Synthesis gas production via the solar partial oxidation of methane-ceria redox cycle: Conversion, selectivity, and efficiency

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ABSTRACT

The importance of methane conversion, syngas selectivity, and oxidizer conversion for efficient syngas production by the partial oxidation of methane using a metal oxide redox cycle is quantified. The operating conditions which enable high conversion of methane to syngas over cerium oxide and conversion of carbon dioxide to carbon monoxide in the subsequent oxidation reaction are identified experimentally. The parametric study considers operating temperatures of 900 and 1000 °C and methane flow rates from 1 to 15 mL min^{-1} g^{-1} in a fixed bed of porous ceria particles. The reduced ceria is reoxidized in a flow of 10 mL min^{-1} g^{-1} CO_2 to produce CO. A trade-off of achieving high methane conversion is observed. For example, at 1000 °C, the cycle-averaged methane conversion increases from 13% for reduction in 15 mL min^{-1} g^{-1} to 60% in 1 mL min^{-1} g^{-1}. For the same change in methane flow rate, the cycle-averaged selectivities decrease from 78% to 39% (CO) and 77% to 40% (H_2) and the oxidizer conversion decreases from 93% to 48%. The maximum projected solar-to-fuel thermal efficiency is 27% for cycling at 1000 °C with reduction in 5 mL min^{-1} g^{-1} methane.

Introduction

Syngas and its components, carbon monoxide and hydrogen, are building blocks for producing prominent chemicals such as liquid fuels and ammonia. In the present study we consider the combination of two attractive processes to produce syngas. The first process is the partial oxidation of methane (R1).

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad (R1)$$

Partial oxidation of methane is an excellent match for production of methanol or Fischer-Tropsch liquid fuels because the H_2/CO ratio of the syngas is 2:1. The second process is water and/or carbon dioxide splitting via a metal oxide redox cycle, which stores solar energy in chemical form by utilizing concentrated solar process heat to drive the reverse combustion reactions.

In the combined approach considered in the present study, the partial oxidation of methane and solar water or carbon dioxide splitting are coupled by the cerium dioxide (ceria) redox cycle, which consists of two heterogeneous reactions. In the ceria reduction reaction (R2), methane reacts with oxygen released by ceria to produce syngas with H_2/CO = 2.
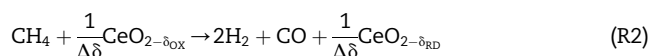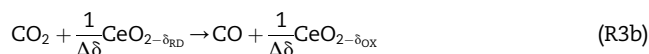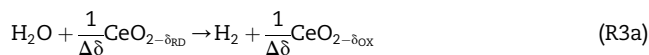
$$CH_4 + \frac{1}{\Delta\delta}CeO_{2-\delta_{ox}} \rightarrow 2H_2 + CO + \frac{1}{\Delta\delta}CeO_{2-\delta_{RD}} \qquad (R2)$$

This step increases the nonstoichiometry of the ceria to a reduced state, δ_{RD}. In the ceria oxidation reactions, steam (R3a) and/or carbon dioxide (R3b) react with the reduced ceria to produce hydrogen and/or carbon monoxide, and the ceria returns to an oxidized state, $\delta_{OX} < \delta_{RD}$.

$$H_2O + \frac{1}{\Delta\delta}CeO_{2-\delta_{RD}} \rightarrow H_2 + \frac{1}{\Delta\delta}CeO_{2-\delta_{ox}} \quad \text{(R3a)}$$

$$CO_2 + \frac{1}{\Delta\delta}CeO_{2-\delta_{RD}} \rightarrow CO + \frac{1}{\Delta\delta}CeO_{2-\delta_{ox}} \quad \text{(R3b)}$$

The cycle is endothermic for both H_2O and CO_2 splitting. As a consequence, solar energy is stored in the products and the syngas has a higher energy content than the methane feedstock. The energetic upgrade factor,

$$U = \frac{\sum_i n_{i,OUT}HHV_i}{\sum_i n_{i,IN}HHV_i} \quad \text{(4)}$$

is the ratio of the total heating value of the products of the cycle to the heating value of the methane feedstock. With complete conversion of methane to synthesis gas and oxidizer to fuel, the energetic upgrade factor is 128% for both H_2O and CO_2 splitting. Because there is an energetic upgrade, combusting the products of the cycle emits 22% less net CO_2 than combusting the methane feedstock. Depending on the oxidizer, the cycle produces the same net products as steam-reforming or dry-reforming of methane. Unlike the reforming reactions, the products of reactions R2 and R3 are in two separate streams: one containing syngas and the other pure hydrogen (R3a) or carbon monoxide (R3b). The separate gas streams are valuable individually or may be mixed to tune the H_2/CO ratio, making the process amenable to synthesis of a wider range of products than either steam- or dry-reforming of methane.

