerobic conversion</td>
<td>CH₄ → CH₂O</td>
<td>(R₆₄) CH₄(g) + 2H₂(g) + O₂(g)</td>
</tr>
<tr>
<td>Super-dry reforming</td>
<td>CH₄/CO₂ → CO/H₂O</td>
<td>(R₆₅) 6CH₄(g) + 2H₂O(g) → 2CO(g) + 3H₂(g)</td>
</tr>
<tr>
<td>Calcium/carbone looping</td>
<td>CaO → CaCO₃</td>
<td>(R₆₆) 2CO(g) + O₂(g) → 2CO₂(g)</td>
</tr>
<tr>
<td>RWGS</td>
<td>CO₂ + H₂ → CO/H₂O</td>
<td>(R₆₇) 3H₂(g) + CO(g) → H₂O(g) + CO₂(g)</td>
</tr>
<tr>
<td>Methanol oxidation</td>
<td>CH₁OH → CH₂O</td>
<td>(R₆₈) 2CO(g) + 2H₂(g) → 2CH₄(g) + 2H₂O(g)</td>
</tr>
</tbody>
</table>

Table 2 Reactions for MeOₓ → MeOₙ hydrocarbon partial oxidation, and calcium/carbone looping reactions illustrated in Fig. 8
Moreover, Ni is a known carcinogenic, thus possessing significant health and safety risks.\textsuperscript{193} Fe-based redox catalysts are also very promising for CL-methane POx owing to their suitable thermodynamic properties for both CH\textsubscript{4} reforming and H\textsubscript{2}O/CO\textsubscript{2} splitting, low cost and minimal environmental impact.\textsuperscript{59,194} However, compared to Ni-based oxygen carriers, Fe-based redox catalysts possess a low reactivity with CH\textsubscript{4} and a low selectivity towards synthesis gas.\textsuperscript{195} Because of their high activity and thermal stability, La-based perovskites with Fe, Mn, or Co as B-site cations have been widely investigated in recent years for CL-methane POx and CL-SMR.\textsuperscript{58–60,64,66,88,89,139,179,196–198} As mentioned above, the structural and compositional tailoring of the redox catalysts can open up extensive possibilities for improvements of CLR processes. Since the objective of this part of the perspective is not to present a comprehensive review of the redox catalysts used for CLR, we briefly summarize some of the strategies that have been demonstrated to enhance the reactivity and selectivity of redox catalysts in the following sections.

**Stabilization by a mixed conductive support.** The redox catalysts typically comprise of a primary metal oxide as an oxygen reservoir and an inert support to stabilize the metal oxide. The appropriate combinations of oxygen carriers and supports can potentially increase the selectivity of synthesis gas and reduce catalyst deactivation.\textsuperscript{199} For example, it has been demonstrated that the use of a mixed conductive support (such as La\textsubscript{0.8}Sr\textsubscript{0.2}FeO\textsubscript{3−δ} or Ca\textsubscript{0.8}Sr\textsubscript{0.2}Ti\textsubscript{0.8}Ni\textsubscript{0.2}O\textsubscript{3−δ}) enables fast solid state O\textsuperscript{2−} flux and electron/ hole exchange\textsuperscript{92,131,200} between the metal oxide crystallites and the surface of oxygen carrier particle, thereby allowing effective oxygen removal and restoration during reactions (R3) and (R4).\textsuperscript{201,202} Importantly, supports that promote the outwards diffusion of active metal should be avoided because such supports can potentially deactivate the redox catalysts via surface enrichment and agglomeration of the active metal oxide crystallites.\textsuperscript{203}

**Core–shell architecture.** The spatial distribution of support in an oxygen carrier particle also significantly affects its activity and selectivity.\textsuperscript{204} For example, Shafieefarhood \textit{et al.}\textsuperscript{59} demonstrated that an Fe\textsubscript{2}O\textsubscript{3}@La\textsubscript{0.8}Sr\textsubscript{0.2}FeO\textsubscript{3} (LSF) core–shell material was 10–200 times more active, selective and resistant to carbon formation than composite iron oxide-based materials comprising inert (Al\textsubscript{2}O\textsubscript{3} and MgAl\textsubscript{2}O\textsubscript{4}), ionic-conductive (YSZ), and mixed-conductive (LSF) supports. Neal \textit{et al.}\textsuperscript{58,60} and Shafieefarhood \textit{et al.}\textsuperscript{205} investigated the mechanism for CH\textsubscript{4} partial oxidation over an Fe\textsubscript{2}O\textsubscript{3}@LSF core–shell material and found four distinct regimes, viz. (i) full oxidation of CH\textsubscript{4} to CO\textsubscript{2}, (ii) competing full oxidation to CO\textsubscript{2} and partial oxidation to CO, (iii) partial oxidation of CH\textsubscript{4} to CO, and (iv) CH\textsubscript{4} decomposition. During deep oxidation in region (i) “loose” lattice oxygen from the iron oxide core transports and evolves into surface oxygen species. In region (ii), both selective and non-selective (i.e. loose) oxygen species compete for CH\textsubscript{4} oxidation, with O\textsuperscript{2−} flux and overall oxygen availability determining the product ratio. In region (iii), dissociatively adsorbed CH\textsubscript{4} species are partially oxidized by O\textsuperscript{2−} species on the surface, resulting in an increase in metallic iron species along with a decrease in the concentration of oxygen surface species. Coke formation in region (iv) results from the depletion of O\textsuperscript{2−} in the iron oxide core and CH\textsubscript{4} decomposition over metallic iron precipitated from the LSF lattice. Transient pulse studies showed that oxygen anion conduction and/or its evolution to electrophilic surface oxygen species is the rate-limiting step in all the reduction regions of interest.\textsuperscript{205} Oxygen atoms maintain a modified Mars–van Krevelen (MvK) mechanism throughout the reaction, while the mechanism of CH\textsubscript{4} oxidation changes from the Eley–Rideal in region (i) to a Langmuir–Hinshelwood-like mechanism in region (iii). These findings indicate that redox catalyst architectures that inhibit the formation of non-selective surface oxygen species while maintaining a steady supply of lattice oxygen to the surface can potentially lead to an improved performance for CL-methane POx.

**Use of promotors.** Ni- and Fe-based oxygen carriers have a high catalytic activity for the decomposition of CH\textsubscript{4} via (R64). Promotion of redox catalysts with a transition metal that is inactive for the dissociation of CH\textsubscript{4}, e.g. Cu, Ag, or Au, can suppress the formation of carbon during the CH\textsubscript{4} reforming step.\textsuperscript{206} In this regard, Imtiaz \textit{et al.}\textsuperscript{207} demonstrated that doping of Fe\textsubscript{2}O\textsubscript{3} with CuO significantly lowers its propensity for coke deposition in a CH\textsubscript{4} atmosphere. The high resistance to carbon deposition of Cu modified oxygen carriers was found to be due to the (partial) coverage of surface Fe with Cu. Some transition metals (e.g. Ru, Rh, Ir, etc.) can expedite the dissociation of C–H bonds in CH\textsubscript{4}\textsuperscript{208} and can therefore enhance the reforming activity of redox catalysts. Shafieefarhood \textit{et al.}\textsuperscript{139} reported a significant improvement in the performance of Rh-promoted CaMnO\textsubscript{2} and La\textsubscript{0.8}Ce\textsubscript{0.2}O\textsubscript{3} redox catalysts for CH\textsubscript{4} reforming. It was found that a higher concentration of CH\textsubscript{4} species on the surface of Rh-promoted catalysts accelerates the extraction of facile oxygen resulting in an enhanced O\textsuperscript{2−} conduction through the bulk of the redox catalyst. Therefore, a higher redox activity and synthesis gas selectivity was observed for Rh promoted redox catalysts at temperatures as low as...
500 °C than for pristine catalysts. Similar findings were reported by Palchelva et al.,226 for Rh promoted La0.8Sr0.2Fe0.8Co0.2Ga0.2O3, which showed a 40% enhancement in CO selectivity for methane conversion at 600 °C. Noble metals, modification with CeO2 nanoparticles can also improve the oxygen storage capacity and mobility in perovskite68 or iron oxides63,64,141,209 which in turn can enhance the availability of lattice oxygen for the methane POx to synthesis gas.

