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Solar Thermochemical CO₂ Splitting Utilizing a Reticulated Porous Ceria Redox System

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ABSTRACT: A solar cavity-receiver containing a reticulated porous ceramic (RPC) foam made of pure CeO₂ has been experimentally investigated for CO₂ splitting via thermochemical redox reactions. The RPC was directly exposed to concentrated thermal radiation at mean solar flux concentration ratios of up to 3015 suns. During the endothermic reduction step, solar radiative power inputs in the range 2.8–3.8 kW and nominal reactor temperatures from 1400 to 1600 °C yielded CeO_{2- δ} with oxygen deficiency δ ranging between 0.016 and 0.042. In the subsequent exothermic oxidation step at below about 1000 °C, CeO_{2- δ} was stoichiometrically reoxidized with CO₂ to generate CO. The solar-to-fuel energy conversion efficiency, defined as the ratio of the calorific value of CO (fuel) produced to the solar radiative energy input through the reactor's aperture and the energy penalty for using inert gas, was 1.73% average and 3.53% peak. This is roughly four times greater than the next highest reported values to date for a solar-driven device. The fuel yield per cycle was increased by nearly 17 times compared to that obtained with optically thick ceria felt because of the deeper penetration and volumetric absorption of high-flux solar irradiation.

1. INTRODUCTION

Solar-driven thermochemical cycles based on metal oxide redox reactions can split H_2O and CO_2 to produce H_2 and CO (syngas), the precursors to the catalytic synthesis of conventional liquid fuels for the transportation sector.¹⁻⁴ In contrast to the thermolysis, these cycles bypass the CO/O_2 and H_2/O_2 separation problem. When coupled to the capture of CO_2 directly from atmospheric air, the solar-made hydrocarbon fuels can be considered carbon neutral.⁵⁻⁹ Among a variety of metal oxides, ceria has emerged as an attractive redox active material because of its ability to rapidly conduct O^{2-} contributing to fast redox kinetics, ^{10,11} as compared to ferrite-based and other nonvolatile metal oxides.^{12–14} The two-step H_2O/CO_2 splitting cycle based on nonstoichiometric ceria is represented by

high-temperature reduction:

$$CeO_2 = CeO_{2-\delta} + \frac{1}{2}\delta O_2 \tag{1}$$

low-temperature oxidation with H₂O:

$$CeO_{2-\delta} + \delta H_2O = CeO_2 + \delta H_2$$
(2)

low-temperature oxidation with CO₂:

$$CeO_{2-\delta} + \delta CO_2 = CeO_2 + \delta CO$$
(3)

In the solar reduction step, ceria is thermally reduced to a nonstoichiometric state. At equilibrium, the oxygen deficiency δ reaches 0.06 at 1500 °C and 10⁻⁵ bar O₂ partial pressure.¹⁵ In the subsequent non-solar oxidation step, the reduced ceria is reoxidized with H₂O and/or CO₂ below about 1400 °C to form H₂ and/or CO.^{16,17} The thermodynamics of ceria-based metal oxides M_xCe_{1-x}O₂, where M = Gd, Y, Sm, Ca, Sr, have also

been studied in relation to their applicability as reactive intermediates in solar thermochemical redox cycles. $^{18}\,$

Pure ceria is crystallographically stable over a wide temperature range of interest, provided its fluorite-type structure is maintained.^{10,16,19} The reduction of CeO₂ to Ce₂O₃ at above 2000 °C caused melting and vaporization.²⁰ In contrast, the partial nonstoichiometric reduction and oxidation according to eqs 1–3 was stable,^{10,21} as observed in 500 consecutive redox cycles.¹⁰ We have recently demonstrated experimentally the solar production of CO and H₂ from CO₂, H₂O, and simultaneously from CO₂ and H₂O using a simple and scalable solar reactor design.^{22,23}

The key indicator of the solar reactor's performance is the solar-to-fuel energy conversion efficiency, $\eta_{\text{solar-to-fuel}}$, defined as

$$\eta_{\text{solar-to-fuel}} = \frac{\Delta H_{\text{fuel}} n_{\text{fuel}}}{P_{\text{solar}} + E_{\text{penalties}}}$$
(4)

where $\Delta H_{\rm fuel}$ is the high heating value of the fuel produced, $n_{\rm fuel}$ is the total amount of fuel produced, and $P_{\rm solar}$ is the solar radiative energy input through the solar reactor's aperture. System specific energy penalties $E_{\rm penalties}$ such as those derived from the consumption of inert gas, electricity, or pumping work for promoting the chemical reactions should be accounted in the denominator. Note that $\eta_{\rm solar-to-fuel}$ does not include the optical efficiency of the solar concentrating system. This definition has a direct impact on the economics of the process. Higher $\eta_{\rm solar-to-fuel}$ implies a smaller solar concentrating system for the same fuel output, which directly translates to lower fuel cost, as—analogous to solar thermal electricity (CSP) plants—

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Figure 1. CeO₂ RPC parts fabricated for the solar cavity-receiver. One set consists of a disk (20 mm thickness, 100 mm o.d.) and four rings (20 mm thickness, 60 mm i.d., 100 mm o.d.).



