Solar fuel processing efficiency for ceria redox cycling using alternative oxygen partial pressure reduction methods

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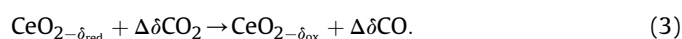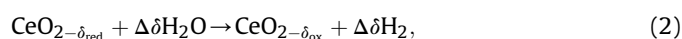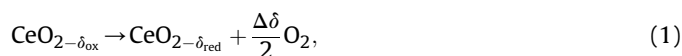
ABSTRACT

Solar-driven non-stoichiometric thermochemical redox cycling of ceria for the conversion of solar energy into fuels shows promise in achieving high solar-to-fuel efficiency. This efficiency is significantly affected by the operating conditions, e.g. redox temperatures, reduction and oxidation pressures, solar irradiation concentration, or heat recovery effectiveness. We present a thermodynamic analysis of five redox cycle designs to investigate the effects of working conditions on the fuel production. We focused on the influence of approaches to reduce the partial pressure of oxygen in the reduction step, namely by mechanical approaches (sweep gassing or vacuum pumping), chemical approaches (chemical scavenger), and combinations thereof. The results indicated that the sweep gas schemes work more efficient at non-isothermal than isothermal conditions, and efficient gas phase heat recovery and sweep gas recycling was important to ensure efficient fuel processing. The vacuum pump scheme achieved best efficiencies at isothermal conditions, and at non-isothermal conditions heat recovery was less essential. The use of oxygen scavengers combined with sweep gas and vacuum pump schemes further increased the system efficiency. The present work can be used to predict the performance of solar-driven non-stoichiometric redox cycles and further offers quantifiable guidelines for system design and operation.

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1. Introduction

The direct solar-driven processing of fuels by the thermochemical splitting of H_2O and CO_2 into H_2 and CO, a mixture called syngas, is a promising pathway for renewable fuel synthesis. The syngas can further be converted into liquid fuels through a conventional Fischer-Tropsch process effectively providing a direct approach for liquid solar fuel processing [1,2]. This approach exhibits a small environmental impact, allows for direct solar energy storage, and permits using conventional energy distribution infrastructure [1–4]. Direct H_2O and CO_2 thermolysis is challenging since temperatures above 2700 K are needed for reasonable reaction convergence [5,6], and efficient high temperature gas separation of a (possible explosive) mixture is required. Thermochemical multi-step cycles have been proposed to circumvent these drawbacks [1,7–9]. Particularly two-step, non-volatile metal oxide-based cycles show promise in avoiding gas separation issues, working at lower temperatures compared to direct thermolysis, enabling relatively simple design and operation, and theoretically achieving high solar-to-fuel efficiencies [10–14]. Ceria non-stoichiometric redox cycling has attracted interest due to its non-volatile characteristics even at high operating temperature, fast kinetics causing high hydrogen generation rates [12,15,16], theoretical high solar-to-fuel efficiencies [13,14,17], and practical demonstration of reasonable efficiencies in working prototypes [18–21]. The two steps water and CO_2 splitting reactions through non-stoichiometric ceria cycling are given as ($\Delta\delta = \delta_{red} - \delta_{ox}$)

$$CeO_{2-\delta_{ox}} \rightarrow CeO_{2-\delta_{red}} + \frac{\Delta\delta}{2}O_2, \qquad (1)$$

$$CeO_{2-\delta_{red}} + \Delta\delta H_2O \rightarrow CeO_{2-\delta_{ox}} + \Delta\delta H_2, \qquad (2)$$

$$CeO_{2-\delta_{red}} + \Delta\delta CO_2 \rightarrow CeO_{2-\delta_{ox}} + \Delta\delta CO. \qquad (3)$$

The endothermic reduction step, eq. (1), operates with reasonable conversion at temperatures ranging between 1400 K and 2100 K. The exothermic oxidation reactions, eqs. (2) and (3), favor lower temperatures in order to ensure a complete oxidation of ceria [12] with a typical temperature range of around 700 K–1100 K. The

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temperature difference between the two steps requires solid phase heat recovery in order to maintain a high solar-to-fuel efficiency [14], which is difficult to realize and increases the system complexity. Therefore, isothermal cycling has been proposed [16,22,23].

Thermodynamic evaluations of the performance of ceria redox cycling have been reported in Refs. [3,13,14,17,24]. Panlener et al. studied the reaction enthalpy of non-stoichiometric ceria in a large range of temperatures and pressures by thermogravimetric measurements [25]. Riess et al. [26] investigated the specific heat of ceria by an adiabatic temperature scanning calorimeter. Lapp et al. [15] performed a parametric thermodynamic analysis of a ceria-based cycling scheme using an ideal mixing model and sweep gassing to maintain a low oxygen concentration atmosphere for the reduction step. They found that effective solid phase heat recovery was crucial in achieving solar-to-fuel efficiencies above 10%. Bader et al. [13] demonstrated numerically that isothermal cycling of ceria was possible at the expense of reduced system performance. Sweep gas was used to reduce the oxygen partial pressure in the reduction chamber, gas phase heat recovery was assumed, and plug flow reactor models in counter flow arrangements were employed in both chambers. Gas phase heat recovery with effectiveness above 95.5% was required for solar-to-fuel efficiencies above 10%. The energy penalty introduced through the use of immense amounts of sweep gas pointed to the need for alternative methods to reduce the oxygen partial pressure during the reduction reaction. Ermanoski et al. [17] showed for the non-isothermal cycling of ceria using ideal mixing in both reaction chambers that the efficiency of the process could be increased by using vacuum pumping schemes for the reduction of the oxygen partial pressure. It is unclear whether this conclusion applies to isothermal operation and whether a further decrease of the oxygen partial pressure in the reduction chamber through non-mechanical methods is required for competitive solar-to-fuel efficiencies provided the use of solid−solid and gas−gas heat recovery components with realistic heat exchange effectiveness.