### 4.1.2 CL methane to chemicals

The selective oxidation of CH4 to value-added chemicals has been studied extensively, but no significant breakthroughs have been achieved that would enable commercial adoption. A key reason lies in the thermodynamic limitations: CH4 is more favorably converted to CO2 and H2O than to C2+ oxygcnates or C2+, hydrocarbons, as evident when comparing the Gibbs free energy changes for the respective reactions (Fig. 2b).210 In consequence, the reactions must be controlled kinetically through suitable catalysts.211 Even if CH4 is converted successfully to the desired products, these products tend to be more reactive than CH4 and can get oxidized readily to CO2, thus lowering the overall yield.

For CL-based CH4 partial oxidation, gaseous O2 is substituted by lattice oxygen. This eliminates the expensive air separation, ensures safer operation and inhibits non-selective oxidation reactions in the gas phase when carried out at high temperatures.212,213 In addition, the use of lattice oxygen is also shown to potentially benefit the product selectivity.214,215 Challenges in the design of suitable redox catalysts relate to the following aspects of CL-based CH4 oxidation processes:213 (i) CL would likely to require higher operating temperature than co-feed which may negate the selectivity benefit of using lattice oxygen, and (ii) the surface and bulk of the CL redox catalyst tend to undergo notable changes during the redox reactions, which makes maintaining a high product selectivity challenging. Below we briefly discuss several CH4 conversion schemes that were shown to be feasible in chemical looping mode.

**Oxidative coupling.** The oxidative coupling of methane (OCM) is a method proposed in the early 1980s to convert CH4 directly into ethane and ethylene according to reactions (R53) and (R54) at temperatures >600 °C.216 The exothermic reactions can be carried out either in “normal” catalytic fashion where oxygen is co-fed with CH4, or in a cyclic redox (chemical looping) operation expressed by reactions (R7) and (R8).212,217,218 For either mode, an upper limit of 25–30% yield for C2, hydrocarbon products has been supposed based on mechanistic considerations,215,217,219 which is near the yields required for economic competitiveness.220–222 Various engineering means have been suggested to improve yields, but no breakthroughs have been achieved to date.211,223,224 It is worth noting that early studies by Atlantic Richfield company, which operated a 12 year program on OCM focusing on the redox mode, reported an approximately 10% higher C2 selectivity under the chemical looping mode compared to the conventional catalytic route.215

The OCM reaction occurs via a complex mechanism including coupled heterogeneous and homogeneous steps (depending on the catalyst) and is initiated by breaking one of the four equivalently strong C–H bonds of the methane molecule to form methyl radicals.214,215,225 The low yields for C2, hydrocarbons obtained so far are largely due to secondary oxidation reactions of these reactive products with oxygen weakly bound to the surface of the catalyst and with oxygen in the gas phase, forming a significant amount of COx.71,222,226,227 More recently, the upper yield limit for C2, products in the absence of gas phase reactions was estimated to be as high as 60% at elevated pressure, which could possibly be achieved via chemical looping.225,228 Experiments with doped-Mg6MnO8 and Mn/Na2WO4/SiO2, a catalyst previously shown to attain single pass C2, product yields of ~25% in co-feed mode,229,230 gave C2+ product yields of 23.2% and 25%, respectively under a chemical looping mode.231–234 In these studies, the selectivity toward the coupling reaction was high, but the H2 molecules formed through the dehydrogenation reaction of ethane competed with CH4 molecules for reacting with activated oxygen on the surface of the catalyst, resulting in a decreasing rate of CH4 activation and consequently lower C2+, yields than expected.222 Hence, improving the activity of the redox catalysts without negatively affecting their selectivity is one important task. In addition, the reaction conditions (e.g. temperature and pressure) probably need to be revised to surpass C2+, product yields of 30%.235 The importance of dopants in Mg6MnO8 was highlighted recently,234 and it was found that Li-doping-induced oxygen vacancies reduce the adsorption energy of methyl radicals and increase the C–H activation barrier, resulting in an increased selectivity towards C2+. For doped Na3WO4 on SiO2-supported MoO3 catalysts (where M = V, Cr, Mn, Fe, Co or Zn) it was found previously that their performance is correlated with their electrical conductivity.236

**Non-oxidative dehydroaromatization.** Non-oxidative dehydroaromatization (DHA) is a promising route to produce C6H6 directly from CH4. Conversion of CH4 to C6H6 via reaction (R65) was first reported in 1993 using a ZSM-5 zeolite modified with Mo or Zn.237 Since then, a wide range of metals and zeolites have been investigated for DHA of CH4, but Mo-modified ZSM-5-based catalysts still remain the most effective.238,239

Despite being a potentially attractive pathway to selectively produce high-value aromatics, CH4 DHA has not yet been commercialized due to the following reasons: Firstly, CH4 DHA (R65) is endothermic and limited by the thermodynamic equilibrium. From Fig. 11, it can be seen that the amount of C6H6 produced is only significant at high temperatures (i.e. > 600 °C). Secondly, the inevitable decomposition of CH4 (R64) under reaction conditions not only lowers the equilibrium yield of C6H6 substantially but also causes coking and catalyst deactivation.241 Consequently, C6H6 selectivity is typically between 60–80% at CH4 conversions of ~ 10%, corresponding to net C6H6 yields of <10% under conditions of practical interest.219 Several strategies have been proposed to overcome these barriers, e.g. the use of membrane reactors to remove H2 produced during reaction242 or the periodic regeneration of the coked catalyst.73 Recently, a CL approach was suggested to potentially address all three limitations of conventional CH4 DHA process as following (Fig. 11): 145 (i) the reactive separation
of H₂ from the products of DHA reaction to enhance the equilibrium CH₄ conversion and C₆H₆ yield, (ii) heat generation by selective H₂ combustion to decrease the overall heat demand, and (iii) in situ steam generation to reduce coking. However, care must be taken because excessive presence of steam can negatively affect catalyst selectivity. Moreover, re-oxidation requirements for CL may affect the active MoCₓ species on Mo/ZSM-5. Using Mo/HZSM-5 (as the DHA catalyst) and Ce₀.₉Gd₀.₁Oₓ (as the SHC redox catalyst) in a composite bed, an approximately three times higher aromatics yield was demonstrated compared to the conventional process employing only Mo/HZSM-5 without periodic regeneration with oxygen.¹⁴⁵

Besides the two-step approach, Brady et al.²⁴⁰ proposed a four-step approach for CL-DHA. In the first step, DHA reaction is performed on a Mo/H-ZSM-5 catalyst at 700 °C to obtain a mixture of CH₄, C₆H₆, and H₂. Subsequently, H₂ present in the DHA effluent is combusted selectively using Fe₂O₃. The H₂O produced in step two is then removed using a high-temperature water adsorbent, e.g. Zeolite 5A, which can be regenerated using a temperature swing. Finally, the reduced oxygen carrier is re-oxidized back to Fe₃O₄ using steam. To increase the conversion of CH₄ and the yield of C₆H₆, the effluent from step three is fed again to the DHA unit in the subsequent cycle. Brady et al.²⁴⁰ demonstrated each of these above steps. Based on extrapolation, the upper limit of aromatics yield for such a process was estimated to be ~43%.²⁴⁰ However, an integrated CL-DHA process under such a multi-step scheme has yet to be demonstrated. Furthermore, the oxidation of Fe to Fe₂O₃ with steam is thermodynamically limited. It is also to be noted that the regeneration of Fe with water instead of air renders the overall process endothermic. The use of water for regeneration by Brady et al.²⁴⁰ may have been (partially) motivated by the lack of H₂ combustion selectivity of Fe₂O₃. Although this CL-enhanced DHA scheme is quite innovative, it could be simplified while accounting for the aforementioned design considerations. For this, other SHC redox catalysts with higher H₂ combustion selectivities should be considered in addition to iron oxides.⁸³,¹⁴⁵