In evaluating the promise of nascent solar thermochemical processes, it is common to use efficiency as a surrogate for cost. Using an equilibrium model and assuming isothermal operation at 950 °C, Krenzke and Davidson predict the solar-to-fuel thermal efficiency of the partial oxidation of methane-ceria redox cycle could reach 40% for H_2O and 39% for CO_2 splitting [1]. Key assumptions in the prior analysis are that the two reactions proceed to equilibrium states in mixed flow reactors and oxygen is released from ceria in reaction R2 to provide $CH_4/O_2 = 2$ required for the partial oxidation of methane (R1).

The primary challenges to reaching the predicted efficiency of the partial oxidation of methane-ceria redox cycle are achieving $CH_4/O_2 = 2$, high methane conversion, and high selectivity toward syngas in the reduction reaction (R2) and achieving high conversion of oxidizer to fuel in the oxidation reaction (R3). According to chemical thermodynamics, both the complete conversion of methane and high syngas selectivity (>97%) are ensured by operating reaction R2 with $CH_4/O_2 = 2$ at or above 900 °C. High equilibrium oxidizer conversion (>80%) in the subsequent oxidation reaction is ensured by limiting oxidation to nonstoichiometries of δ>0.05. For systems that do not achieve the equilibrium product distribution or for which $CH_4/O_2 > 2$, unconverted methane and oxidizer may constitute a significant additional heating requirement. For syngas selectivities less than 100%, which are promoted by

$CH_4/O_2 < 2$, water and carbon dioxide formed by the reaction between methane and ceria also increase the required energy input for the cycle.

Prior experimental studies of the partial oxidation of methane over cerium-based oxides provide comparison of methane conversion and selectivity toward syngas for mixed ceria-ferrite [2–7] or ceria-zirconia [8–10] oxides. Li et al. found increasing iron content in $Ce_{1-x}Fe_xO_{2-\delta}$ (x = 0–0.5) increases the methane conversion at 850 °C, but decreases the selectivity toward syngas [3]. The morphology of the metal oxide is also known to impact conversion and selectivity. For reduction of macroporous $Ce_{0.8}Zr_{0.2}O_2$ at 800 °C in methane, Zheng et al. attribute a decrease in methane conversion and an increase in syngas selectivity to the collapse of the macroporous architecture and loss in surface area with increasing calcination temperature [10]. Zhu et al. observed that increasing the reaction temperature (800−900 °C) increases both methane conversion and syngas selectivity for $Ce_{0.5}Fe_{0.5}O_{2-\delta}$ [5]. High methane conversion (77%) and high selectivity toward hydrogen (87%) and carbon monoxide (86%) were obtained at 900 °C with a methane flow rate of 5.6 mL min^{-1} g^{-1} [5].

Isothermal cycling data for undoped ceria are limited to temperatures up to 850 °C. Undoped ceria is particularly attractive for the solar process because it has been shown to enable high oxidizer conversion at 500 °C [11]. Repeatable cycling with ceria is facilitated by limiting the nonstoichiometry below 0.2 to avoid carbon deposition [11,12]. In the prior work, high selectivity toward hydrogen (87%) and carbon monoxide (92%) but low methane conversion (24%) were observed at 850 °C [3]. Based on the improvement of conversion and selectivity with increasing temperature observed by Zhu et al. for $Ce_{0.5}Fe_{0.5}O_{2-\delta}$ [5], higher temperatures are anticipated to favor improved methane conversion without sacrificing selectivity.

To determine the actual expected efficiency of the cycle, it is necessary to quantify the conversion of oxidizer (H_2O or CO_2) to fuel. None of the prior work evaluated the partial oxidation of methane-ceria redox cycle using pure carbon dioxide or steam as the cycle would be operated commercially. The oxidant in the prior work was dilute oxygen [3,4,6,7], dilute steam [5,8,10–13] or dilute carbon dioxide [11,12,14]. We note that oxidation of ceria by oxygen or air results in an exothermic redox cycle and is not suitable for storing solar energy in chemical form. Studies of water and carbon dioxide splitting over ceria that target a ceria cycle with reduction in sweep gas or vacuum rather than methane have evaluated only a narrow nonstoichiometry range δ<0.06 [15], or have also used dilute oxidizer [16–19].

In the present study we quantify the importance of methane conversion, syngas selectivity, and oxidizer conversion on the thermal efficiency of the solar-to-fuel conversion. Experimentally, we identify the conditions which enable high conversion of methane to syngas over ceria and conversion of carbon dioxide to carbon monoxide. In the experimental study, we examine the influences of operating temperature, methane flow rate, and nonstoichiometric state on the production of syngas from methane and fuel from oxidizer over ceria in a fixed bed reactor. Key results are conversion of methane and selectivity toward syngas in the reduction of