Figure 2. (a) Schematic of the solar reactor configuration and (b) experimental setup at ETH's High-Flux Solar Simulator.

the major cost component derives from the investment of the solar collecting and concentrating infrastructure. A thermodynamic analysis indicates the potential of reaching $\eta_{\text{solar-to-fuel}}$ of 20% in the absence of heat recovery and exceeding 30% by recovering the sensible heat of the hot products.^{10,18,24} A recent techno-economic analysis for the production of methanol from H₂O and CO₂ via solar redox cycles further indicates that, with $\eta_{\text{solar-to-fuel}}$ approaching 20% and an overall system efficiency from solar to methanol of 7.1%, the fuel price would reach a break-even point and competitiveness vis-à-vis other renewable-based alternatives.²⁵

The peak and average measured values of $\eta_{\text{solar-to-fuel}}$ reported for the solar-driven splitting of CO₂ were 0.8 and 0.4%, respectively.²² Both the efficiency and the cycling rates in the solar reactor were limited largely by thermal losses, resulting from poor conductive and radiative heat transfer across the ceria structure. Several metal oxide structures and supports such as monolithic vertical pins,²⁶ textured plates,²⁶ foams,^{26–29} 3D ordered porous structures,³⁰ honeycombs,¹⁴ felts,²³ and monolithic and lattice type structures^{22,31} have been examined for solar thermochemical applications. Microporous structures with pore size in the μ m range, such as monoliths or felts, display rapid oxidation rates thanks to their high specific surface areas but are limited by their heat transfer rates because of opacity to incident radiation, leading to undesired temperature gradients across the structure.^{22,23} In contrast, macroporous structures with pore size in the millimeter range, such as foams and honeycombs, can achieve uniform heating thanks to deeper penetration and volumetric absorption of concentrated solar radiation. However, when these structures are coated with metal oxides, they often suffer from mechanical instability,^{27,28} side reactions with the support,¹⁴ and a relatively low mass loading of reactive material.^{14,28,29}

In the present study, we report on the synthesis and experimental assessment of a novel reticulated porous ceramic (RPC) foam made of pure CeO₂ for thermochemical redox cycling in a solar reactor. The ceria-made RPC acts as the reactive material itself and inherently combines the advantages of volumetric radiative absorption, rapid reaction rates, and high mass loading of reactive material. This ultimately results in experimentally measured values of $\eta_{\text{solar-to-fuel}}$ that are significantly higher than those previously reported.

2. EXPERIMENTAL SECTION

Material Synthesis. The ceria RPCs were manufactured by the replication method.³² A slurry of cerium(IV)-oxide powder (particle size <5 μ m, 99.9% purity, Sigma Aldrich) and water at a ratio 5:1 was prepared according to a previously published recipe.³³ The organic deflocculating agent Dolapix CE 64 (Zimmer & Schwartz) was added in a ratio 0.83 wt % of solid load. Mixing and deagglomeration were achieved by roller milling. Polyvinyl alcohol binder (Optapix RA 4G, Zimmer & Schwartz) was dissolved under continuous stirring at 85 °C. The slurry was then cooled to ambient temperature and antifoaming agent (Contraspum KWE, Zimmer & Schwartz) was added. Cylindrically shaped organic polyurethane sponges of 10 ppi