Direct conversion of CH₄ to CH₃OH. Direct conversion of CH₄ to CH₃OH (and/or formaldehyde) via (R50) is thermodynamically feasible. However, despite over a century of research the development of such a process remains a challenge owing to (i) a large energy barrier associated with the activation of the C–H bonds of CH₄, and (ii) a lower stability of CH₃OH than CH₄, resulting in further oxidation of CH₃OH to CO₂.²⁴³ Consequently, CH₃OH is currently produced on a commercial scale from synthesis gas derived from coal or CH₄.²⁴⁴

To date, no heterogeneous catalyst exists that can activate CH₄ according to reaction (R50) while simultaneously inhibiting CH₃OH oxidation at practical yields.²⁴⁵ Interestingly, in nature monoxygenase (MMO) enzymes convert CH₄ selectively into CH₃OH at ambient temperature.²⁴⁶ The active sites in these enzymes, i.e. binuclear iron and copper centers, can be mimicked using zeolite frameworks. However, so far with Fe and Cu-based zeolites a high selectivity for CH₃OH is only achievable at very low CH₄ conversions (<0.1%).²⁴⁷,²⁴⁸ The low CH₃OH yields of the direct aerobic conversion of CH₄ to CH₃OH process is a thermodynamic feature that cannot be overcome by the choice of catalyst. Nonetheless, this thermodynamic constraint can be circumvented by using a CL approach and soft oxidants such as H₂O or N₂O.²⁵⁷,²⁵⁸ For example, using a Cu-exchanged mordenite zeolite, Sushkevich et al.²⁵⁵,²⁵⁶ reported an anaerobic CL process based on the reaction (R66) to avoid the over-oxidation of CH₃OH. In the proposed three-step process, the Cu-exchanged mordenite zeolite was first activated at 400 °C in a flow of either dry O₂ or He, followed by exposure to CH₄ at 200 °C and 7 bar to form methoxy species. Subsequently, the methoxy species were desorbed in the form of CH₃OH under a flow of a H₂O/He mixture. Once the desorption step was complete, the second reaction cycle was started by heating the zeolite again to 400 °C under a flow of dry O₂ or He. This process resulted in a normalized CH₃OH production rate of ~20 μmole CH₃OH g⁻¹ catalyst⁻¹ h⁻¹ (based on a cycle time of 6.7 h) with a selectivity of 97%, which is considerably higher than the CH₃OH production rate of 1.81 μmole CH₃OH g⁻¹ catalyst⁻¹ h⁻¹ reported for a continuous process using O₂ as the oxidant.²⁵⁴
4.2 Chemical looping for C₂⁺ valorization

4.2.1 ODH of light alkanes. As illustrated in Section 2, the chemical looping strategy has been explored to intensify the production of ethylene, an important commodity chemical with a worldwide production capacity exceeding 150 million tonnes per year. Compared to the well-established, yet energy- and carbon-intensive ethane (and naphtha) cracking processes, the CL-ODH approach (Fig. 12) has the potential to reduce the energy consumption and CO₂ emissions for ethylene production by as much as 87%. The significant process intensification of CL-ODH is enabled by: (i) built-in air separation via chemical looping; (ii) higher ethane conversion with autothermal operations via the in situ oxidation of hydrogen; and (iii) simplified downstream product separation due to the higher ethylene yield and the combustion of hydrogen. We note that extensive research has been conducted for catalytic ethane ODH in the presence of gaseous oxygen, but with limited success. The key challenges for catalytic ODH resides in the cost of oxygen, safety issues related to the oxygen/ethane co-feed, the lack of catalysts with high activity and selectivity, and the complexity for the removal of oxygenate byproducts. To date, no suitable ODH catalysts have been identified to achieve sufficiently high olefin yields (~70%) such that ODH could replace the conventional steam cracking processes. Moreover, most of ODH reactions were carried out at very low ethane partial pressures (<0.1 bar) due to safety concerns. In contrast, CL-ODH avoids direct contact between ethane and oxygen, provides integrated oxygen separation, and has demonstrated superior olefin yields (>70%) at practical ethane partial pressures (≥0.8 bar). In principle, the same CL-ODH strategy can be applied to other light alkanes such as propane and butane. The following discussions provide a brief account of the chemical looping studies related to ethane and propane conversion to light olefins.

The chemical looping operations illustrated in Fig. 12 can be realized by two types of redox catalysts with distinct functionalities. Type I redox catalysts function primarily as SHC materials. Using Type I catalysts, ethylene production is realized by a combination of dehydrogenation (DH) or cracking reaction (for olefin and hydrogen production) and SHC reaction (for the in situ oxidation of the hydrogen byproduct, reaction (R16)). In comparison, Type II redox catalysts catalyze ethane ODH reactions while donating their active lattice oxygen.

Type I: SHC redox catalysts. While it could be argued that Type II redox catalysts are more desirable due to their multi-functionality, Type I redox catalysts could offer better flexibility since they can be tuned independently for various operating conditions and reactor configurations. For instance, SHC redox catalysts have been explored to enhance both DH and thermal cracking reactions with a temperature range varying from 450 to 900 °C.

The use of SHC to enhance catalytic DH reactions (Route a in Fig. 12) was proposed in the late 1990s by Imai et al. in the context of propane dehydrogenation. While both co-feeding oxygen and redox mode operation using lattice oxygen were investigated, the latter was surmised to be superior based on both experimental data and reactor simulations. Resulting from their significant potential, various oxides were explored as SHC redox catalysts in the temperature range of 550–800 °C. Representative materials showing high (>90%) SHC selectivities, defined as the conversion of the hydrogen divided by the conversion of all combustible species, include Sb₂O₃, In₂O₃, WO₃, Bi₂O₃, PbCrO₄, doped ceria, ion-exchanged ZSM-5, etc. Bi, In, Pb, and Sb oxides often suffer from a poor redox stability owing to relatively low melting temperatures of their reduced states. Ceria doped with W, Bi, Cr or Pb, were found to be stable in the temperature range 500–600 °C with selectivities of up to 98% for hydrogen combustion in the presence of C₂ and C₃ hydrocarbons and oxygen storage capacities as high as 2 wt%. Mn- and La-containing perovskites also showed a high SHC selectivity and stability in the presence of C₃ hydrocarbons at 550 °C. It is noted, however, that the SHC selectivity tends to decrease with increasing temperature due to the lower activation energy for hydrogen combustion compared to hydrocarbon oxidation. Therefore, these early SHC studies focusing mostly on operating temperatures <650 °C were exclusively geared towards dehydrogenation applications in combination with a DH catalyst such as supported PGM (e.g., Pt) and chromium oxides.

