Ceria as a Thermochemical Reaction Medium for Selectively Generating Syngas or Methane from H₂O and CO₂

William C. Chueh and Sossina M. Haile

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To enable the transition away from a fossil-fuel-based energy economy, it is essential to address, in addition to energy extraction from sustainable resources, the problem of energy storage. We pursue in this work a storage strategy that relies on the capacity of selected nonstoichiometric metal oxides to capture solar heat, and the changes in oxidation state are utilized to produce a chemical fuel. For the production of hydrogen the reaction cycle is given as:

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\begin{align*}
\text{(Temperature } T_1) & \text{ MO} & \rightarrow & \text{ MO} \_\text{d} + \delta / 2O_2 \\
\text{(Temperature } T_2) & \text{ H}_2O & \text{ + MO} \_\text{d} & \rightarrow \text{ MO} + \delta H_2 \\
\text{Total} & \text{ H}_2O & \rightarrow & \text{ 1/2O}_2 + H_2
\end{align*}
\]

We demonstrate not only H₂ generation by this strategy, but also direct and rapid production of high-energy-density fuels compatible with the existing energy infrastructure. In particular, we selectively generate syngas (CO + H₂: a chemical feedstock that can be converted to liquid fuels) using CO₂ in addition to H₂O as inputs, and, when the ceria is treated with a base-metal catalyst, we directly produce CH₄. Beyond fuel generation, the effective conversion of CO₂ into useful chemical feedstocks represents a potential carbon mitigation strategy.

Because of the attractiveness of chemical fuels for energy storage and the relative ease with which heat can be extracted from other inputs, the thermochemical production of H₂ has received significant though sporadic interest during the past few decades. In contrast to other metal oxides used for thermochemical cycles, such as Zn/ZnO and FeO/FeOₓ, ceria offers the advantage of an oxygen nonstoichiometry change within the framework of a fixed crystal structure along with exceptionally high rates of oxygen chemical diffusivity. These features suggest the complete availability of the change in the metal cation valence for fuel production without limitations due to formation of an impermeable oxide scale or slow, bulk diffusion. Furthermore, ceria-based oxides are known as active catalyst supports and oxygen storage materials with high resistance to carbon deposition. These observations, as well as recent demonstrations of H₂ production from CeO₂ [10–15] led us to consider the possibility of using ceria-based oxides for simultaneous thermochemical reduction of H₂O and CO₂ to produce carbon-containing fuels.

We selected 15% samarium-doped ceria (SDC) to serve as a test-bed for ceria-based fuel production, because the thermodynamics of reduction are well-characterized. Hence, the value of oxygen nonstoichiometry, δ, in the chemical formula SmₓCe₁₋ₓO₁₋₂δ is known for a given temperature and oxygen partial pressure. We examined the fuel production half-cycle using porous SDC, pretreated at 1500 °C for 24 h, to simulate possible deactivation resulting from sintering and then lightly reduced the material to a specified δ value (typically 0.05 for experimental convenience). Undoped ceria has been shown to reach a δ value of 0.10 at 1500 °C and pO₂ of 10⁻⁶ atm (1 atm = 1.013 x 10⁵ Pa), with higher δ values possible at higher temperatures and/or lower pO₂ values (see Supporting Information Figure S1 for experimental oxygen evolution data). The input H₂O and/or CO₂ were reacted with the partially reduced SDC (specific surface area 0.2 m²g⁻¹) in a packed-bed reactor and the effluent gas was monitored by gas chromatography (GC). The average fuel production rate, r, is determined by averaging the rate over the time required to reach 90% of total fuel produced. The extent of reaction, X, is computed as the ratio of fuel produced to the theoretical fuel productivity, as set by the initial oxygen deficiency.