We developed a thermodynamic model for evaluating optimal operating conditions (system pressure, oxygen partial pressure, reduction temperature, oxidation temperature, heat recovery, and irradiation concentration ratio) for various system configurations of non-stoichiometric cycling of ceria using concentrated solar irradiation. Particularly, we focused on the reduction step and on the incorporation of alternative methods − mechanical and chemical − for reducing the oxygen partial pressure. The understanding of the influence of working conditions, component choices, and system configurations on system performance is required for the determination of the optimal operation conditions and design of practical system configurations for increased solar fuels processing efficiencies.

2. Thermodynamic model

2.1. Model development

Five thermochemical fuel production systems investigated are depicted in Fig. 1. They differed in their approaches to reduce the oxygen partial pressure in the reduction chamber, namely: three mechanical schemes using i) sweep gas (scheme a) [14,15], ii) vacuum pump (scheme b) [18], and iii) the combination thereof (scheme d); and two combined mechanical-chemical schemes using i) sweep gas and a chemical scavenger (scheme c), and ii) using the combination of sweep gas, vacuum pump, and a chemical scavenger (scheme e). All five systems used two continuously and simultaneously operating reaction chambers for the separated reduction and oxidation reactions. The systems incorporated two

heat exchanges to recover the heat from the exhaust (sweep gas and products). Solid phase heat recovery was incorporated between the reduced and oxidized ceria streams.

In scheme (a) inert gas was used to sweep away the produced oxygen during the reduction and correspondingly maintaining a desired oxygen partial pressure at the entrance (process 3−4). The sweep gas flow and the ceria flow was considered in a counterflow arrangement [13], i.e. the pressure and temperature will stay constant while the concentration of oxygen and the δ of ceria vary only in axial direction. Compared to the ideal mixing flow design used in Refs. [15,18], the counterflow arrangement maximized the p_{O_2} in the sweep gas at the outlet of the reduction chamber and minimized the p_{O_2} at the outlet of the oxidation chamber, resulting in a reduced sweep gas demand and reactant input. The inert gas was preheated in a heat exchanger and further heated by concentrated solar energy to the reduction temperature, T_{red}, before entering the reduction chamber. The states 5 to 8 described a full, closed ceria cycle. The ceria was cooled to the oxidation temperature, T_{ox}, in the process 5−6 while rejecting Q_{ceria} (not needed for isothermal operation), and isothermally reacted with the oxidizing agents (H_2O, CO_2) in the oxidation chamber during the process 6−7. Finally, the ceria temperature was heated to T_{red} (process 7−8) and then isothermally reduced in the reduction chamber (process 8−5). The oxidizer was preheated in the heat exchanger by effluent and further heated to T_{ox} by concentrated solar energy (process 10−11). Since the oxidation reaction was an exothermic process, the energy needed to heat the oxidizer from T_{10} to T_{11} may be less than the heat released by the reaction and hence a heat exchanger was used for further exhaust cooling after heat recovery (process 13−14).

The processes of scheme (b) were similar to the processes in scheme (a) concerning the oxidation process and the ceria cycling process. However, the oxygen generated in the reduction chamber was not swept away by inert gas. Instead a vacuum pump was employed continuously removing the produced oxygen during the reduction and maintaining a desired oxygen partial pressure in the chamber.

In scheme (c), sweep gassing was combined with a chemical oxygen scavenger (process 1′−2′) in which the oxygen in the sweep gas is reacted with an active metal (e.g. magnesium) to further reduce the oxygen partial pressure. Magnesium has been reported to be an alloying element in metals industries acting an important chemical oxygen scavenger which is widely used is large scale metal alloy production [27,28]. Magnesium oxide can be recycled through various thermochemical and electrochemical processes which are commonly used for industrial magnesium production [29].

Scheme (d) was a combination of both mechanical approaches, namely sweep gassing and vacuum pump. Scheme (e) combined scheme (d) with the chemical scavenger.

Additional assumptions used in the model were: *i*) the system was evaluated at steady state, *ii.a*) for scheme (a), counterflow arrangement was assumed for both reduction and oxidation chamber, *ii.b*) for scheme (b), counterflow arrangement was assumed in the oxidation chamber and the oxygen was uniformly distributed in the reduction chamber, *iii*) gases were modeled as ideal gases, and *iv*) temperatures of the reactants in the reduction and oxidation chambers were considered constant and uniform.

Additionally, we used ideal mixing models for the reduction and oxidation chambers to account for a less favorable reaction chamber design configuration. The ideal mixing model considered the equilibrium p_{O_2} that was created by the water at T_{ox}, influencing the non-stoichiometry at oxidation. In this case, the p_{O_2} in the oxidation chamber was determined by optimizing it for largest cycle efficiency while ensuring it was smaller than p_{O_2} of water dissociation at T_{ox}.