![Fig. 12 Schematic of CL-ODH, redox catalyst types, and reaction schemes. Ethane is used as an example for light alkanes for illustration purpose.](image-url)
Another challenge with the DH and SHC concept resides in the incompatibility of the catalysts and their operating conditions. While physical and chemical interactions between the catalysts themselves can be avoided by spatially separating them (e.g. in a packed bed using different DH and SHC reactors), surface sites and dominating reaction pathways on DH catalysts can be affected by the steam generated from the SHC material. For instance, steam can lead to undesirable reforming reactions on PGM-containing catalysts. For oxide-based DH catalysts, steam (or air during the regeneration step) can affect the oxidation state of the active metal, induce changes in the surface compositions, and hence negatively affect the DH performance. Except for very few studies, the aforementioned studies used hydrogen and a hydrocarbon mixture (e.g. hydrogen, ethane, and ethylene) to evaluate the redox catalysts’ SHC performances. The incompatibility issues between DH and SHC have largely been unaddressed to date. Development of DH catalysts that are stable under redox conditions and in the presence of steam is therefore the key to apply the DH + SHC concept for CL-ODH.

SHC redox catalysts can also be integrated with thermal cracking reactions (Route b in Fig. 12). Unlike surface-catalyzed DH reactions, thermal cracking proceeds via gas-phase radical reactions and so steam generated by SHC would not negatively affect cracking reactions. Under this approach, the CL-ODH reactions proceed via parallel gas-phase and surface pathways, i.e. hydrogen generated from gas phase cracking reactions is selectively combusted on the surface of the redox catalysts.

In some cases, the redox catalyst surface can also function as a radical initiator to enhance the gas phase reactions (i.e. surface-initiated homogeneous reactions). It is noted that the initiation of radicals from alkanes typically requires temperatures close to or higher than 700 °C. While such a temperature range is not uncommon for CLC, the inverse relationship between SHC selectivity and reaction temperature for most oxide redox catalysts dictates that many of the SHC catalysts reported for DH + SHC, which are geared towards operating at 650 °C or lower, would not be compatible with thermal cracking reactions. The high operating temperature can also be challenging for oxides or metals with low melting points or high vapor pressures. To address these challenges, Dudek et al. investigated a number of Mn-containing redox catalysts including CaMnO₃, SrMnO₃, and Mg₆MnO₈ for selective hydrogen combustion using hydrogen and ethylene mixtures at temperatures up to 850 °C. The effect of promoters was also studied by impregnating Na₂WO₄ on each of these oxides. In general, Na₂WO₄ was effective in inhibiting the formation of COₓ, but negatively affected the redox activity of the mixed oxide. The operating temperature windows, i.e. the optimal temperature ranges with a high activity and selectivity towards hydrogen combustion, for the six redox catalysts investigated ranged between 550 and 850 °C. The large and tunable operating temperature window opens up the potential opportunity for integration of a SHC redox catalyst with thermal cracking. The effectiveness of CL-ODH under thermal cracking conditions was confirmed with Na₂WO₄ promoted Mn–Mg and Mn–Si oxides. Resulting from their high activity and high temperature SHC selectivity, ethylene yields up to 68% were demonstrated with CO₂ selectivities as low as 1.9%. Negligible coking was observed in these studies. This is not surprising considering the redox catalysts’ high activity for lattice oxygen donation, which can actively inhibit coke formation. Na₂WO₄ was important for obtaining a high olefin selectivity since it enriches on the oxide surface and suppresses the deep oxidation of hydrocarbons. In the case of the Mg₆MnO₈ system, a mixed oxide with a cation deficient rocksalt structure, near surface Mn⁴⁺ was suppressed by more than 85%. Further characterizations by low energy ion scattering (LEIS), in situ XRD, and differential scanning calorimetry indicated that the Na₂WO₄ is likely to form a molten layer on the oxide surface under the operating conditions and thus acts as a physical blocker to suppress surface catalyzed C–H bond activation. The corresponding process analysis further highlighted the advantages of CL-ODH of ethane over steam cracking. These include higher single-pass yields, a reduction in the total energy demand by > 80% and a reduction in CO₂ emissions by > 80%. Importantly, CL-ODH is self-sufficient from a process heat requirement point of view, making it a highly efficient and low emission technology ideal for distributed systems.

Type II: ODH redox catalysts. Many heterogeneous catalysts used in conventional ethane ODH (where oxygen is co-fed with the ethane) are redox-active. In the presence of gaseous oxygen (or, as was shown recently, mild oxidants such as steam), the reaction proceeds through a MVK mechanism in which ethane is activated and dehydrogenated by surface metal-oxide species, thereby reducing the metal oxide and creating oxygen vacancies. The vacancies on the surface are subsequently replenished by gaseous oxygen, which is dissociated and incorporated at surface sites different from the ODH reaction sites. The overall reaction is therefore facilitated by the migration of oxygen anions through the lattice and/or on the surface. The most common redox-active heterogeneous catalysts for ODH of light alkanes are based on vanadium oxide with different supports, such as alumina or silica. Nickel oxides and cobalt oxides have also been examined.

Since a key characteristic for the MVK mechanism is that the overall reaction can be carried out under a “swinging mode”, i.e. separating the reduction and oxidation into two sequential steps identical to chemical looping operations, it is not surprising that many of the redox-active catalysts can act as redox catalysts in CL-ODH schemes. For example, Hosain and de Las reported a number of cyclically stable VOₓ/γ-alumina-based catalysts for the CL-ODH of ethane in a continuous fluidized bed process consisting of an ODH reactor and a catalyst regenerator. Ethylene selectivities ranging from 80–90% at temperatures between 550–600 °C were reported. The corresponding ethane conversions, however, were relatively low (<10%). The same class of catalysts was also used for the CL-ODH of propane in the simulated fluidized bed process and propylene selectivities of > 90% were obtained at up to 25% conversion of propane. The good performance of the most promising
redox catalyst, VO_2/CaO-γ-Al_2O_3, was attributed to an intermediate acidity of the catalyst and moderate active site–support interactions. Encouraging results for ethane CL-ODH were also obtained with Mo-based redox catalysts, which gave ethylene selectivities of 93–95% and conversion up to 66.5% at 600 °C. The oxygen storage capacity of these Mo-based redox catalysts was relatively low (<0.4 wt%), resulting in a decreasing conversion of ethane with time. Nonetheless, in a continuously operating riser reactor system, an ethane conversion of 12% at ethylene selectivities >90% was obtained with a mixed Mo-Te-V-Nb oxide supported on γ-Al_2O_3 when the contact time of ethane feed and redox catalysts was 1–2 s at 500–575 °C. The same authors also showed that the performance of Mo-based redox catalysts is strongly affected by the support material (Al_2O_3, Ga_2O_3, or Y_2O_3), leading to an increased ethane conversion and ethylene selectivity with a decrease in the content of MoO_3; the best results were obtained with 5 wt% MoO_3 on alumina, giving 90% selectivity for ethylene at an ethane conversion of 30%. Novotny et al. investigated the effect of impregnating MoO_3 onto an Fe_2O_3-based redox catalyst, which improved the oxygen storage capacity from 0.28 wt% to 0.62 wt%. A MoO_3 and Fe_2O_3 enriched surface layer was formed upon calcination. At 600 °C, the ethylene selectivity was as high as 62% while CO_2 formation was suppressed when compared to pure Fe_2O_3. Supported chromium oxide catalysts are widely used in catalytic dehydrogenation, e.g., the commercial CATOFIN® process. Chromium oxides were also shown to perform reasonably well in CL-ODH of propane with potential use in a moving bed process. The oxygen storage capacity was determined to be crucial for the performance of the redox catalyst, and slightly higher oxygen capacities (up to ~0.5 wt%) resulted in higher yields of propylene (~46% at 630 °C). More recently, Chen et al. used to use Mo-VO mixed oxides as the redox catalyst for CL-ODH of propane to propylene. Attracting propylene yield (89% propylene selectivity at 36% pro-pane conversion) over 100 redox cycles was obtained at 500 °C due to the tailored bulk lattice oxygen via atomic-scale doping of Mo in the redox catalyst. Although promising results were obtained from these redox catalysts, the toxicity of Cr and V and thermal stabilities of Mo and V oxides could affect their practical applicability especially in circulating bed systems.

