Chemical Engineering Science 146 (2016) 302–315

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Model of transport and chemical kinetics in a solar thermochemical reactor to split carbon dioxide

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HIGHLIGHTS

- A 3-D model of a solar reactor for the isothermal ceria redox cycle is presented.
- Reaction rate parameters are extracted for the redox reactions at 1773 K.
- Recovery of 90% of the sensible heat of the gases is achieved.
- For CO_2 splitting, CO is produced at 3.6×10^{-4} mol s^{-1} for a 4.2 kW solar input.

ARTICLE INFO

Article history:
Received 4 January 2016
Received in revised form
25 February 2016
Accepted 1 March 2016
Available online 7 March 2016

Keywords:
Ceria
Kinetics
Solar reactor
Heat exchanger
Radiation
Packed bed

ABSTRACT

Solar thermochemical reactors to carry out the nonstoichiometric reduction and oxidation of cerium dioxide (ceria) to split water and carbon dioxide provide a pathway to store sunlight in a chemical fuel. One of the challenges in the design of these reactors is understanding the complex coupling of heat and mass transfer and redox chemistry. To elucidate this coupling, we present a three-dimensional, transient model of a recently developed prototype solar reactor that implements an isothermal, pressure-swing ceria redox cycle. Radiative transport is modeled by a hybrid Monte Carlo/finite volume approach and paired with the transport and chemical processes within a fixed bed of porous ceria particles. Morphology specific reaction rate coefficients for the gas–solid reactions in ceria are extracted for the first time from global rate measurements in a bench-top reactor at 1773 K. Results demonstrate the interdependent spatial and temporal variations in temperature, species concentration and reaction rates, and provide insight on the effects of optical properties on reactor performance. For a solar input of 4.2 kW, the reactor achieves nearly isothermal cycling at 1791 K with carbon monoxide produced continuously at 3.6×10^{-4} mol s^{-1}. At this temperature, global reaction rates are driven by advective mass transport rates and the intrinsic material thermodynamics. Predicted surface temperatures and fuel production rates compare favorably to measured data.

1. Introduction

A sustainable approach to produce synthetic fuels and to store solar energy in chemical form is to use concentrated sunlight to split water and carbon dioxide via thermochemical metal-oxide redox cycles. Excellent reviews of solar redox cycles are available in recent publications (Agrafiotis et al., 2015; Muhich et al., 2015a; Smestad and Steinfeld, 2012). The products, hydrogen and carbon monoxide, can be combusted directly, used in a fuel cell, or further processed to liquid fuels, hence providing a pathway to convert the abundant yet intermittently available energy from the sun into a storable and transportable fuel.

In the present study we consider conversion of sunlight to fuel via the cerium dioxide (ceria) redox cycle (Abanades and Flamant, 2006; Chueh and Haile, 2010). Ceria undergoes partial reduction in an endothermic reaction at temperatures above 1600 K in a low oxygen partial pressure environment (Eq. (1)). Hydrogen and carbon monoxide are produced via the exothermic reactions (2a) and (2b) when the reduced ceria is reoxidized with H_2O and CO_2.

$$CeO_{2-\delta_{ox}} = CeO_{2-\delta_{rd}} + \frac{\delta_{rd}-\delta_{ox}}{2}O_2 \quad (1)$$

$$CeO_{2-\delta_{rd}} + (\delta_{rd}-\delta_{ox})H_2O = CeO_{2-\delta_{ox}} + (\delta_{rd}-\delta_{ox})H_2 \quad (2a)$$

$$CeO_{2-\delta_{rd}} + (\delta_{rd}-\delta_{ox})CO_2 = CeO_{2-\delta_{ox}} + (\delta_{rd}-\delta_{ox})CO \quad (2b)$$

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http://dx.doi.org/10.1016/j.ces.2016.03.001
0009-2509/

Fuel is produced in proportion to the change in the non-stoichiometry between reduction and oxidation, $\delta_{rd} - \delta_{ox}$. In the present study, we investigate a "nearly isothermal", pressure swing redox cycle (Bader et al., 2013; Hao et al., 2013; Krenzke and Davidson, 2015; Roeb and Sattler, 2013; Venstrom et al., 2014). The driving potential to produce fuel is generated at approximately 1773 K by maintaining low O_2 partial pressures during reduction ($\sim$10 Pa) via an inert sweep gas. The isothermal redox cycle is an alternative to the "temperature swing" cycle in which reaction (2) is carried out after cooling the ceria by hundreds of degrees to produce a larger difference in nonstoichiometry (Chueh et al., 2010; Furler et al., 2012a, 2012b; Krenzke and Davidson, 2015; Lapp et al., 2012). Although the temperature swing cycle is favored by the material thermodynamics (Panlener et al., 1975), it requires recovery of the sensible heat of the ceria to avoid irreversible heat losses during cycling (Ermanoski et al., 2013; Krenzke and Davidson, 2015; Lapp et al., 2012). However, solid phase heat recovery has proven difficult to implement in solar thermochemical reactors. Proposed reactor concepts for solid phase heat recovery require moving components that are subjected to large thermal gradients (Diver et al., 2010; James et al., 2006; Lapp and Lipinski, 2014; Lapp et al., 2013). The isothermal cycle eliminates the need for solid phase heat recovery between the reaction steps, reduces thermal stresses in the reactor components and simplifies the overall reactor design. The efficiency of both isothermal and temperature swing cycles will gain from gas phase heat recovery.

