



Chemical looping: To combustion and beyond



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ABSTRACT

Chemical looping combustion (CLC) is a rapidly emerging technology for clean combustion of fossil and renewable fuels which allows production of sequestration-ready CO₂ streams with only minor efficiency penalties for CO₂ capture. While initial interest in chemical looping was almost exclusively focused on combustion, we demonstrate here that the underlying reaction engineering principle forms a highly flexible platform for fuel conversion: Replacing air with steam or CO₂ as oxidizer yields the chemical looping analogue to steam and dry reforming, resulting in the production of high purity hydrogen streams without the need for further clean-up steps and a novel route for efficient CO₂ activation via reduction to CO, respectively. Furthermore, by controlling the degree of carrier oxidation, incomplete, i.e. partial oxidation of the fuel to synthesis gas is attained. Finally, appropriate selection of oxygen carrier materials even allows simultaneous desulfurization of the effluent stream, resulting in a strongly intensified process for highly efficient, low-emission conversion of S-contaminated fuel streams. Based on new results from our own research, the present paper presents a brief overview over the potential of chemical looping processes for methane conversion with a particular focus on the key role of engineered carrier materials as enablers for this class of processes.

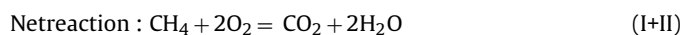
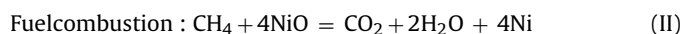
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1. Introduction

Reliable supply of energy is a basic foundation for sustained development and economic growth of modern society. At the present, the world's energy needs are met predominantly through the combustion of fossil fuels, with no significant change predicted for at least the next few decades. In combination with the continuously increasing global energy demand, and in the absence of effective countermeasures, fossil fuel based energy production is hence predicted to result in an increase in energy-related CO₂ emissions from ~30 Gt in 2008 to ~43 Gt in 2035 [24]. Therefore, major efforts are underway to develop more efficient energy technologies and economically viable CO₂ capture and sequestration technologies.

Chemical looping combustion (CLC) is emerging in this context as a particularly promising combustion technology which offers an elegant and efficient route towards clean combustion of fossil fuels [2,16,30]. In CLC, the combustion of a fuel is broken down into two, spatially separated half-steps: The oxidation of an oxygen carrier (typically a metal) with air and the subsequent reduction of this carrier via reaction with a combustible fuel. The overall net reaction

yields a conventional combustion, as illustrated below using Ni as “carrier” and methane as fuel:



It is noteworthy that over the full cycle the “oxygen carrier” undergoes the same cyclic reduction-oxidation as a catalyst (in the well-established Mars-van Krevelen mechanism) and, in fact, fulfills the same function as a catalyst, i.e. it facilitates the reaction without being formed or consumed in the reaction.

The two reaction steps are typically conducted in two separate reactors which are coupled through the carrier transport between the reactors, most commonly in a circulating fluidized bed (CFB) configuration (Fig. 1). However, due to the issues associated with the transport of large amounts of solids (in particular attrition of the carrier material), fixed-bed reactors with periodic switching of the reactor feed from oxidizing (air) to reducing conditions (fuel) – i.e. a temporal rather than a spatial separation of the two reactions steps – are also being actively investigated. While this configuration minimizes the issues associated with the mechanical strength of the carrier, control of temperatures in the reactor is a challenge in the fixed-bed process [36].

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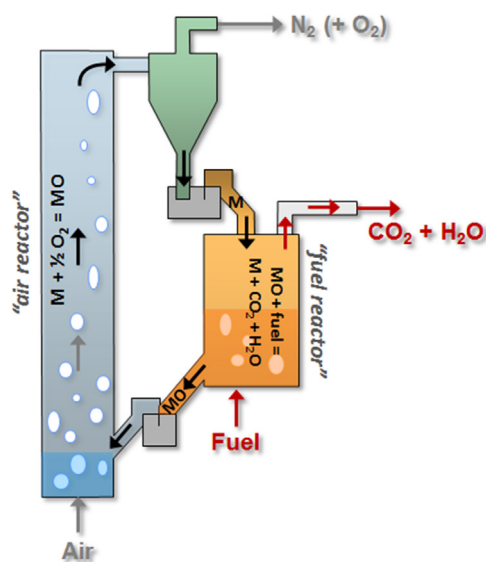


Fig. 1. Schematic of a typical circulating fluidized bed (CFB) reactor configuration for chemical looping combustion. An oxygen carrier ("M") is periodically oxidized with air in the air reactor, and reduced in contact with a fuel in the fuel reactor.