Aside from the redox-active oxides commonly found in heterogeneous DH and ODH catalysts, alkali metal-promoted, Ruddlesden–Popper structured, La_xSr_yFeO_3–δ redox catalyst was recently shown to be active for CL-ODH of ethane. Up to 90% ethylene selectivity and 61% conversion were observed at 700 °C, with near 100% H_2O selectivity. An important finding from this study was that electrophilic surface oxygen species (such as O^- and O_2-), which limit the selectivity of the ODH reaction and account for the deep oxidation of the alkanes and olefins, can be suppressed by enrichment of alkali metal oxide on the surface of the redox catalyst. A thin layer of Li_2O on the surface likely served as a barrier to inhibit the outward diffusion of O^- and its evolution into electrophilic oxygen species on the surface.

A common challenge with these Type II ODH redox catalysts is the lack of oxygen storage capacity. Most of the redox catalysts reported to date exhibit < 1 wt%, and in many cases < 0.5 wt%, oxygen storage capacity. As noted above, the utilization of lattice oxygen in CL-ODH is significantly more efficient than that in CLC. For instance, combusting one mole of propane under CLC consumes ten moles of lattice oxygen whereas under CL-ODH it consumes only one. The order of magnitude increase in oxygen utilization efficiency makes these low capacity redox catalysts potentially feasible for industrial applications, provided that high olefin selectivity, redox activity, and stability are demonstrated. Another challenge is the trade-off between conversion and selectivity especially in many of the V- and Mo-based redox catalysts, i.e., higher alkane conversion (e.g., by increasing the residence time) often leads to a significantly decreased olefin selectivity. This could result from the re-adsorption of the olefin products and/or the presence of distinct active sites for selective and non-selective reactions. In-depth understanding of the active sites and reaction pathways would be crucial for rational optimization of the redox catalysts. Although a large body of literature is available on conventional, catalytic ODH systems, the exact mechanisms for many redox-active ODH catalysts are still under debate. Dynamic nature of redox catalysts undergoing chemical looping reactions also makes mechanistic investigation on CL-ODH even more challenging than catalytic ODH. Therefore, further investigation on the mechanistic aspects of the redox catalysts is an important, yet challenging task. Although we did not separately discuss ethane and propane CL-ODH in this section, we note that propane (and C_4+) is significantly less stable than ethane. The tendency for C-C bond cleavage makes it more difficult to develop highly selective redox catalysts for CL-ODH of propane and C_4+ to olefins. Thus, a redox catalyst optimized for CL-ODH of ethane may not automatically be applicable for propane and C_4+ conversion.

### 4.2.2 Epoxidation of olefins

The epoxidation of olefins (R51) is another example for oxidation reactions where yields are generally low due to the non-selective oxidation of the educts and the epoxides; yet, these catalytic reactions are of enormous relevance for the chemical industry. So far, only the epoxidation of ethylene has been realized industrially using molecular oxygen as the sole oxidant. The selectivity to ethylene oxide is typically in the range of 85–90% at ~10% ethylene conversion with optimized silver-based catalysts. A chemical looping approach was recently explored to undertake the epoxidation reaction by substituting co-fed molecular oxygen with lattice oxygen (Fig. 13). Here, Ag (15 wt%) was impregnated onto the perovskite SrFeO_3 that possesses an oxygen storage capacity of up to ~2 wt%. The main rationale for selecting SrFeO_3 was its excellent ability to spontaneously release O_2 at relatively low temperatures. The authors proposed that oxygen was transported from subsurface SrFeO_3 to the surface of the redox catalyst and thus formed oxygen adatoms on the silver surface. The vital role of atomic oxygen adsorbed on the silver surface for catalyzing the oxidation of ethylene has been discussed extensively in the literature, as well as the availability of subsurface oxygen to achieve a high ethylene oxide selectivity. Furthermore, it was found in
previous studies that higher selectivities could be obtained with low surface area supports, a characteristic of most redox catalysts used in chemical looping applications. The selectivities and conversions reported by Chan et al. were, however, very low (the ethylene oxide selectivity was <20% and the ethylene conversion was <4% at 270 °C). Previous work showed that the dispersion of Ag, the morphology and temperature treatment of the support all affect, besides operational parameters, the performance of the catalyst. It is also possible that the exposed surface of SrFeO3 is largely responsible for non-selective oxidation reactions and the activity of the oxide substrate to catalyze non-selective oxidation reactions should not be overlooked. Another challenge observed by Chan et al. was the low rate of oxidation when the redox catalyst was regenerated in air, causing a gradual loss in oxygen capacity. A similar problem was reported for vanadium phosphorous oxide redox catalysts, as will be discussed in Section 4.2.3. The problem was overcome by modifying the SrFeO3 with 5 mol% CeO2, which also improved the cyclic stability and ultimately gave 60% selectivity towards ethylene oxide at 10% ethylene conversion. The authors proposed that CeO2 may have acted as oxygen gateway (see Section 3.2.2) and thus improved the re-oxidation of the redox catalyst. The challenge for further improvement will thus be to find oxygen storage materials with sufficient reduction/regeneration activities at temperatures <300 °C while suppressing over-oxidation of ethylene. Despite the relatively low reaction temperatures of 200–280 °C typically employed for the epoxidation of ethylene, Ag-based catalysts tend to deactivate owing to the sintering of the silver particles, and this may be even more problematic when the redox catalysts are regenerated in an exothermic oxidation reaction.

In principle, the chemical looping epoxidation approach can certainly also be applied to the selective oxidation of propylene, where it was shown recently that mixed metal oxides are catalytically active in a conventional oxygen co-fed mode. For a mixed MoO3/Bi2SiO5 catalysts supported on SiO2, propylene oxide selectivities of 55% were reported at a propylene conversion of 22% at 400 °C. Previous work showed that the dispersion of Ag, the morphology and temperature treatment of the support all affect, besides operational parameters, the performance of the catalyst. It is also possible that the exposed surface of SrFeO3 is largely responsible for non-selective oxidation reactions and the activity of the oxide substrate to catalyze non-selective oxidation reactions should not be overlooked. Another challenge observed by Chan et al. was the low rate of oxidation when the redox catalyst was regenerated in air, causing a gradual loss in oxygen capacity. A similar problem was reported for vanadium phosphorous oxide redox catalysts, as will be discussed in Section 4.2.3. The problem was overcome by modifying the SrFeO3 with 5 mol% CeO2, which also improved the cyclic stability and ultimately gave 60% selectivity towards ethylene oxide at 10% ethylene conversion. The authors proposed that CeO2 may have acted as oxygen gateway (see Section 3.2.2) and thus improved the re-oxidation of the redox catalyst. The challenge for further improvement will thus be to find oxygen storage materials with sufficient reduction/regeneration activities at temperatures <300 °C while suppressing over-oxidation of ethylene. Despite the relatively low reaction temperatures of 200–280 °C typically employed for the epoxidation of ethylene, Ag-based catalysts tend to deactivate owing to the sintering of the silver particles, and this may be even more problematic when the redox catalysts are regenerated in an exothermic oxidation reaction.