At the University of Minnesota, we have developed a 4 kW_{th} solar reactor prototype with integrated gas phase heat recovery to implement the isothermal ceria redox cycle and have demonstrated continuous, production of CO from CO_2 (Hathaway et al., 2015). Prior publications present the supporting analyses for design and operation of the reactor (Bader et al., 2015; Hathaway et al., 2015; Venstrom et al., 2014) and the gas heat recovery system (Bala Chandran et al., 2015b; Banerjee et al., 2015). In the present study, we present a transient, three-dimensional (3-D) numerical model of the reactor that couples heat and mass transport processes with the chemical reactions for splitting CO_2. Surface reaction rate coefficients are extracted from experimental data for an isothermal bench top reactor (Venstrom et al., 2014). Prior numerical transport models for isothermal and temperature swing ceria-based reactors are limited in scope to heat transfer analyses (Furler and Steinfeld, 2015; Lapp and Lipinski, 2014; Lapp et al., 2013) or only consider kinetics for the reduction step (Bala Chandran et al., 2015a; Keene et al., 2014, 2013).

2. Reactor

The reactor (Fig. 1) has a cylindrical receiver cavity lined with six tubular reactive elements each integrated with a ceramic heat exchanger. Concentrated sunlight enters the 347 mm long, 305 mm diameter cavity through an open 42 mm diameter aperture. Each reactive element is a concentric assembly of two alumina tubes. Within the solar cavity, the annulus is filled with 590 g of 5 mm cylindrical, ceria particles. The particles are 75% porous and the void fraction in the packed bed is 45%. The tubular assemblies extend beyond the solar cavity to integrate with a tubular heat exchanger. The heat exchanger tubes are filled with alumina reticulate porous ceramic (RPC) to enhance heat transfer

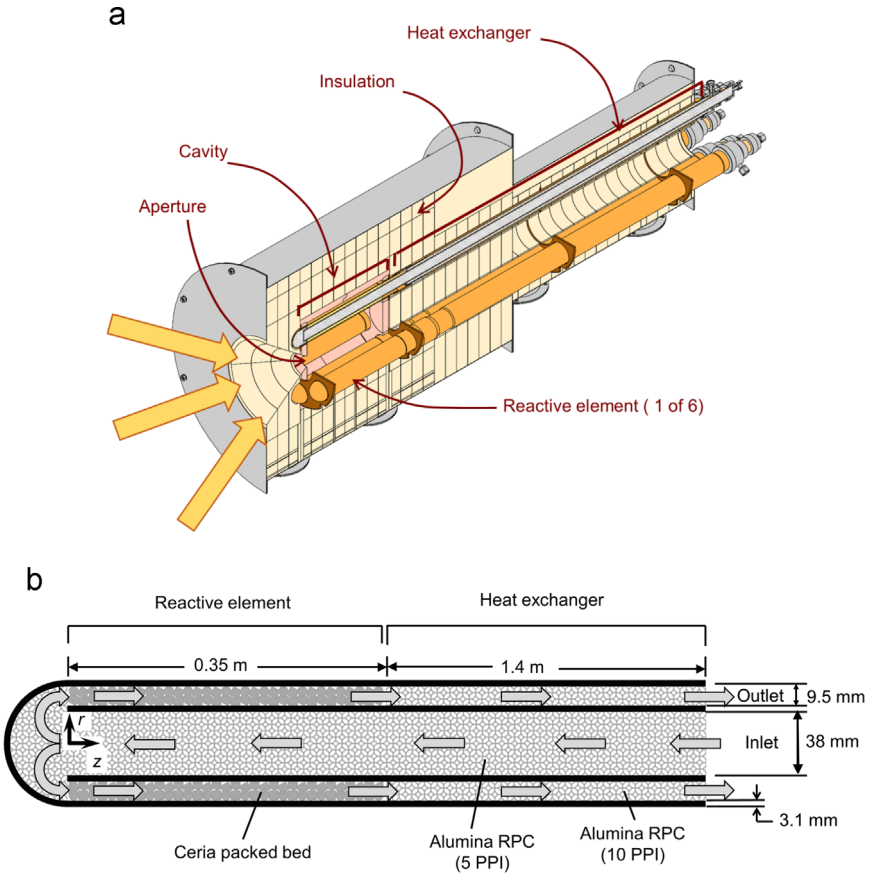

Fig. 1. Cross section of the solar reactor: (a) overview showing the cavity and integrated heat exchanger and (b) details of the reactive element and heat exchanger assembly. Arrows indicate gas flow direction. (The aspect ratio is distorted to better visualize the reactive element.)