Table 1. Ope	erating Conditions	and Results of (CO ₂ Splitting	Cycles for	Three Sol	ar Radiative	Power Inpu	ıts
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power input during reduction (kW)	2.8	3.4	3.8
power input during oxidation (kW)	0	0	0
duration of reduction step (min)	22	22	22
nominal reactor temp. (°C)	1420	1530	1600
mean heating rate (°C min ⁻¹)	30	35	39
peak heating rate (°C min ⁻¹)	83	110	130
mean specific O_2 evolution rate (mL min ⁻¹ g ⁻¹ CeO ₂)	0.044 ± 0.002	0.083 ± 0.003	0.113 ± 0.004
peak specific O_2 evolution rate (mL min ⁻¹ g ⁻¹ CeO ₂)	0.078 ± 0.003	0.163 ± 0.006	0.216 ± 0.008
total specific O_2 evolution (mL g ⁻¹)	1.056 ± 0.038	2.01 ± 0.073	2.764 ± 0.101
absolute O ₂ evolution (mL)	1492.1 ± 53.7	2840.1 ± 103.1	3905.5 ± 142.7
nonstoichiometry δ	0.016 ± 0.001	0.031 ± 0.001	0.042 ± 0.002
mean specific CO evolution rate (mL min ⁻¹ g^{-1} CeO ₂)	0.043 ± 0.001	0.126 ± 0.004	0.158 ± 0.005
peak specific CO evolution rate (mL min ⁻¹ g ⁻¹ CeO ₂)	0.127 ± 0.004	0.365 ± 0.011	0.526 ± 0.015
total specific CO evolution (mL g ⁻¹)	1.465 ± 0.043	4.107 ± 0.121	5.690 ± 0.166
absolute CO evolution (mL)	2070.0 ± 60.8	5803.2 ± 171.0	8040.0 ± 234.6
molar ratio (CO:O ₂)	1.39 ± 0.09	2.04 ± 0.14	2.06 ± 0.14

(Foam-Partner, Fritz Nauer AG) were used as the skeletal structure and completely immersed into the ceria slurry. After 24 h drying at ambient temperature, a second coating of the initial slurry was applied. The coated foams were fired in a furnace (Nabertherm GmbH) at 1600 °C to completely burn and vaporize the organic polyurethane matrix and sinter the ceramic body. Figure 1 shows photographs of the fabricated ceria RPC parts for the solar cavity receiver.

Solar Reactor Configuration and Setup. The solar reactor design and peripheries were previously described^{22,23} and are shown schematically in Figure 2. The main features are summarized here. The solar reactor consisted of a cavity-receiver with a 4 cm-diameter aperture for the access of concentrated solar radiation. The reactor front was sealed by a 24 cm-diameter, 3 mm-thick clear fused quartz disk window. A compound parabolic concentrator (CPC)³⁴ incorporated onto the aperture to further boost the solar concentration ratio (the solar concentration ratio C is defined as C $= P_{\text{solar}}/(IA)$, where P_{solar} is the solar radiative power intercepted by the aperture of area A, normalized to the direct normal solar irradiation I. C is often expressed in units of "suns" when normalized to I = 1 kW m^{-2}) to mean values of up to 3015 suns. The ceria RPC, which is the novel and key component in this setup, was contained within the cavity as a cylinder composed of four 20 mm-thick, 60 mm-i.d., 100 mm-o.d. rings, and a single 20 mm-thick, 100 mm-o.d. disk. The total mass of the CeO₂ cylinder was 1413 g. The cavity was insulated by Al₂O₃ and sheathed by an outer shell made of Inconel 600. An annular gap between the RPC and insulation enabled uniform radial flow across the porous RPC cylinder. Temperatures were measured at the outer surface of the RPC (B-type thermocouples), insulation, and Inconel wall (K-type thermocouples). Argon (99.999% purity) and CO₂ (99.998% purity) flow rates were regulated by electronic mass flow controllers (Bronkhorst F-201C). Reacting gases were injected through four radial inlet ports and product gases exited the reactor axially through an outlet port at the rear plate. Product gas composition was monitored by gas chromatography (Varian 490), supplemented by a paramagnetic alternating pressure based O2 detector (Siemens Oxymat 6) and infrared-based detectors for CO and CO₂ (Siemens Ultramat).

Experimentation was performed at the High-Flux Solar Simulator (HFSS) of ETH Zurich. An array of seven Xe-arcs, close-coupled to truncated ellipsoidal reflectors, provided an external source of intense thermal radiation, mostly in the visible and IR spectra, that closely approximated the heat transfer characteristics of highly concentrating solar systems such as solar towers and dishes.³⁵ The radiative flux distribution at the focal plane was measured optically using a calibrated CCD camera focused on a water-cooled, Al_2O_3 -plasma coated Lambertian (diffusely reflecting) target. The solar radiative power input through the aperture P_{solar} was calculated by integration of the radiative flux over the aperture area and verified with a water calorimeter. During a typical redox cycle, the reactor was heated to the

desired reduction temperature by increasing P_{solar} while purging with Ar. Following reduction, the HFSS was turned off ($P_{\text{solar}}=0$) and the reactor was cooled to the desired oxidation temperature. Subsequently, oxidation was initiated by introducing CO₂ into the reactor, and it was terminated when CO evolution approached zero.