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## 4.2.3 Maleic anhydride production

ODH in a redox mode was demonstrated commercially by DuPont for the oxidation of n-butane to maleic anhydride to produce maleic acid (R53). Up to 6500 kg h⁻¹ of maleic acid were produced using a vanadium phosphorous oxide (VPO) redox catalyst in a circulating fluidized bed reactor operated at ~400 °C. The process was developed over a period of more than ten years, as summarized by Contractor, also highlighting the challenges associated with redox catalyst and reactor design. Selectivity of near 80% was claimed at a conversion of 40%. Nevertheless, the plant was shut down in the early 2000s, partially owing to economic reasons related to a rapidly changing market situation for different raw materials and intermediates, but also owing to problems with catalyst loss through attrition and deteriorating oxidation kinetics of the VPO catalyst, which resulted in a gradual loss in oxygen capacity during operation such that O2 had to be co-fed. We also note that the oxygen capacity of the VPO redox catalyst was rather low to begin with, corresponding to merely a few monolayers of lattice oxygen near the catalyst surface.

## 4.3 Chemical looping involving liquid and solid fuels

### 4.3.1 Liquid fuels driven processes

The CLBC approach can readily be extended to liquid hydrocarbons. In fact, it has been successfully employed to reform various liquid fuels, such as alcohols (e.g. methanol or ethanol), glycerol, waste cooking oil, liquid alkanes (e.g. dodecane), kerosene, heavy oil, and biomass tar. In addition to reforming, liquid fuels can also decompose or completely oxidize in the fuel reactor. For example, Ochoa et al. explored the nature of the surface species and gaseous products formed during...
4.3.2 Solid fuels driven processes. Owing to the slow rates of solid-solid reactions, using solid fuels directly for CLBC is challenging. Therefore, solid fuels (such as biomass or coal) are typically gasified in a separate unit and the resulting synthesis gas is fed to the chemical looping process designed for gaseous fuels.371–374 To avoid dilution of the synthesis gas with \( \text{N}_2 \), the gasification reaction needs to be carried out with pure \( \text{O}_2 \) or a mixture of \( \text{O}_2 \) and \( \text{steam/CO}_2 \). Therefore, an air separation unit but also enhances the rate of gasification.375,376 However, special care must be taken when using viscous liquids such as tar or heavy oil to avoid their condensation upstream and/or downstream of the fuel reactor. Similar to Type II ODH process, the chemical looping approach has been applied for the oxidative cracking of naphtha. Process simulations indicate that over 50% energy and \( \text{CO}_2 \) savings can be achieved via the chemical looping route.112 Using perovskite-based redox catalysts, Dudek et al.57 demonstrated close to 70% olefin selectivity with a \( \text{CO}_2 \) selectivity as low as 0.3%.

4.4 Synergy between oxide and calcium/carbonate looping

CaO-Based sorbents, often in the form of naturally-occurring lime, are used widely in applications such as flue gas desulfurization387–389 and sorption-enhanced steam methane reforming (SE-SMR) to produce \( \text{H}_2 \).390–393 In SE-SMR, \( \text{CO}_2 \) is removed continuously in the WGS reaction step, thus shifting the equilibrium to the product side according Le Chatelier’s principle.394 The \( \text{H}_2 \) yield can thereby be increased to ~97 vol% at 550 °C.395 The WGS reaction is relevant also in gasification reactions, and generally in schemes where mixtures of \( \text{CO}, \text{CO}_2, \text{H}_2 \) and \( \text{H}_2\text{O} \) co-exist at high temperature, and so sorbents for \( \text{CO}_2 \) are conventionally used.396 Lately, CaO-based sorbents have also gained considerable attention for carbonate looping (CaL).397–405 A post-combustion \( \text{CO}_2 \) capture technique.402,406 A key advantage of using \( \text{CaO} \) for the sorption of \( \text{CO}_2 \) is its high theoretical uptake of 0.78 g \( \text{CO}_2 \) per g \( \text{CaO} \), according to reaction (R68) in Table 2. The carbonation reaction is exothermic whereas the reverse reaction, known as the calcination reaction, is endothermic, giving a stream of concentrated \( \text{CO}_2 \).407 Carbonate and oxide (chemical) looping processes can be combined to improve efficiencies of both processes, as discussed below.

4.4.1 Reaction schemes

Chemical looping with sorbent enhancement for heat-neutral sorbent regeneration. Besides permitting higher yields of \( \text{H}_2 \) in the SE-SMR/gasification scheme, the exothermic carbonation reaction can provide a large amount of heat for the strongly endothermic methane reforming or the gasification reaction. Meanwhile, the regeneration of the sorbent via the highly endothermic calcination reaction is critical and requires high reaction temperatures (> 750 °C). Performing the calcination reaction in the presence of an exothermic reaction would balance the heat requirements. Such exothermic reaction could be the oxidation of a reduced oxygen carrier, as suggested by Lyon and Cole,161,408 e.g. the simultaneous oxidation of the
Ni-based reforming catalyst. However, a relatively high ratio of Ni to CaCO₃ (> 0.75) would be required to balance the heats of reaction, resulting in an increase in the catalyst cost, and the CO₂ produced is diluted with N₂ when air is used for the re-oxidation of Ni. In addition, the oxidation of the reforming catalyst at high temperature is likely to promote its sintering and deactivation.

**Chemical looping with sorbent enhancement for CO₂ capture.** The simultaneous oxidation and calcination reactions eliminate the benefit of CaO-based sorbents to produce a pure stream of CO₂. In CaO-based CO₂ capture architectures, the calcination reaction can be performed in a reactor operated in an oxy-fuel mode, where the heat is provided by combusting additional fuel (e.g. natural gas) in an atmosphere containing O₂ diluted with CO₂. Replacing molecular oxygen with an oxygen carrier that reduces in an exothermic reaction while fully combusting the fuel would enable both the balancing of the endothermicity of the calcination reaction and generating a pure stream of CO₂. A few redox pairs, e.g. CuO/Cu or Mn₂O₃/Mn₃O₄, can be reduced exothermally with CH₄ and other hydrocarbons. This feature can be applied to integrate the heat released from the CLC reduction step with the endothermic calcination step to produce concentrated CO₂. A reaction scheme where CuO-based chemical looping combustion is combined with SE-SMR is shown in Fig. 14a and at least three reactors are required to obtain separate streams of H₂ and CO₂.

For carbonate looping as a CO₂ capture technique, heat integration is vital to be economically competitive with other CO₂ capture techniques. In analogy to the SE-SMR process, CuO-based oxygen carriers have mostly been investigated to render the heat exothermic during the exothermic calcination step. Unlike the CLC reduction step that is often endothermic, the regeneration step is always exothermic for monometallic oxides. Therefore, integration of the heat released in the CLC regeneration step with the sorbent calcination step can also result in concentrated CO₂ if a heat transfer agent is used to avoid direct contact between the air (in the regeneration step and the oxidizer) and CO₂ (from calcination in the calciner). Both ALSTOM and General Electric proposed and investigated such schemes (details on these two processes have been summarized by Fan). In ALSTOM’s Hybrid Combustion–Gasification Process for hydrogen generation, a CaSO₄ oxygen carrier is employed to generate the heat for the calcination of the CaO sorbent. Instead of oxidizing the oxygen carrier in the vicinity of the CaCO₃, bauxite is used to transfer the heat from the oxidation reactor to the calcination reactor. Similarly, General Electric’s Fuel-Flexible Advanced Gasification–Combustion Process also adopted CLC reactions to provide the heat for calcination. In this case, an iron oxide-based oxygen carrier was used as the heat transfer agent.

**Sorption-enhanced methane reforming coupled with chemical looping conversion schemes.** The thermodynamic properties of some oxygen carriers permit the splitting of CO₂ or H₂O to produce CO or H₂ upon oxidation (see Section 4.1.1). Since the rate of reduction of many oxygen carriers, e.g. Fe₂O₃, with primary fuels such as CH₄ is low, it was proposed to convert CH₄ first to a synthesis gas over a catalyst (e.g. Ni; in analogy to the dry reforming of methane (DRM)) and use the synthesis gas to reduce the oxygen carrier. Depending on the oxidant used (CO₂ or H₂O) for the subsequent regeneration of the oxygen carrier, CO or H₂ can readily be produced.

