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Carbon capture and utilization via chemical looping dry reforming

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A B S T R A C T

Chemical looping combustion (CLC) is a clean energy technology for CO_2 capture that uses periodic oxidation and reduction of an oxygen carrier with air and a fuel, respectively, to achieve flameless combustion and yield sequestration-ready CO_2 streams. While CLC allows for highly efficient CO_2 capture, it does not, however, provide a solution for CO_2 sequestration.

Here, we propose chemical looping dry reforming (CLDR) as an alternative to CLC by replacing air with CO_2 as the oxidant. CLDR extends the chemical looping principle to achieve CO_2 reduction to CO, which opens a pathway to CO_2 utilization as an alternative to sequestration. The feasibility of CLDR is studied through thermodynamic screening calculations for oxygen carrier selection, synthesis and kinetic experiments of nanostructured carriers using cyclic thermogravimetric analysis (TGA) and fixed-bed reactor studies, and a brief model-based analysis of the thermal aspects of a fixed-bed CLDR process.

Overall, our results indicate that it is indeed possible to reduce CO_2 to CO with high reaction rates through the use of appropriately designed nanostructured carriers, and to integrate this reaction into a cyclic redox ("looping") process.

Keywords: Chemical looping; CO_2 utilization; Nanomaterials; Fixed bed reactors; Periodic reactor operation

1. Introduction

Carbon dioxide (CO_2) is widely recognized as the leading greenhouse gas (GHG) contributor to global warming. Among anthropogenic GHG emissions, combustion of fossil fuels is the leading cause of CO_2 emissions, constituting ~80% of the national U.S. GHG emissions from all sources on a CO_2 equivalent basis (U.S. E.P.A., 2010). Currently, the U.S. is deriving ~83% of total energy consumption from fossil fuels, and no significant change is anticipated for at least the next two decades (U.S. E.I.A., 2010). Worldwide trends mirror those in the U.S. closely. Hence, large global efforts are under way to develop efficient and affordable technologies to capture and sequester CO_2.

Among current CO_2 capture methods, chemical looping combustion (CLC) is a particularly promising emerging technology, which combines flameless NO_x-free combustion of fossil or renewable fuels with the efficient production of sequestration-ready CO_2 streams (Hossain and de Lasa, 2008; Ishida and Jin, 1994; Lyngfelt et al., 2001). In CLC, an oxygen carrier, typically a metal, is first oxidized with air in one reactor (oxidizer) and then reduced in contact with a fuel in a second reactor (reducer). The effluent of the reducer is a virtually pure mixture of CO_2 and steam so that following condensation of steam a high-pressure, sequestration-ready CO_2 stream is obtained (Ishida and Jin, 1994). However, while CLC is a highly efficient technology for CO_2 capture, it does not offer a solution for CO_2 sequestration. The lack of a secure and proven sequestration technology motivates efforts in our laboratory to develop alternate, chemical-looping derived process schemes, including the incorporation of CO_2 utilization within a CLC-based process.

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Nomenclature

C_P	heat capacity (J/kg K)
ΔH_R	heat of reaction (J/mol)
M_{act}	molecular weight of reactive component in solid carrier (kg/mol)
M_{CO_2}	molecular weight of CO_2 (kg/mol)
T_0	initial temperature (C)
T_{max}	maximum temperature (C)
ΔT_{max}	maximum temperature rise (C)
v_g	gas velocity (m/s)
v_h	heat front velocity (m/s)
v_r	reaction front velocity (m/s)
w_{act}	weight fraction of reactive component in solid carrier
w^{in}_{g,CO_2}	weight fraction of CO_2 in the feed
ρ	density (kg/m^3)
ε_s	porosity
ξ	stoichiometric factor (ratio of number of moles of gas to moles of solid in the oxidation reaction)

One alternative chemical looping process that has already been explored in some depth is chemical looping steam reforming (CLSR), which has been proposed as a means of H_2 production with integrated CO_2 capture by replacement of air with steam in the oxidizing reactor (Solunke and Veser, 2010; Takenaka et al., 2005; Zafar et al., 2006). Here, we propose chemical looping dry reforming (CLDR) as an alternate CLC process, in which CO_2 is used as an oxidant instead of air or steam. The CLDR configuration is shown in Fig. 1. Utilizing methane as a fuel, CLDR produces a net reaction similar to the dry reforming of methane as shown below where the stoichiometric half-reactions are based on a metallic 'M' oxygen carrier:

$$\text{oxidizer}: 4M + 4CO_2 \rightarrow 4MO + 4CO \quad \text{(R1)}$$

$$\text{reducer}: 4MO + CH_4 \rightarrow 4M + CO_2 + 2H_2O \quad \text{(R2)}$$

$$\text{netreaction}: CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O \quad ((R3) = (R1) + (R2)) \quad \text{(R3)}$$