3. RESULTS AND DISCUSSION

A summary of the operating conditions and results are listed in Table 1. Figure 3 shows the nominal reactor temperature and



Figure 3. Nominal reactor temperature and O_2 and CO evolution rates during three individual redox cycles for different solar radiative power inputs during the reduction step. Experimental conditions: 2.8, 3.4, and 3.8 kW solar radiative power input and 2 L min⁻¹ Ar during the reduction step; no solar radiative power input and 2 L min⁻¹ CO₂ + 0.1 L min⁻¹ Ar during the oxidation step.

 O_2 and CO evolution rates during three single redox cycles. During reduction, $P_{solar} = 2.8$, 3.4, and 3.8 kW and the Ar flow rate was 2 L min⁻¹ (SLPM; mass flow rates calculated at 273.15 K and 101 325 Pa). During oxidation, $P_{solar} = 0$ and the gas flow rate was 2 L min⁻¹ CO₂ and 0.1 L min⁻¹ Ar. The temperature of the ceria RPC rose rapidly with increasing solar radiative power input, from the initial 740 °C at 0.8 kW to 1420 °C at 2.8 kW, 1530 °C at 3.4 kW, and 1600 °C at 3.8 kW. Additionally, as P_{solar} increased from 2.8 to 3.8 kW, both peak and average heating rates increased from 80 °C min⁻¹/30 °C min⁻¹ to 130 °C min⁻¹/39 °C min⁻¹. As expected, higher temperatures ultimately lead to higher O₂ yields during reduction and subsequently higher CO yields during oxidation.

In all three runs, O₂ evolution was observed at above 900 °C and continued to be evolved for the duration of the reduction step. After 22 min, the solar radiative power input was interrupted, resulting in a decrease in temperature and a sharp decrease in O₂ production. Shortly after, CO₂ was introduced to the reactor and CO evolution was observed immediately as the temperature continued to decrease. The CO production was characterized by a relatively slow increase in its rate, followed by a decrease at nearly the opposite slope. This behavior is partly attributed to the smaller specific surface area of the RPC relative to that of other porous structures,^{10,22,23,30} which generally exhibit initial rapid CO rates followed by an exponential decline. Another factor is the continuing reduction in temperature as the oxidation proceeded, as thermodynamics^{10,15,18} and kinetics¹⁰ are highly dependent upon temperature. Specific O2 evolution during 22 min at 3.8 kW was 2.764 \pm 0.101 mL g⁻¹ CeO₂, which corresponds to δ = 0.042 ± 0.002 . Subsequent specific CO evolution during 36 min was 5.690 \pm 0.166 mL g⁻¹ CeO₂. The molar ratio of CO produced to O_2 released was 2.04 \pm 0.14 and 2.06 \pm 0.14 for the experimental runs at 3.4 and 3.8 kW, implying that the oxygen nonstoichiometry was fully exploited for fuel production and corresponded to a net stoichiometric reaction $CO_2 = CO + \frac{1}{2}O_2$. For replicate runs at 2.8 kW (the lowest P_{solar}), the molar ratio was 1.39 ± 0.09 due to slower kinetics at lower temperatures during the oxidation step, caused in turn by the lower temperature levels achieved during the reduction step. Since $P_{\text{solar}} = 0$ during the oxidation step, the temperature levels for both reduction and oxidation steps are determined by $P_{\rm solar}$ during reduction.

It is evident that, as the duration of the reduction step is extended at a constant solar radiative input, δ and the total fuel production increase. However, the O2 evolution rate and the degree of reduction per unit time become diminishingly smaller as the heating rate decreases and δ approaches its thermodynamic equilibrium value asymptotically. Therefore, for a constant P_{solar} during reduction, the maximum $\eta_{\text{solar-to-fuel}}$ does not necessarily occur at the maximum δ . Accordingly, based on the O2 evolution data of Figure 3, the optimum duration of the reduction step for maximum $\eta_{\text{solar-to-fuel}}$ was determined, yielding 22 min at 2.8 kW, 18 min at 3.4 kW, and 16 min at 3.8 kW. Note that since the oxidation is performed until completion and for $P_{\text{solar}} = 0$, the optimum duration of the reduction step becomes independent of the oxidation step provided δ is fully exploited for fuel production (i.e., molar ratio $CO:O_2 = 2$). For each of the three solar radiative power inputs, CO₂ splitting redox cycles were performed in adherence to the optimal durations of the reduction steps. Figure 4 shows the cycle performed with the optimal duration of the reduction step of 16 min at 3.8 kW. O₂ and CO evolution and temperatures were consistent with those shown in Figure 3 for all three solar radiative power inputs. The operating conditions and results are summarized in Table 2.