Under all conditions explored (inlet H₂O/CO₂ = 2:1; T = 400–900 °C, pH₂O = 0.06–0.13 atm) we observed rapid reoxidation of the neat SDC and production of syngas with 100% selectivity and without any indication of carbon deposition. For example, at 900 °C, a technologically desirable H₂/CO ratio of 2:1 was achieved, with 90% of ceria oxidized in under 2 min (r = 0.2 L·g⁻¹·h⁻¹; Figure 1). The absence of a surface passivation layer allowed the oxidation reaction to proceed to completion, achieving X = 1 within experimental error (see Supporting Information Table S1). While oxidation of high-surface-area ceria by oxidized gases (primarily CO₂) has been previously reported, the majority of these studies involved precious-metal catalysts. The observation that such a reaction can proceed rapidly in the absence of any metal catalyst despite a very low specific surface area is unprecedented and indicates a strong inherent catalytic activity of ceria. Throughout the thermochemical cycling, we found that SDC is stable, with H₂ and CO production rates being essentially unchanged even after more than 50 cycles (see Supporting Information Figures S2–S3), an advantageous consequence of high activity in the absence of a high-specific surface area.

To shed light on the process of fuel production over ceria, kinetic analyses of CO₂ and H₂O reduction were carried out separately. Under differential reactor conditions of relatively low re-
actant partial pressures (0.01–0.08 atm) and moderate temperatures (500–700 °C), it was possible to slow the reaction sufficiently so that the temporal dependence of $H_2$ and CO production could be accurately captured by GC (see Supporting Information Figure S4). When considering the water splitting reaction, it should be noted that water uptake in ceria has been reported to be insignificant and is, in any case, limited to the grain boundaries.[24] Given our large grain size as well as the observation that the $H_2$O-to-$H_2$ dissociation is similar to that of $CO_2$-to-CO (see Supporting Information Figures S5–S6) and that the amount of $H_2$ produced corresponds closely to the initial oxygen vacancy content, water uptake in our sample is neglected. In the case of $CO_2$ reduction by nonstoichiometric ceria, $CO_2$-to-CO conversion was achieved without carbon deposition, as verified by post situ temperature programmed oxidation (TPO).

Overall, we found a higher activation energy for $CO_2$ dissociation (to CO and $O_2$) $(0.80\pm0.02$ eV) than for $H_2$O dissociation $(0.52\pm0.02$ eV). Furthermore, the reaction order, $n$, for CO production was $0.77\pm0.02$ (assuming a power law for the reaction rate, $r=k[CO_2]^n[O_2]^{m}$), as compared to $0.54\pm0.01$ for $H_2$ production. These results suggest a surface-reaction-limited process, despite the micrometer-scale structural features of the coarse oxide. In the case of a reaction limited by bulk (amibipolar) diffusion of oxygen into the reactive oxide, the fuel production kinetics would be independent of the nature of the gas phase species. As further evidence of a surface-limited process, the kinetics of $H_2$ production over SDC decorated with Rh catalyst particles showed a threfold increase in rate relative to the catalyst-free material (see Supporting Information Figure S5). The rapid kinetics and concomitant complete extent of reaction for ceria stand in sharp contrast to the diffusion-limited oxidation of metals such as Zn or of reduced oxides such as FeO, which are largely limited to reaction at their surface with the oxidant gas stream.

In contrast to high-temperature fuel production, significant amounts of solid carbon and/or $CH_4$ are thermodynamically preferred when $H_2$O and CO$_2$ are reacted with reduced SDC at temperatures below 715 °C. For example, at 650 °C ca. 89% of the C atoms are expected to be in the form of solid carbon, and further reductions in temperatures increasingly favor $CH_4$ (see Supporting Information Figure S7). Despite thermodynamic driving forces, however, experiments conducted at these temperatures (400 to 700 °C) and even at an extremely low space velocity $(4300$ h$^{-1}$) did not yield any $CH_4$ or solid carbon (as confirmed by a subsequent TPO experiment on the reacted SDC) and resulted in a 100% product selectivity for syngas (Figures 2 and 3).

Because the thermodynamics for $CH_4$ production are favorable at moderate temperatures, we hypothesized that introduction of a catalyst that interacts more strongly with carbon than does ceria could enable production of $CH_4$ rather than syngas.

