

Thermochemical performance of ceria coated-macroporous 3D-printed black zirconia structures for solar CO/H₂ fuels production

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ABSTRACT

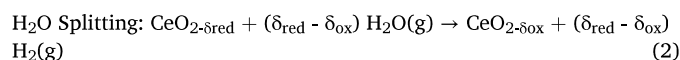
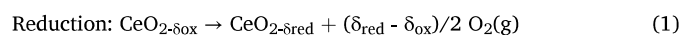
The use of macroporous structured ceria for the solar thermochemical splitting of CO₂ and H₂O to produce clean fuels through two-step redox cycles was investigated. The research aimed to assess the reactivity of 3D-printed black zirconia gyroid structures coated with a microporous layer of pure CeO₂ for producing CO and H₂. Such porous designs are intended to increase both the absorption of solar radiation and the available surface area for the solid-gas reaction. It was observed that the structure degraded more at the top of the reactor cavity, where the formation of Ce_xZr_{1-x}O₂ solid solutions occurred at the coating/substrate interface. Besides, the porous ceria structure remained after redox cycles in the samples not directly exposed to solar radiation. Consequently, the solar reactor achieved CO and H₂ production rates of up to 5.4 and 1.9 mL min⁻¹ g⁻¹ with fuel yield over 0.2 mmol g⁻¹, and the material maintained its performance over several consecutive cycles without any loss of reactivity. This indicates a strong potential for producing solar fuels at a large facility using custom 3D-printed ceria-coated structures.

1. Introduction

In today's world, the challenge to humankind is the gradual transition from fossil fuels to renewable fuels to reduce human-caused emissions of greenhouse gases [1]. To this end, harnessing sunlight is interesting since it is a free, clean, and abundant renewable resource. Concentrated solar power (CSP) particularly stands out as it can drive high-temperature thermochemical processes that convert CO₂ and H₂O into valuable sustainable fuels, such as syngas and hydrogen [2].

Direct thermolysis of H₂O or CO₂ requires temperatures above 2000 °C for a significant degree of dissociation, which is far too high for practical applications [3]. Another approach to convert heat directly into chemical fuels is through thermochemical two-step cycles using non-stoichiometric oxides. Among several potential candidates, ceria (CeO₂) is usually considered the leading material for thermochemical cycles due to its thermal stability and favorable fast oxidation rate [4]. Abanades and Flamant [5] pioneered work on using ceria to produce H₂

through a two-step solar-driven water-splitting cycle. As H₂ and O₂ are produced separately, there is no need for a high-temperature gas-phase separation step, and the two reactions involved are:



The terms δ_{ox} and δ_{red} represent the oxygen non-stoichiometry of ceria when it is oxidized and reduced, respectively. When ceria is reduced to CeO_{2- δ} , it undergoes an endothermic process that requires temperatures higher than 1000 °C to release O₂ from its crystal fluorite structure. The change in ceria's stoichiometry impacts the yield of fuel production, and this change depends on temperature and oxygen partial pressure. Some researchers have suggested doping ceria as a potential strategy to enhance fuel production yields [6]. Ceria crystallizes in a fluorite-type structure. The O²⁻ anions are surrounded by Ce⁴⁺ cations,

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