Average and peak solar-to-fuel energy conversion efficiencies are defined as

$$\eta_{\text{solar-to-fuel, average}} = \frac{\Delta H_{\text{CO}} \int r_{\text{CO}} \, \mathrm{d}t}{\int P_{\text{solar}} \, \mathrm{d}t + E_{\text{inert}} \int r_{\text{inert}} \, \mathrm{d}t} \tag{5}$$

$$\eta_{\text{solar-to-fuel,peak}} = \frac{2r_{\text{oxygen}}\Delta H_{\text{CO}}}{P_{\text{solar}} + r_{\text{inert}}E_{\text{inert}}}$$
(6)



Figure 4. Nominal reactor temperature and O_2 and CO evolution rates during a redox cycle for an optimal reduction time. Experimental conditions: 3.8 kW solar radiative power input and 2 L min⁻¹ Ar during the reduction step; no solar radiative power input and 2.5 L min⁻¹ CO₂ during the oxidation step.

where r_{CO} is the molar rate of CO production during oxidation, $r_{
m oxygen}$ is the molar rate of O₂ evolution during reduction, $\Delta H_{
m CO}$ is the heating value of CO, P_{solar} is the solar radiative power input, r_{inert} is the flow rate of the inert gas during reduction, and E_{inert} is the energy required to separate the inert gas (assumed 20 kJ mol⁻¹).³⁶ $\eta_{\text{solar-to-fuel,avg}}$ is calculated by integration of the CO production and energy consumption over the complete redox cycle. It also accounts for the solar energy needed to reheat the reactants up to the reduction temperature. This is because the solar reactor is cool-down and reheated between the redox steps during cyclic operation. Therefore, integration of P_{solar} (eq 5) accounts for the required reheating once the oxidation step is completed. The definition of $\eta_{\text{solar-to-fuel,avg}}$ (eq 5) is valid regardless whether the process is being performed in a batch, continuous, or semibatch/semicontinuous mode, since the integration is carried out for the duration of the complete cycle. In the present case, $P_{solar} = 0$ during the exothermic oxidation step. The use of P_{solar} without interruption can be accomplished by the operation of two solar reactors side-byside, one undergoing oxidation while the other undergoing reduction, by switching the concentrated solar beam between the two reactors.³⁷ The same applies for a single solar reactor in which the reactive solid material is transported from the reduction zone to the oxidation zone and vice versa,³⁸ or for a single solar reactor used exclusively for the reduction step while the reduced metal oxide is transported to an external (nonsolar) reactor for the oxidation step and recycled to the solar reactor. 39,40 On the other hand, $\eta_{\rm solar-to-fuel,peak}$ is calculated based on the peak O2 evolution rate attained during reduction assuming stoichiometric fuel production rate. This assumption is justified by closing the net mass balance for the complete cycle (i.e., $\dot{CO}_2 = \dot{CO} + \frac{1}{2}O_2$). Figure 5 shows $\eta_{\text{solar-to-fuel,avg}}$ $\eta_{\text{solar-to-fuel,peak}}$ the optimal duration of the reduction step, and the nominal reactor temperature as a function of the solar radiative power input during the reduction step. The highest efficiency values achieved were $\eta_{\text{solar-to-fuel,avg}} = 1.73\%$ and $\eta_{\text{solar-to-fuel,peak}}$ = 3.53% for a solar radiative power input of 3.8 kW. These are more than 4 times greater than the next highest efficiency reported in the literature for CO_2 conversion to CO using solar energy.^{2,22,41,42} Previous experimental work performed in a similar solar reactor configuration with porous monolithic bricks resulted in $\eta_{\text{solar-to-fuel,avg}}$ = 0.4% and

Table 2. Operating Conditions and Results of CO₂ Splitting Cycles for Three Solar Radiative Power Inputs Performed at Optimal Duration of the Reduction Step