This reaction concept can be extended by adding a CaO-based sorbent (Fig. 14b). Analogously to SE-SMR, the heat of sorption from the carbonation reaction (reaction (R68)) balances the endothermic reforming and reduction reactions. In the following oxidation step, CO₂ is released from the sorbent and oxidizes the oxygen carrier while producing CO. The chemical looping concept, where in theory three moles of CO₂ per mole CH₄ are converted to four moles of CO, has been termed super-dry reforming of methane (R67). Importantly, in such a process the formation of an equilibrium mixture of CO₂, CO, H₂O and H₂ is circumvented during the...
reforming step, thus avoiding a loss in CO yield through the RWGS reaction \((R71)\). So far, the process has been demonstrated by mixing different materials, viz. CaO supported on \(\text{Al}_2\text{O}_3\) as \(\text{CO}_2\) sorbent, \(\text{Fe}_2\text{O}_3\) supported on \(\text{MgAl}_2\text{O}_4\) as oxygen carrier, and \(\text{NiO}\) supported on \(\text{MgAl}_2\text{O}_4\) as the \(\text{CH}_4\) reforming catalyst, rather than multifunctional redox catalysts. While the theoretical advantages over conventional dry-reforming of \(\text{CH}_4\) are apparent, there is still scope for improvement (besides improving the materials used). For example, it was proposed to run the process isothermally. Equilibrium thermodynamics dictate that the release of \(\text{CO}_2\) from the \(\text{CO}_2\) sorbent requires very low \(\text{CO}_2\) partial pressures and for that, an inert gas would likely be needed in the oxidation step (where \(\text{Fe}\) is oxidized by the \(\text{CO}_2\) released from the sorbent). This will inevitably dilute the product gas \(\text{CO}\). The product gas \(\text{CO}\) is diluted further with \(\text{CO}_2\) because the conversion of \(\text{CO}_2\) to \(\text{CO}\) over \(\text{Fe}\) is thermodynamically limited and the ratio of \(\text{CO}/\text{CO}_2\) in the product gas will decrease further as the \(\text{Fe}\)-based oxygen carrier is oxidized via \(\text{FeO}\) to \(\text{Fe}_3\text{O}_4\).

### 4.4.2 Material design.

The performance and function of CaO-based sorbents can be further improved by doping with active oxides\(^{414,421,422}\), addition of supports\(^{423}\), acid modifications\(^{424,425}\), and morphology control\(^{421,426}\). One of the most studied combined oxide and carbonate looping schemes is CuO-based chemical looping combustion coupled with SE-SMR\(^{427-430}\). In this process, at least three materials are required: A catalyst for the reforming of \(\text{CH}_4\), a sorbent for \(\text{CO}_2\), and \(\text{CuO}\) as the oxygen carrier that can be reduced by various fuels in an exothermic reaction. If \(\text{CH}_4\) is used as the fuel, the \(\text{Cu}/\text{Ca}\) ratio needs to be \(>3.1\) to achieve thermally neutral conditions in the calcination step based on the enthalpies of reaction at 900 °C. However, this figure varies somewhat and is subject to the process design, the type of fuel (e.g. using \(\text{CO}\) as the fuel, the ratio would be 1.3) and the heat management strategy\(^{431,432}\).

Three active components make the design of suitable, “trifunctional” materials rather challenging\(^{433}\). Current research thus focuses largely on the development and optimization of separate particle systems\(^{434-436}\) or bi-functional \(\text{Ca–Cu}\)\(^{422,437-440}\) or \(\text{Ca–Ni}\)\(^{441-443}\) composites and uses commercially available Ni-based catalyst particles\(^{444,445}\). The \(\text{CO}_2\) capture capacity of the CaO-based sorbents is linked strongly with the available surface area, which is known to decay due to sintering when the sorbents undergo cycling of carbonation and calcination\(^{446-448}\). Producing stable particles with a porous CaO structure in the vicinity of low surface area CuO in a Ca–Cu composite material requires appropriate support materials, e.g. MgO\(^{449}\) or \(\text{Ca}_2\text{Al}_2\text{O}_3\)\(^{450}\). Recent works\(^{405,414,451}\) at ETH Zürich have shown how such support materials function as structural stabilizers at the microscopic level and how subtle phase transitions affect the cyclic performance of the CaO-sorbents (Fig. 15). Another recent study...

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**Fig. 15** Morphological changes during cyclic operation of a Ca–Mg mixed oxide-based sorbent. (a–c) SEM images of FIB cross-sections. (d–f) HAADF-STEM images with EDX maps of Ca and Mg at different stages of \(\text{CO}_2\) capture/regeneration cycles. Scale bars: 1 µm for (a–c) and 700 nm for (d–f).\(^{451}\)
reported an interesting phase transition based approach to
effectively enhance sorbent stability for the hydrogen production
from bio-glycerol.452

Conventional design strategies aim to limit the mobility of
active species and their growth by using inert support materials
that act as physical barriers.199 New approaches have shown that
the active species in a sorbent or redox catalyst may well be
mobile, but their self-diffusion is limited if the simultaneous
formation of a new phase with the active species is thermo-
dynamically more preferred.453 For example, Dang et al.452
demonstrated that calcium cobalt, a layered bi-functional
material acting as both sorbent and catalyst for the sorbent
enhanced reforming of glycerol could effectively be stabilized
because the components CaCO3 and CoO homogenized into
calcium cobalt on an atomic level in every calcination stage of
the cyclic process instead of remaining segregated and sintering.
Well-ordered structures, such as layered oxides, spinels or
perovskites are particularly suitable for such approaches.452,454

For reaction schemes such as the super-dry reforming of
methane, catalyst and oxygen storage material are usually
separated spatially.455 Work by Hosseini et al. demonstrated
that both the reforming of methane through the catalyst and
the reduction of the oxygen storage material can be realized by
the same redox catalyst particle provided it is designed carefully
in a core–shell structure.456

5. Summary and perspective

The chemical and petrochemical industry generates an annual
revenue in excess of $4 trillion while consuming 40.9 quad-
rillion BTU of energy and emitting 2.5 Gigatons of CO2 (2014
numbers provided by IEA).457 The significant energy intensity
and CO2 emissions associated with this important industrial
sector offer excellent opportunities for process intensification,
energy conservation, emission reduction, as well as profitability
enhancement. We believe that CLBC represents a promising
new frontier in chemical reaction engineering, catalysis, and
particle technology to address the aforementioned challenges
and opportunities. As discussed in Section 2, the unique
advantages of CLBC largely reside in its ability to significantly
improve a chemical (and energy) conversion process from a
thermodynamic second law standpoint: a strategically designed
CLBC scheme, when coupled with tailored oxygen carrier or
redox catalyst, can significantly reduce process exergy loss and/
or facilitate chemical transitions that would otherwise be
impossible under a conventional scheme. From an economic
standpoint, reactive separation enabled by oxygen carriers in
CLBC offers excellent potential to simplify conventional pro-
cesses and to reduce the number of unit operations. With the
continued technical progress in CLC, a promising carbon
capture technology that addresses the carbon intensive,$1.4 trillion power generation sector, we argue that chemical
looping beyond combustion offers equally and perhaps even
more exciting opportunities due to their potential for more
efficient lattice oxygen utilization, higher product value, and
relative ease for scale-up compared to full scale utility plants.