Accordingly, we explored $CH_4$ generation using SDC onto which 10 wt% Ni was deposited (Ni-SDC). Ni is a well-known CO hydrogenation and methanation catalyst[25] and has been shown to strongly interact with ceria supports to enhance the performance of dry methane reforming.[26] The reduced material was exposed to mixtures of diluted $CO_2$ and $H_2$O $(CO_2/H_2O=2:1$) at temperatures between 400 °C and 700 °C. The results, shown in Figures 2 and 3, reveal a remarkably high selectivity for $CH_4$ generation, defined as $S=4V_{CH_4}(4V_{CH_4}+V_{H_2}+V_{CO})$, where $V$ is the component gas volume, reaching almost 80% at 400 °C. Considering the sum of all fuels generated, the extent of reaction is again 1 within experimental error (see Supporting Information Table S1). Post situ TPO analysis of reacted samples indicated the absence of solid carbon. Overall, the product composition is in good agreement with thermodynamic expectations, which predict the $CH_4$ yield to decrease with increasing temperature, becoming negligible at 700 °C.

In contrast to experiments in the absence of Ni, the profiles of fuel production in the presence of the catalyst show a temporal evolution that is not a simple monotonic decay (Figure 2). In particular, at lower temperatures the $H_2$ production curve is essentially flat before decreasing, whereas CO production is initially negligible, then rises and falls. We propose that, in the presence of Ni, surface carbonaceous species—collectively referred to as C(s)—form on the metal catalyst surface[28] and/or near the metal/ceria interface and that these intermediate species react with the rapidly produced hydrogen to yield $CH_4$. Because C is consumed owing to deposition, it is not available to form CO. As the reaction progresses, the local hydrogen concentration is no longer sufficient to remove the surface C(s) and the Ni becomes deactivated, leaving $CO_2$ to be reduced to CO as it would in the absence of Ni. Simultaneously, the residual carbon react with excess $H_2$O to generate additional CO and $H_2$, effectively regenerating the Ni surface for subsequent cycles. Analysis of the product gases indeed indicates an initial depletion in carbon relative to the reactant gases followed by an excess of carbon in the products (see Supporting Information Figure S8). The net carbon formation implied by the difference between the carbon in the reactants and that in the products over the full course of the reaction was found to be zero, consistent with the TPO data for the reacted sample. It is noteworthy that the general form of the
fuel production profiles presented in Figure 2 was obtained not only for Ni but also for Pt and Rh as catalysts on SDC, suggesting the universality of this reaction pathway.

To further probe the hypothesis that transient carbonaceous species play a key role in CH\textsubscript{4} production over Ni–SDC, we searched for direct evidence of CO\textsubscript{2} splitting to C(s) and CO. First, 85 ± 5 μmol g\textsuperscript{-1} of CO\textsubscript{2}, a quantity insufficient for complete oxidation of the reactant ceria, was injected over reduced ceria for 6 min at 500 °C (pCO\textsubscript{2} = 0.032 atm) and the product stream monitored. For both SDC and Ni–SDC, CO\textsubscript{2} conversion was complete; that is, no CO\textsubscript{2} was detected in the effluent gas. However, while the CO\textsubscript{2} was nearly entirely converted to CO over reduced SDC, the conversion to CO over Ni–SDC was negligible, Figure 4, which implies that the CO\textsubscript{2} is, in the latter case, almost entirely converted to C(s). The occurrence of C(s) was verified post situ by a TPO experiment (Figure 4b). For Ni–SDC, we observed a large oxidation peak (maximum ca. 525 °C), with an integrated intensity (corresponding
to 89 ± 5 μmol g⁻¹ SDC of deposited C(s)) that accounts for ca. 100% conversion of the injected CO₂. In contrast, no carbon oxidation peak was observed for neat SDC. Therefore, in the absence of H₂O, and under reactant-limited conditions, CO₂ is completely reduced to C(s) over Ni–SDC, whereas it is converted only to CO over reduced SDC. These observations suggest that the inactivity of neat SDC for methane generation is related to the absence of C(s) formation on the oxide surface upon dissociation of CO₂.