power input during reduction (kW)	2.8	3.4	3.8
power input during oxidation (kW)	0	0	0
duration of reduction step (min)	22	18	16
nominal reactor temp. (°C)	1510	1566	1597
mean heating rate (°C min ⁻¹)	35	47	54
peak heating rate (°C min ⁻¹)	110	122	139
mean specific O_2 evolution rate (mL min ⁻¹ g ⁻¹ CeO ₂)	0.065 ± 0.002	0.100 ± 0.004	0.135 ± 0.005
peak specific O_2 evolution rate (mL min ⁻¹ g ⁻¹ CeO ₂)	0.109 ± 0.004	0.168 ± 0.006	0.226 ± 0.009
total specific O_2 evolution (mL g ⁻¹)	1.513 ± 0.055	1.876 ± 0.069	2.256 ± 0.083
absolute O ₂ evolution (mL)	2137.9 ± 77.7	2650.8 ± 97.5	3187.7 ± 117.3
nonstoichiometry δ	0.024 ± 0.001	0.029 ± 0.001	0.035 ± 0.001
mean specific CO evolution rate (mL min ⁻¹ g ⁻¹ CeO ₂)	0.064 ± 0.002	0.118 ± 0.003	0.140 ± 0.004
peak specific CO evolution rate (mL min ⁻¹ g ⁻¹ CeO ₂)	0.213 ± 0.006	0.397 ± 0.007	0.476 ± 0.013
total specific CO evolution (mL g ⁻¹)	1.916 ± 0.052	3.690 ± 0.100	4.564 ± 0.124
absolute CO evolution (mL)	2707.3 ± 73.5	5214.0 ± 141.3	6448.9 ± 175.2
molar ratio (CO:O ₂)	1.27 ± 0.08	1.97 ± 0.13	2.02 ± 0.13
$\eta_{ m solar-to-fuel,avg}$ (%)	0.73 ± 0.04	1.44 ± 0.05	1.73 ± 0.04
$\eta_{\text{solar-to-fuel,peak}}$ (%)	2.29 ± 0.02	2.92 ± 0.01	3.53 ± 0.05



Figure 5. Solar-to-fuel energy conversion efficiency (average and peak) for the complete cycle, optimal duration of the reduction step, and nominal reactor temperature as a function of the solar radiative power input for the reduction step. Error bars indicate the standard deviation from the experimentally measured and averaged values.

 $\eta_{\text{solar-to-fuel,peak}} = 0.8\%^{22}$ Experiments performed on the simultaneous splitting of H₂O and CO₂ using porous ceria felt resulted in $\eta_{\text{solar-to-fuel,avg}} = 0.15\%$ and $\eta_{\text{solar-to-fuel,peak}} = 0.31\%^{23}$ We attribute the higher values obtained in this work to a more efficient radiative heat transfer to the reactive material during the reduction step and the higher mass loading of CeO₂ inside the cavity.

The advantage of the macrostructured RPC vis-à-vis the microstructured felt (both made of pure ceria) is seen clearly when comparing experimental results using the same solar reactor under same operating conditions. Figure 6 shows the specific (per unit mass of ceria) and absolute production rates of O_2 during the reduction step and of CO during the oxidation step obtained with RPC (left graphs; this study) and felt (right graphs; ref 23). The experimental conditions for both structures were 3.4 kW solar radiative power input and 2 L

min⁻¹ Ar during the reduction step, and 0.8 kW solar radiative power input and 3 L min⁻¹ CO₂ + 2 L min⁻¹ Ar during the oxidation step. The specific amounts and rates of O2 released per gram CeO₂ are comparable for both structures, but the absolute values are much greater for the RPC (4.00 l) than for the felt (0.24 l). This is partly due to the fact that the bulk density of the RPC is larger and more mass could fit into the reactor (1413 g for RPC vs 90 g for felt). However, more mass loading that is not uniformly heated to the reduction temperature would have a detrimental effect on $\eta_{\text{solar-to-fuel}}$ because more solar energy would be "wasted" on heating unreacted material. Thus, the main cause of the superior performance of the RPC as compared to the felt is linked to heat transfer. The macropore structure of the RPC enabled deeper penetration and volumetric absorption of concentrated solar radiation, as aforementioned, which in turn resulted in a



Figure 6. Specific (upper graphs) and absolute (lower graphs) production rates of O_2 during the reduction step and of CO during the oxidation step obtained with RPC (left graphs; this study) and felt (right graphs; ref 23). Experimental conditions: 3.4 kW solar radiative power input and 2 L min⁻¹ Ar during the reduction step; 0.8 kW solar radiative power input and 3 L min⁻¹ CO₂ + 2 L min⁻¹ Ar during the oxidation step. Sample mass: 1413 g for RPC, 90 g for felt.