Although CLBC has attracted increasing attentions over the
past 5–10 years, we note this emerging research area is far
from being adequately explored particularly considering its
significant complexity and excellent potential. From scientific
and engineering standpoints, CLBC represents an “ultimate”
multidisciplinary and multiscale challenge that requires expert-
ise in various areas including, but not limited to, chemical
looping, heterogeneous catalysis, material science, particle
technology, reaction and reactor engineering, and process
and system engineering. This is due to the uniquely intertwined
nature of CLBC. For instance, redox catalyst performance
cannot be treated in an isolated manner since it is significantly
affected by reactor design and gas–solids contacting patterns as
well as the multi-step redox scheme configuration. Meanwhile,
the redox catalyst can undergo significant changes in its surface
and bulk properties within a CLBC cycle that exceeds complex-
ities typically observed in heterogeneous catalysts. Such
complexities, while daunting, are closely associated with the
unique advantages CLBC has to offer. They can and should be
addressed through continued research via interdisciplinary
efforts. From a practical standpoint, redox catalysts with high
stability and satisfactory long-term performance are critical for
CLBC. Moreover, reactor designs that facilitate suitable redox
catalyst particle circulation, gas–solids contacting patterns,
residence time distributions, and heat integration between
multiple reactors are important to enable these promising
CLBC technologies.

This article aims to cover all the CLBC schemes to the best of
our knowledge. Although a number of promising approaches
such as oxidative dehydrogenation of light alkanes and alkene
epoxidation are under investigation, significantly greater
opportunities still exist both within and beyond these CLBC
topics. From a reaction chemistry standpoint, the chemical
looping approach is analogous to the MvK mechanism com-
monly encountered in catalytic oxidation reactions. As illu-
strated in Fig. 16, CLBC carries out catalytic oxidation cycles
via a step-wise MvK with macroscopic spatial or temporal
separation of the lattice oxygen removal and replenishment
events. This is in contrast with conventional MvK, where the
catalytic cycle is completed on the surface of an oxide catalyst
under steady-state operations. The step-wise operations in
CLBC offers both significant advantages (reactive separation,
process intensification, and energy/cost reduction) and potential
challenges (surface and/or phase changes of the redox catalytic
under redox cycles). Considering their similarities, it would not
be unreasonable to anticipate catalytic reactions operated under
MvK mechanism to be potentially suitable candidates for CLBC.
Table 3 summarizes a number of such candidate reactions.

Compared to the limited CLBC reactions investigated to date,
a significantly number of potential reactions are yet to be
explored. In addition, the regeneration step in CLBC, which
was demonstrated to be effective for H2 and CO production
via CO2/H2O splitting, could be investigated for hydrogenation
or carboxylation reactions. Carriers other than oxygen, e.g. nitrogen
Fig. 16 Comparison of O₂ co-feeding (MvK) and chemical looping modes for partial oxidations and their applications on conversions of hydrocarbon to chemicals (transformation between alkane, alkene, alcohol, aldehyde, ketone, acid, and aromatics).

Table 3 Partial oxidation reactions facilitated by oxide catalysts via the Mars van Krevelen mechanism. The overall oxidation reactions are numbered from (R73) to (R111) and these reactions can potentially be realized by CLBC.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Products</th>
<th>Reaction</th>
<th>Heterogeneous catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Formaldehyde</td>
<td>(R73) CH₄ + 2CO₂ → CH₂O + 2CO + H₂O</td>
<td>V₂O₅/SiO₂, Fe₃[MoO₄]₆⁴⁵⁴⁶⁰</td>
</tr>
<tr>
<td>Methanol</td>
<td>Formaldehyde</td>
<td>(R74) CH₃OH + 1/2O₂ → CH₂O + H₂O</td>
<td>Fe₂O₃/TiO₂, SnO₂–MoO₃⁴⁶²</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Acetic acid</td>
<td>(R76) C₂H₅OH + O₂ → CH₃COOH + H₂O</td>
<td>V₂O₅/TiO₂⁴⁶³</td>
</tr>
<tr>
<td>O₂-cofeeding (MvK) Mode</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td>1-Butene</td>
<td>(R86) C₄H₁₀ + 1/2O₂ → C₄H₈ + H₂O</td>
<td>P-Doped Fe–Mo mixed oxide⁴⁶⁶</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>Glutaraldehyde</td>
<td>(R89) C₅H₁₀ + 5/2O₂ → 2CH₃COOH + H₂O</td>
<td>V₂O₅/SiO₂⁴⁵⁸</td>
</tr>
<tr>
<td>Ethyl lactate</td>
<td>Ethyl pyruvate</td>
<td>(R90) C₅H₁₀O₂ + 1/2O₂ → C₅H₈O₃ + H₂O</td>
<td>Fe₂O₃/TiO₂⁴⁸¹</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>Cyclohexanone</td>
<td>(R91) C₆H₁₂ + 1/2O₂ → C₆H₁₀O₂ + H₂O</td>
<td>V₂O₅/TiO₂⁴⁸¹</td>
</tr>
<tr>
<td>Glucose</td>
<td>Lactic acid</td>
<td>(R93) C₆H₁₂O₆ + O₂ → C₆H₁₀O₃ + 3CO₂ + 3H₂O</td>
<td>Fe₂O₃/TiO₂⁴⁸¹</td>
</tr>
<tr>
<td>5-Hydroxymethylfurfural</td>
<td>2,5-Furandicarboxylic acid</td>
<td>(R94) C₆H₁₀O₇ + 3/2O₂ → C₆H₁₄O₄ + 4H₂O</td>
<td>Fe₂O₃/TiO₂⁴⁸¹</td>
</tr>
<tr>
<td>Benzene</td>
<td>Maleic acid</td>
<td>(R95) C₆H₆ + 9/2O₂ → C₆H₄O₃ + 2CO₂ + 2H₂O</td>
<td>V₂O₅/SiO₂⁴⁸³</td>
</tr>
<tr>
<td>Toluene</td>
<td>Benzoic acid</td>
<td>(R96) C₆H₅CH₃ + O₂ → C₆H₄O₂ + H₂O</td>
<td>V₂O₅/SiO₂⁴⁸³</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>Benzaldehyde</td>
<td>(R97) C₆H₅CH₂OH + 3/2O₂ → C₆H₅COOH + H₂O</td>
<td>V₂O₅/SiO₂⁴⁸³</td>
</tr>
<tr>
<td>p-Cresol</td>
<td>p-Hydroxybenzyl alcohol</td>
<td>(R98) C₆H₅CH₂OH + 1/2O₂ → C₆H₅COOH</td>
<td>V₂O₅/SiO₂⁴⁸³</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>Styrene</td>
<td>(R100) C₆H₁₁ + 1/2O₂ → C₆H₈ + H₂O</td>
<td>Mn₃Ti₄O₁₃ [x = 0–0.15]⁴⁸⁴</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>Phthalic anhydride</td>
<td>(R101) C₆H₁₀ + 3O₂ → C₆H₄O₃ + 3H₂O</td>
<td>V₂O₅⁴⁸⁵</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>Phthalic anhydride</td>
<td>(R102) C₁₀H₈ + 9/2O₂ → C₆H₄O₃ + 2CO₂ + 2H₂O</td>
<td>V₂O₅-Based catalysts⁴⁸⁶</td>
</tr>
</tbody>
</table>
carriers, also offer exciting potential for chemical syntheses. Aside from these, significant progress still needs to be made towards in-depth understanding of redox reaction mechanisms, catalyst design and optimizations, reactor and process design and operations, as well as process scale up for the existing CLBC approaches. To summarize, we believe that CLBC represents a largely uncharted and extraordinarily exciting area of research and potential applications.

Conflicts of interest

Authors have no conflict of interest to declare.

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