



Investigation of long term reactive stability of ceria for use in solar thermochemical cycles



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ABSTRACT

The use of an intermediate reactive material composed of cerium (IV) oxide (ceria) is explored for solar fuel production through a CO₂-splitting thermochemical redox cycle. To this end, powder and porous ceria samples are tested with TGA (thermogravimetric analysis) to ascertain their maximum fuel production potential from the CeO₂ → CeO_{2-δ} cycle. A maximum value of the non-stoichiometric reduction factor δ of ceria powder was 0.0383 at 1450 °C. The reactive stability of a synthesized porous ceria sample is then observed with carbon dioxide splitting at 1100 °C and thermal reduction at 1450 °C. Approximately 86.4% of initial fuel production is retained after 2000 cycles, and the mean value of δ is found to be 0.0197. SEM (scanning electron microscopy) imaging suggests that the porous ceria structure is retained over 2000 cycles despite apparent loss of some surface area. EDS (energy dispersive x-ray spectroscopy) line scans show that oxidation of porous ceria becomes increasingly homogenous throughout the bulk material over an increasing number of cycles. Significant retention of reactivity and porous structure demonstrates the potential of porous ceria for use in a commercial thermochemical reactor.

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1. Introduction

Given the finite nature of fossil fuel reserves, at present the most widely used source of energy, it is of interest to develop alternative avenues by which energy may be provided in the future. Of particular interest is solar energy, which is renewable and widely available. Given its intermittence, the issue of *solar energy storage*, however, is a critical challenge that must be addressed if the solar resource is to be extensively utilized. One possible pathway is the storage of solar-derived energy in the form of chemical fuels produced by regenerative thermochemical cycles. Many types of thermochemical cycles have been proposed, including both primarily stoichiometric (e.g. iron oxides) and non-stoichiometric (e.g. cerium oxide) mechanisms. While some involve many processes, those of interest here proceed with two steps. The exothermic oxidation of a reactive metal to produce fuel is the first step. The second uses endothermic thermal reduction that removes oxygen from the reactive material, renewing it to the original state for another cycle of fuel production [1]. With water as an oxidizing

agent, the resultant chemical fuel is high-purity hydrogen [2,3] [4]. When a mixture of water and carbon dioxide oxidizes the material, the result is syngas, a combination of hydrogen and carbon monoxide [5–8]. Xiao et al. summarized recent advances in thermochemical cycling, reviewing a large range of reactive materials for the production of hydrogen and syngas [9]. These products can be directly utilized, or syngas can be further processed to obtain other hydrocarbon-based fuels (e.g. Fisher–Tropsch process).

The intermediate reactive material at the core of the thermochemical redox cycles discussed previously is of considerable significance. Ideally, this material will evolve a large quantity of fuel during the oxidation step and during reduction quickly release all of the oxygen previously incorporated, thereby retaining reactivity for subsequent cycles. Among the first and most popular stoichiometric materials considered were iron oxides such as magnetite (Fe₃O₄) and hematite (Fe₂O₃) [10–13]. While these iron oxides have exhibited promising oxidative potential, they are often supplemented with the addition of other metals (Co, Mn, Ni, etc.) and/or zirconia substrates to avoid the deactivating effects of sintering at high reduction temperatures [14–17]. For example, Song et al. demonstrated a synthesis of iron with mesoporous Si-doped alumina that exhibited a significant reduction in deactivation for hydrogen productivity over three cycles [18]. Zinc oxide is another

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popular choice for stoichiometric thermochemical cycling. During the reduction step, however, zinc oxide experiences a significant vaporization effect that necessitates quenching or other steps to recuperate the original reactive state [19,20].

Recently, cerium(IV) oxide, i.e. ceria, has been examined as a candidate for thermochemical cycling. Equation (1) shows the non-stoichiometric release of oxygen during thermal reduction of ceria at high temperature. Equations (2) and (3) demonstrate the evolution of hydrogen or CO from the oxidizing agents of water or carbon dioxide, respectively [21].



When performed below ceria's melting point of approximately 2000 °C, the reduction proceeds globally in a non-stoichiometric fashion. The figure of δ in the above steps represents the degree of non-stoichiometry present in the process, which also describes its fuel production potential. More specifically, the dimensionless δ can be defined as the number of moles of vacancies per mole of cerium. These vacancies are created by the mobility of oxygen in the ceria lattice during the reduction step, noted in Equation (1). The particular value of δ depends highly on material structure and reactive conditions. Bulfin et al. recently developed a model for the thermal reduction of ceria that predicts temperature and local oxygen partial pressure to significantly impact δ . In particular, an environment of increased oxygen partial pressure is shown to have a substantially damaging effect on δ . A theoretical maximum value of $\delta = 0.32$ was determined for conditions of 2000 °C and an oxygen partial pressure of 10^{-7} bar. Potential commercial cycles employing ceria would likely operate with much lower values of δ , for the previously mentioned conditions approach the melting point of ceria and requires exceptionally low pressure. Bulfin's model predicts a δ of approximately 0.04 for perhaps more practical conditions of 1600 °C and 10^{-3} bar [21].

