Stability of Earth Abundant Redox Materials for Efficient Thermochemical Production of Solar Fuels

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In APSRC 2017 and 2016 we presented the production of syngas using ceria and mixed manganese oxides doped with Ce for water and carbon dioxide splitting (WS and CDS respectively) in a thermochemical cycle hybridized with Concentrated Solar Thermal (CST). Solar thermochemical redox cycles are viewed as a viable pathway to produce syngas. Syngas is an important intermediate in the creation of commercial products like gasoline, diesel, methanol and ammonia. Using a carbothermal reduction step such as methane partial oxidation (MPO) can alleviate some of the process challenges by decreasing the reduction temperature and increasing the fraction of the oxygen carrier undergoing reaction. Recent studies on metal oxides for MPO–CDS/WS solar thermochemical redox cycles have demonstrated potential improvements to the steady-state solar-to-fuel efficiency. A major challenge is engineering redox materials that can maintain reactivity, stability and fast kinetics over many cycles, achieve high non-stoichiometry in the reduction step, and promise large-scale production at low cost.

This year, we have extended the previous study by exploring the viability of these materials for CO_2 splitting over 100 cycles. Fig. 1 shows the H_2 and CO evolution rates for the 3% Ce Mn_3O_4. After some initial oscillations and decline in peak CO production rate for both the reduction and oxidation step, the step-yields stabilized from the 50th cycle onward with an average yield of 3.5 (±0.07) 10^{-3} molH_2 g^{-1}, 0.8 (±0.08) 10^{-3} molCO g^{-1}, and 1 (±0.09) 10^{-3} molCO g^{-1} during methane partial oxidation and CO_2 splitting, respectively. The initial decrease in the peak rates is attributed to the sintering of the nanoparticles, which decreases the available surface area slowing the reduction and oxidation kinetics. This initial surface area decrease is comparable to the behavior observed with the nanostructured Mn_3O_4. However, the impact on the H_2 and CO yield is significantly smaller as the noteworthy bulk-diffusivity of the oxygen ions in both the 3% Ce Mn_3O_4 and CeO_2 keeps driving the redox reactions toward the thermodynamic equilibrium. The slight decline in performance can likely be mitigated by optimization of the operating mode in a fluidized bed reactor or through the inclusion of a compatible secondary phase.
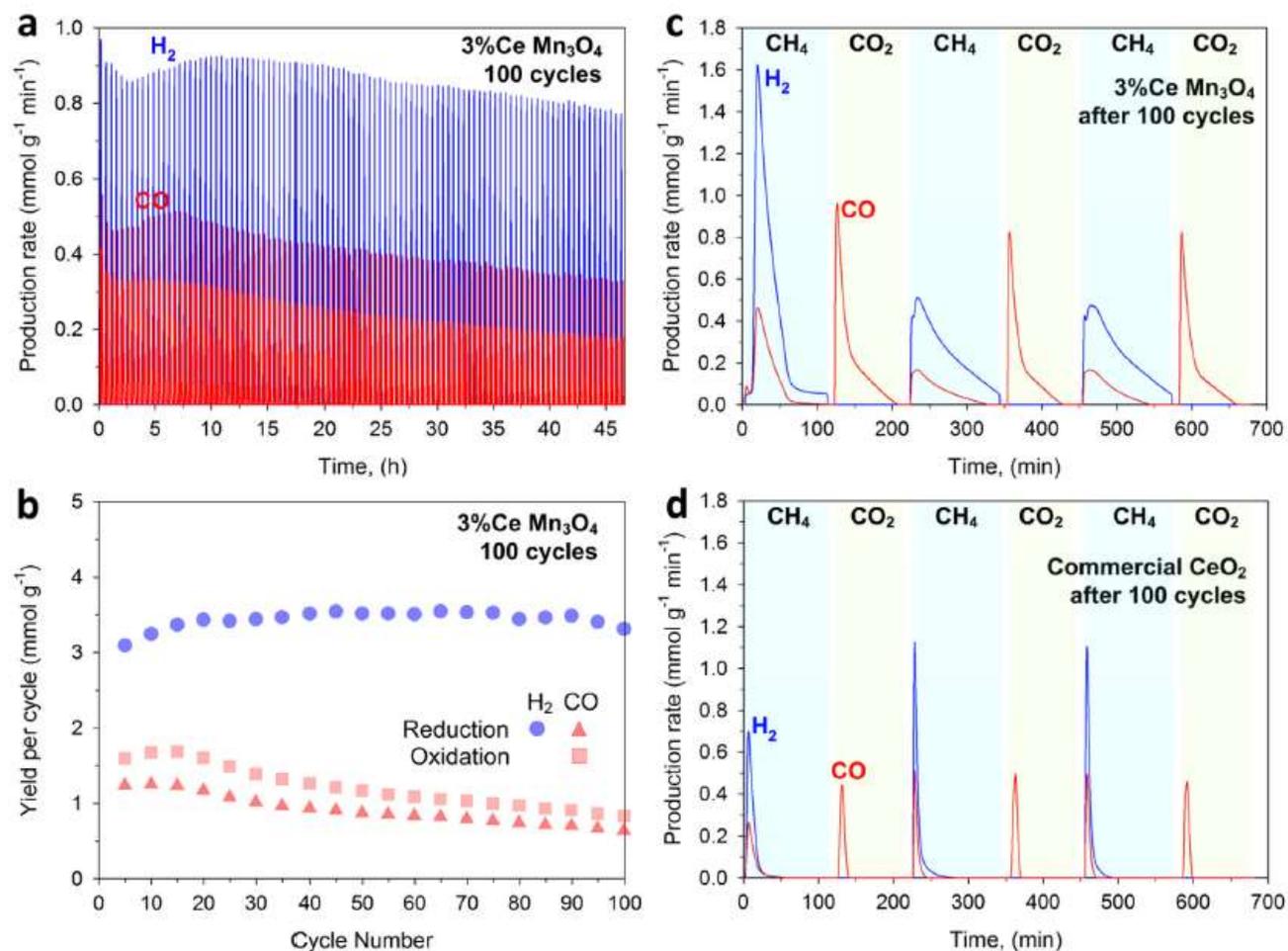
Figure 1: Investigation of the long-term CO_2 splitting kinetics and mid-term stability over consecutive 100 redox cycles. (a) H_2 and CO production rates of the 3% Ce Mn_3O_4 during 100 isothermal cycles of methane partial oxidation and CO_2 splitting and its (b) H_2 and CO yields in every 5th cycle. H_2 and CO production rates of the (c) 3% Ce Mn_3O_4 and (d) commercial CeO_2 over 3 extended cycles after 100 cycles of methane partial oxidation and CO_2 splitting.