The thermodynamic cycle efficiency of the demonstrated reaction scheme can be evaluated by comparing the heat content of the fuel (syngas; H₂/CO = 2:1) produced under equilibrium condition to the energy requirement of the endothermic steps. Such a comparison assumes no heat recovery of the exothermic steps and the solar-thermal heating efficiency was estimated by assuming a blackbody receiver (see Supporting Information Table S4). In the case that ceria attains a relatively conservative oxygen nonstoichiometry of 0.05 after the oxygen evolution step and cycling between 800 and 1500 °C, we obtain an efficiency of 13.2%. On introducing the possibility of 50% heat recovery, the estimated efficiency increases to 22.9%. Additional enhancement in efficiency can be achieved if the ceria oxygen nonstoichiometry is increased. The rapid fuel production kinetics for a ceria-based cycle may provide significant advantage over systems with slower kinetics but comparable thermodynamic efficiencies.[27, 28]

In conclusion, we report a highly effective methodology for the rapid production of chemical fuels from thermal (ideally, solar-thermal) energy using a relatively abundant and inexpensive oxide and without the need for precious-metal catalysts. By tuning the reactant composition and judicious use of a base-metal catalyst, it is possible to obtain the fuel of choice: H₂, CO, syngas, or CH₄. Although the specific material composition employed here may not be the ultimate system of choice for commercial applications, the approach is now clearly demonstrated and opens up new avenues for storing thermal energy.

**Experimental Section**

**Materials:** Sm₀.₁₅Ce₀.₈₅O₂ (Nextech SDC15) was ball-milled with 30 wt% starch in ethanol, uniaxially pressed into a pellet, and sintered at 1500 °C for 24 h. The pellet was then lightly crushed and sieved to obtain particle sizes between 150 and 500 μm. 10 wt% Ni–SDC was prepared via incipient wetness impregnation by dissolving nickel nitrate. After calcining at 750 °C, the powder was sintered at 1350 °C for 24 h, pressed into a pellet, lightly crushed, and sieved as described above. SDC without the addition of metal catalyst was also prepared identically as the 10 wt% Ni–SDC and used for mechanistic comparisons.

**Methods:** Samples containing 1000 mg of SDC were loaded into a 10 mm diameter continuous flow packed bed reactor with the particles held in place by a porous quartz frit. Reaction gases were delivered by digital mass flow controllers, and the effluent gas was measured by a Varian CP-4900 gas chromatograph equipped with Porapak Q and Molecular Sieve 5 A columns. H₂, CH₄, CO and CO₂ concentrations were converted to flow rates using an internal N₂ standard, which also served as a diluent. In some cases, Ar was also used as a diluent. GC calibration curves were established using analytical-grade premixed gases. The reduction of ceria was achieved by flowing a mixture of H₂, H₂O, and Ar at either pO₂ = 2.0 x 10⁻¹⁷ atm at 800 °C or 3.8 x 10⁻¹⁸ atm at 900 °C. Humidification was achieved by bubbling the reaction gas through a H₂O bubbler inside a temperature-controlled bath. pO₂ was calculated by assuming gas phase equilibrium and verified using an oxygen sensor. The oxidation of ceria was achieved by passing diluted water vapor and/or CO₂ over the packed bed of ceria particles. The temperature excursion upon oxidation of the ceria in no case exceeded 6 °C. The TPO experiments were performed on the same setup described above using O₂/N₂ mixtures as the oxidant. Brunauer–Emmett–Teller (BET) specific surface areas were measured using a Micrometrics Gemini 2380.

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Figure 4. a) Rate of CO production upon reacting CO₂ with reduced ceria, with and without Ni catalyst. b) A post situ temperature-programmed oxidation experiment reveals that all of the CO₂ was converted to C(s) over Ni–SDC, and none was converted over SDC.
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Ceria as a Thermochemical Reaction Medium for Selectively Generating Syngas or Methane from H₂O and CO₂

Doped CeO₂ with a low specific surface area is thermochemically cycled between MO₂ and MO₂₋₄ using H₂O and CO₂ as oxidants. The system rapidly and selectively produces syngas in the absence of a metal catalyst, and CH₄ in the presence of Ni. The Ni catalyst, which permits intermediate C to form on its surface, is proposed to shift the product from syngas to CH₄.