more uniform temperature distribution and prevented overheating of the surfaces directly exposed to the high-flux irradiation. In contrast, the micropore structures of felts or monolithic bricks (μ m range pore size) were optically thicker to the solar spectrum and absorbed the impinging radiation primarily on the exposed innermost surface of the cylinder, causing larger temperature gradients across the thickness of the structure and, consequently, restraining the reaction to the innermost layers only. SEM micrographs of the felt after the experiments corroborated the large temperature gradient, as significant sintering was detected in the innermost layers exposed to the high-flux irradiation, but negligible sintering occurred in the outer layers.²³ This thesis is further supported by radiative heat transfer analysis of the RPC and monolithic bricks via Monte Carlo ray-tracing at the pore-scale on the exact 3D digital geometry obtained by computer tomography.43,44 Within the limits of the numerical truncation error (i.e., mesh refinement) and the accuracy of geometrical representation (i.e., tomography resolution), the results obtained by this methodology approached the exact solutions. Mean values of the effective extinction coefficient obtained were 280 m⁻¹ for the RPC and 40 000 m⁻¹ for the monolith bricks, indicating a 2 orders of magnitude higher optical thickness for the latter.

During the oxidation step, the RPC and felt structures exhibited substantially different temporal behavior. For the felt, a rapid increase in the CO rate was followed by an exponential decline and completion of the reaction after a short period of time. For the RPC, the CO evolution proceeded at a considerably slower rate and was characterized by a bell shaped curve with a long tale. Peak reaction rates, normalized by the mass of ceria, were about nine times lower for the RPC (RPC: 0.33 ± 0.01 mL min⁻¹ g⁻¹ CeO₂. Felt: 2.85 ± 0.13 mL min⁻¹ g⁻¹ CeO₂). The complete oxidation took more than four times

longer for the RPC (RPC: 60 min; felt: 14 min). This behavior is attributed to the fact that the oxidation rate is mainly controlled by the availability of reactive surface exposed to CO_2 .¹⁰ BET measurements (TriStar 3000, Micromeritics) indicated specific surface areas of 6.0 m² g⁻¹ for the felt and less than 0.1 m² g⁻¹ (detectable limit) for the RPC. Based on tomographic scans, a specific surface area of 1.45×10^{-4} m² g⁻¹ was determined for the RPC. Nevertheless, the absolute CO production with the RPC (8.27 l) was nearly 17 times that of the felt (0.49 l) because of the higher mass loading, which was 15.7 times that of the felt.

Although the ceria RPC is composed of relatively thick struts $(\sim 1 \text{ mm})$, the rate of O₂ evolution appears to be limited by its heating rate rather than chemical kinetics. Figure 7 shows the time-integrated oxygen evolution, expressed in terms of δ_i , as a function of time during the reduction step for a radiative power input of 3.8 kW. The gray region indicates the thermodynamic equilibrium value of δ as calculated based on the measured nominal reactor temperature with an uncertainty of ± 30 °C. The O_2 partial pressure was assumed to be uniform throughout the reactor and to vary with time as measured by GC. Also shown in Figure 7 are the curves for the measured temperature and O₂ partial pressure. Equilibrium was assumed to be dictated by two equilibrium constants representative of (1) the formation of oxygen vacancies and electrons localized on cerium lattice sites and (2) a defect reaction resulting from the reaction of oxygen vacancies and electrons. Equilibrium modeling was based on experimental data from Panlener et al.¹⁵ and the fitting process described by Scheffe et al.¹⁸ The experimentally determined δ matches the value at equilibrium within the range of temperature uncertainty. This points to the ability of ceria to conduct O²⁻ rapidly and approach



Figure 7. Time-integrated oxygen evolution (black dashed), expressed in terms of δ , as a function of time during the reduction step for a solar radiative power input of 3.8 kW. The gray region indicates the thermodynamic equilibrium value of δ , as calculated based on the nominal reactor temperature (*T*) measured with an uncertainty of ±30 °C, and the O₂ partial pressure (p_{O_2}) measured by GC. Also shown are the curves for the measured *T* and p_{O_2} .

equilibrium. The reduction rate was thus primarily controlled by heat transfer.

The RPC structure withstood the cyclic rapid heating and cooling without degradation. Figure 8 shows SEM micrographs taken before and after 14 redox cycles. No changes of the surface and structure were observed. Isolated cracks occurred during the first runs, but the number did not grow over time and the cavity shape was maintained throughout the experimental campaign. Thermal stresses were diminished by assembling the cavity from multiple parts, allowing for thermal expansion.