Many forms and structures of ceria, such as powders [22], doped and ceramic-supported structures [23–26], monolithic foams [27–29], and felts [5] have been examined for thermochemical cycling applications. Solar simulating reactors have also incorporated monolithic ceria structures to demonstrate their feasibility for practical implementation [5,27–29]. While ceria has been noted for its oxygen storage capacity and its redox potential, on-sun reactors often suffer from very low solar-to-fuel efficiencies on the order of approximately 1–2%. As reactor design improves, efficiency increases are possible. For instance, Lapp et al. modeled a dramatic increase of reactor efficiency from 3.5% to 16% with moderate heat recovery [30]. Furthermore, for successful utilization in a solar thermochemical reactor, the physical structure of ceria needs to be optimized for maximum fuel production and reduction potential. While initial production rates over the first few cycles are important to the preliminary selection of promising reactive material candidates, stability of long term production over thousands or tens of thousands of cycles is arguably of equal significance for the purposes of successful commercialization. To this end, Chueh and Haile performed 500 thermochemical cycles of porous ceria. Hydrogen production decreased by 25% after 100 cycles, and production held relatively stable thereafter [31]. To date, however, literature is largely lacking in the study of ceria over an extended number of cycles. This study will focus on the reactive potential of several ceria structures as well as an extended test of the most promising candidate over 2000 cycles. Reactivity data over many

cycles will further characterize the potential for the utilization of ceria in a commercially viable solar thermochemical reactor.

2. Experimental methods

2.1. Data acquisition

All experiments were conducted with TGA (thermogravimetric analysis) (Netzsch STA 449 *Jupiter*) and analyzed with a combination of Netzsch Proteus Thermal Analysis and Microsoft Excel. A control experiment is required for each unique set of experimental conditions. This corrective run accounts for the effects of thermal buoyancy and gas flow changes on the mass change recorded by the balance. After each experiment is run, per manufacturer recommendation, the mass change from the associated corrective run is subtracted from the results. This subtraction ensures that the data reflects mass change due to only a specimen's reaction in the experimental conditions.

For morphological inspection, specimens were set in epoxy (ExpoCure 20-8130-032) to prepare them for polishing. Thereafter, they were imaged with SEM (scanning electron microscopy) and EDS (energy dispersive x-ray spectroscopy). Images were obtained with a Jeol SEM-6400. SEM images provide insight into the morphological structure of specimens and how their structures may change over time. EDS line scans characterize elemental composition of specimens so that potential gradients of reactivity within individual particles may be identified. Unreacted ceria powder and SPF-G ceria were used as standards to quantify the EDS O/Ce atomic data along with a two-point linear calibration curve.

2.2. Sample preparation

Three forms of ceria were used in this study: micron-sized powder, nano-sized powder, and a synthesized porous structure. The micron-sized powder (Alpha Aesar 12925) contains particle sizes ranging from 5.2 to 8 microns in diameter. Nano-sized powder (Sigma–Aldrich 544841) is comprised of particles with diameters less than 25 nm. The porous ceria sample was prepared using a sacrificial pore formation using graphite (SPF-G) method. This method entails mixing graphite particles into ceria powder and oxidizing the mixture in air at high temperature. During this process, the graphite reacts to form carbon monoxide and is emitted from the structure. After ceria particles sinter, the result is a solid, porous ceria structure that is free of graphite. More details on this procedure can be found in the recent work by Allen et al. [32]. For this study, equal parts (by mass) of micron-sized ceria, mesh 325 graphite, and mesh 40 graphite powders were combined and heat treated in an alumina tube furnace.

2.3. Experimental procedure

During experimentation, samples were housed in alumina crucibles. UHP (ultra high purity) argon was used as inert flow and was passed through an Agilent adsorbent bed to remove any residual traces of oxygen and other impurities prior to introduction to the TG. UHP carbon dioxide was used as received as the oxidizing agent. Before experimentation, the TG was evacuated and backfilled with argon to remove oxygen and water vapor from the reactive chamber. The balance was allowed to equilibrate at ambient temperature and pressure for at least one hour prior to the initiation of each experiment.

Two primary sets of experiments were conducted, both using oxidation under 120 cm³/min of carbon dioxide and thermal reduction under 120 cm³/min of argon. Additionally, a 20 cm³/min argon flow was present at all times as a protective gas stream.

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