Dry reforming is one of the more established pathways for CO_2 utilization. For example, in typical methane dry reforming, methane (another greenhouse gas) and CO_2 are processed at elevated temperatures (>700 °C) over a catalyst (typically nickel or a noble metal) to produce syngas with a maximum H_2/CO ratio of 1 (Fan et al., 2009; Vernon et al., 1992) according to:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \text{(R4)}$$

Typical challenges with current dry reforming technologies are catalyst cost and deactivation due to coking, as well as product selectivity for syngas (Choudhary and Choudhary, 2008; Moon et al., 2004).

The proposed CLDR process differs significantly from conventional catalytic dry reforming processes. While the target of conventional dry reforming is high syngas yield, CLDR results in fundamentally different stoichiometry (compare (R4) to (R3)), with the target of maximum CO yield and no selectivity for H_2 (assuming complete combustion of the fuel), i.e. CLDR yields a process which is optimized for CO_2 activation.

Another advantage of chemical looping dry reforming lies in its fuel flexibility. Chemical looping processes can, in principle, work with any fuel as long as the oxidized carrier shows sufficient reactivity with this fuel. CLC has to-date been demonstrated with methane (Mattisson et al., 2001; Ryden et al., 2008), synthesis gas (Mattisson et al., 2007), biofuels (Cao et al., 2006), and even direct coal feeds (Leion et al., 2007, 2009). In contrast, the catalyst in catalytic dry reforming is highly sensitive to the nature of the fuel, with coking and selectivity forming major obstacles for industrial realization of such processes.

Finally, CLDR can, in principle, handle dilute CO_2 streams as feed for the oxidizer (as long as the other feed gas components do not negatively interact with the carrier, i.e. as long as they are essentially chemically inert), while yielding a highly concentrated CO_2 stream at exit of the reducer. Therefore, CLDR can be conceptualized as a process that also concentrates dilute streams of CO_2.

In this contribution, we present results from a proof-of-concept study which aims to evaluate the potential of CLDR through a combination of thermodynamic calculations for carrier selection, synthesis and characterization of highly active and high-temperature stable nanostructured oxygen carriers,

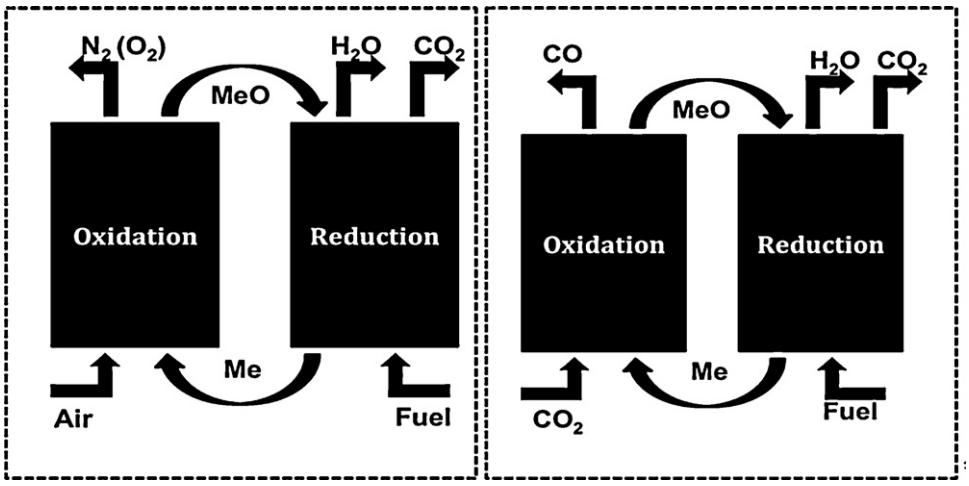

Fig. 1 – Schematic for (left) chemical looping combustion (CLC) and (right) chemical looping dry reforming (CLDR), shown with reduction of CO_2 to CO and full oxidation of a generic carbon-based fuel.