No hydrocarbons were detected among the gaseous products by GC and no carbon formation was observed either. This is in agreement with previous studies.^{22,23,45} As verification, O_2 was

injected into the solar reactor while increasing the temperature to 1000 °C to combust any carbon deposition, but neither CO nor CO₂ was detected. Thus, the conversion of CO₂ was accomplished with total selectivity toward CO. A thin layer of ceria dust, deposited on the CPC, was derived from ceria sublimation, ^{15,23,46} but the percentage of material loss by sublimation was negligible. Nevertheless, this imposes an upper limit in the reduction temperature at about 1550 °C. Operation under vacuum pressures and/or application of dopants should permit lower reduction temperatures for a given δ .^{15,18} The CO₂-to-CO chemical conversion at peak CO production rate was 37.2%. No attempt was undertaken to increase the CO₂-to-CO chemical conversion. It can, in principle, be increased to 100% by simply lowering the CO_2 flow rate but at the expense of adversely affecting $\eta_{\text{solar-to-fuel}}$. If unreacted CO₂ needs to be removed from the product gases, several separation techniques are readily available (e.g., physical/chemical absorption, pressure/temperature swing adsorption, membrane technology, cryogenics), but then again introducing a concomitant energy penalty.⁴⁷ No attempt has been undertaken yet to maximize $\eta_{
m solar-to-fuel}$ of the redox cycle. Measures to accomplish that include (1) doping ceria for faster kinetics and lower reduction temperatures and, consequently, reradiation losses; (2) operating under vacuum pressures for lower reduction temperatures and inert purge gas elimination; (3) optimizing the optical thickness of the porous structure for efficient volumetric absorption of concentrated solar radiation; and (4) recovering the sensible heat between the temperature swings of the redox cycles.

5. SUMMARY AND CONCLUSIONS

A reticulated porous ceramic (RPC) structure made of pure CeO_2 was manufactured for the solar CO_2 -splitting via thermochemical redox cycling. The RPC was tested using a solar cavity-receiver directly exposed to concentrated radiation,



Figure 8. SEM micrographs of unreacted (top) and reacted RPC after 14 redox cycles (bottom): (a) strut, (b) outer surface of the strut, (c) inside the strut.

resulting in total selectivity and stoichiometric conversion of CO₂ to CO. Based on experimental runs initially performed with 22-min reduction at different solar radiative power inputs, the optimum duration of the reduction step for maximum $\eta_{
m solar-to-fuel}$ was determined, and additional redox cycles were performed accordingly. At 3.8 kW, specific O2 evolution was 2.256 \pm 0.08 mL g⁻¹ CeO₂ during the reduction step and specific CO production was 4.56 ± 0.12 mL g⁻¹ CeO₂ during the oxidation step, yielding $\eta_{\text{solar-to-fuel,avg}} = 1.73\%$ and $\eta_{\text{solar-to-fuel,peak}}$ = 3.53%. These are the highest solar-to-fuel energy conversion efficiency values reported to date for a solar-driven device converting CO₂ to CO, and more than four times greater than previously reported values. The superior reactor performance is attributed to the relatively large density and macroporosity of the RPC, which enabled high mass loading and volumetric absorption of concentrated solar radiation. This thesis was verified by comparing RPC and felt structures under same experimental conditions and further supported by Monte Carlo radiative heat transfer on 3D geometries obtained by computer tomography. Further optimization of the RPC structure is feasible by selecting the porosity and pore size distribution to achieve efficient volumetric radiative absorption and uniform temperature distribution. A comparison of the solar thermochemical approach with alternative technologies,^{2,48} such as those based on photo/electrochemical routes, reinforces the favorable prospects of metal oxide redox cycles for large-scale fuel production at high $\eta_{\text{solar-to-fuel}}$ and, consequently, at competitive costs.

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Notes

The authors declare no competing financial interest.

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NOMENCLATURE $A = aperture area (m^2)$ C =solar concentration ratio E_{inert} = energy required to recycle/separate inert gas (J mol⁻¹) $E_{\text{penalties}}$ = system specific energy penalties (J) $\Delta H_{\rm CO}$ = heating value of carbon monoxide (J mol⁻¹) I = direct normal solar irradiation (W m⁻¹) $n_{\rm fuel}$ = total amount of fuel produced (mol) $P_{\text{solar}} = \text{solar radiative power input (W)}$ p = pressure (Pa)ppi = pores per inch $r = \text{molar rate (mol s}^{-1})$ $T = \text{temperature } (^{\circ}\text{C})$ t = time(s) δ = nonstoichiometry $\eta_{\text{solar-to-fuel,avg}}$ = average solar-to-fuel energy conversion efficiency

 $\eta_{\text{solar-to-fuel,peak}}$ = peak (instantaneous) solar-to-fuel energy conversion efficiency

Abbreviations

CCD = charge-coupled device

- CPC = compound parabolic concentrator
- GC = gas chromatography
- HFSS = high-flux solar simulator
- RPC = reticulated porous ceramic
- SLPM = standard liters per minute, calculated at 273.15 K and 101 325 Pa

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