Among the main advantages of CLC in comparison to conventional (mixed) combustion are the fact that the combustion is flame-less, it operates at sufficiently low temperatures to avoid NO_x formation in the (air-blown) oxidizer, and it completely suppresses prompt- NO_x formation by avoiding any contact between the fuel and air. Most importantly, however, CLC ideally produces a pure mixture of CO_2 and H_2O as combustion gases, from which highly concentrated high-pressure (i.e. sequestration-ready) CO_2 -streams can be produced via condensation of the water. By avoiding a mixing of the fuel with air, CLC thus entirely avoids nitrogen dilution of the effluent gases from the fuel oxidation step and hence any of the capital and energy intensive CO_2 separation steps that are needed for CO_2 capture in virtually any other "clean combustion" scenario. The chemical looping concept is hence unique among combustion processes as it results in only minor efficiency penalties for CO_2 capture compared to competing approaches (such as oxyfuel combustion or post-combustion CO_2 capture via CO_2 sorbent materials) [10,27].

While initial interest in chemical looping was almost exclusively focused on combustion, the reaction engineering principle behind chemical looping – i.e. the splitting of a reaction into two spatially separated reaction half-steps which are coupled through the periodic oxidation and reduction of an "oxygen carrier" – has recently been applied to further fuel conversion reactions beyond combustion [2,15]. For example, syngas formation in a chemical looping process configuration have started to attract some attention in recent years. In these process schemes, either steam is co-fed with methane in the fuel reactor, resulting in the "looping equivalent" of autothermal reforming (ATR) of methane, i.e. steam reforming with supplemental oxygen, or the process feeds are kept unchanged from the original CLC process, but the degree of fuel oxidation is controlled (typically via use of appropriate carriers or control of carrier residence time) such that incomplete, i.e. partial oxidation to synthesis gas ($\text{CO} + \text{H}_2$) results [13,41]. In both cases the avoidance of nitrogen dilution of the product streams is again among the main advantages of the "looping configuration" over the respective conventional processes.

Beyond direct oxidation, chemical looping has also shown promise as a novel reforming process: By replacing air as the oxidizer feed with steam or CO_2 , respectively, yields the chemical looping analogue to steam and dry reforming. However, in contrast

to the conventional reforming process, chemical looping results in the first case directly in the formation of high purity hydrogen streams as the effluent of the oxidizer, which can be fuel cell-ready without the need for further CO removal or other carbon clean-up steps [18,47]. Similarly, the second case results in the activation of CO_2 via reduction to CO , opening the path to efficient CO_2 utilization [33].

Finally, appropriate selection of oxygen carrier materials even allows to make use of the chemical looping process scheme for simultaneous, integrated desulfurization of the effluent stream, resulting in a novel, strongly intensified process for highly efficient, low-emission conversion of S-contaminated fuel streams [46,48].

A key to success for all these emerging chemical looping processes is the oxygen carrier: The carrier needs to fulfill a range of very stringent requirements, including: high reactivity in both the oxidation and the reduction reaction; good selectivity for the desired (total or partial) oxidation of the fuel; excellent high-temperature stability over thousands of redox cycles; strong coking resistance as well as resistance against other fuel contaminants; and excellent attrition resistance if used in a transport reactor configuration. Major efforts are hence dedicated to identifying suitable carriers, and increasing activity and robustness of candidate materials.

The present contribution, which is based on a keynote presentation at the 10th symposium on natural gas conversion (NGCS-10, Doha), aims to give a brief overview of these emerging chemical looping processes, using mostly new results from recent work in our own research group on chemical looping processes for methane conversion as illustrative examples. A particular focus will be on the discussion of carrier selection and how synthesis of nanostructured carrier materials can result in particularly active and robust carriers for this class of processes, highlighting the role of engineered materials as enablers for new and emerging reaction engineering concepts.

2. Chemical looping combustion

The application of the chemical looping principle to combustion has experienced an explosive development over the past ~15 years with an ever increasing volume of publications which has by now reached hundreds of papers published annually covering the broad range of engineering challenges associated with chemical looping combustion, including reactor design and operation, thermodynamic analysis of the exergetic efficiency of different processes, and the design, synthesis, and kinetic evaluation of improved carrier materials. This vast amount of work is reflected in an ever increasing number of review articles on this topic, and the interested reader is referred to these for a more in-depth review on the application of chemical looping to combustion processes [2,16,30]. Here, we will focus on a brief discussion of the design of carrier materials for chemical looping combustion, utilizing our work on the design of nanostructured carrier materials for this reaction as illustrative example.

Few chemical processes impose as demanding operating conditions on a catalytic material as chemical looping combustion does: The oxygen carrier (which fulfills the definition as a reaction catalyst when seen over the entire redox cycle, although it strictly acts as a reactant in either of the two half reactions) needs to withstand sintering at very high-temperatures (typically ~800–1000 °C for CLC), show fast oxidation and reduction kinetics over many redox cycles, and, if used in a transport reactor, has to show sufficient mechanical strength to avoid attrition (which not only destroys the carrier but also results in the contamination of the effluent stream with ultra-fine particulates). Broadly, two approaches towards this issue can be found in the literature [3,25,31]: The use of natural ores

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