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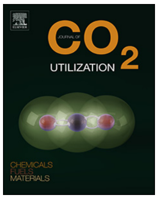

Solar thermochemical CO_2 splitting using cork-templated ceria ecoceramics

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ABSTRACT

This work addresses the solar-driven thermochemical production of CO and O_2 from two-step CO_2-splitting cycles, using both ceria granules prepared from cork templates (CG) and ceria foams from polyurethane templates (CF). These materials were cycled in a high-temperature indirectly-irradiated solar tubular reactor using a temperature-swing process. Samples were typically reduced at 1400 °C using concentrated solar power as a heating source and subsequently oxidised with CO_2 between 1000–1200 °C. On average, CO production yields for CG were two times higher than for CF, indicating that the morphology of this three-dimensionally ordered macroporous (3-DOM) CeO_2 improves the reaction kinetics. Their performance stability was demonstrated by conducting 11 cycles under solar irradiation conditions. Slightly increasing the reduction temperature strongly enhanced the reduction extent, and thus the CO production yield (reaching about 0.2 mmol g^{-1} after reduction at 1450 °C in inert gas), while decreasing the oxidation temperature mainly improved the CO production rate (up to 1.43 µmol s^{-1} g^{-1} at 1000 °C). Characterisation of the 3-DOM structure, by means of XRD and SEM, provided insights into the reactivity behaviour of the developed materials. The pre-sintered ceria granules retained their structure after cycling. The fact that the mean cell size of CG is smaller (at least one order of magnitude) than that of CF suggests that its exposed surfaces enhanced reaction rates by a factor of two. Moreover, the maximum fuel production rate of CG was roughly three times greater than that reported previously for a ceria reticulated porous foam with dual-scale porosity.

1. Introduction

The conversion of sunlight directly to chemical fuels such as synthesis gas (or syngas – primarily a CO/H_2 mixture), hydrogen alone, or further to liquid fuels, offers the potential to efficiently store solar energy, transport it and utilise it on demand [1–3]. Thus, the generation of renewable solar fuels, derived from the sun, water and carbon dioxide and based on existing concentrated solar power (CSP) technology, is gaining considerable attention. The impact of solar fuels would be of utmost importance to ensure a sustainable energy future. Several methods for producing solar fuels, such as electrochemical, thermochemical and photochemical processes have been developed [4]. The use of solar radiation to drive a two-step thermochemical cycle based on redox materials benefits from the favourable thermodynamics arising from high temperature operation, the entire solar spectrum utilisation, the avoidance of the costly solar-to-electric conversion (used in electrolytic processes), and the elimination of CO/O_2 or H_2/O_2 gas separation. The latter is regarded as a tricky problem for one-step splitting methods [5]. Comprehensive literature reviews on solar thermochemical processes have been carried out [6–11]. Basically, two distinct types of metal oxides are being considered for the splitting of H_2O and/or CO_2: the volatile oxide cycles (ZnO/Zn or SnO_2/SnO) and the non-volatile oxide cycles such as Fe_3O_4/FeO or CeO_2/$CeO_{2-\delta}$. This study is focused on the cerium oxide redox pair.

On paper, the two-step cyclic process appears reasonably simple: concentrated solar radiation (a focused beam of sunlight) heats the metal oxide up to 1400 °C or more, driving its endothermic reduction and releasing oxygen. The reduced oxide is then cooled to 1000 °C or below (temperature-swing cycle), while a flow of steam and/or carbon dioxide re-oxidizes it, liberating hydrogen or carbon monoxide. Making such technology practical and cost-effective, however, poses noteworthy engineering challenges.

One of the most critical aspects is solar-to-fuel energy conversion efficiency, which in turn depends upon the redox material and the solar

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