Metal Oxide Redox Cycles as Process Engineering Tools for Effective Carbon Utilization and Capture

Casper Brady
Advisor: Bingjun Xu
Committee: Raul Lobo, Ankita Majumder, Feng Jiao, and Yushan Yan

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Rising CO₂ concentrations, an ever-changing energy landscape, and the need for higher efficiencies in energy conversion technologies necessitate dramatic changes in the way human society uses and recycles carbon. Metal oxide redox cycles offer unique process engineering tools for combating these issues. These flexible technologies can couple with other high temperature processes to shift thermodynamic limitations in reactions via chemical looping for reactive separation, enable thermodynamically unfavorable reactions in thermochemical cycles, and extend the lifetime of catalysts by selective scavenging of catalyst poisons. Herein we develop a myriad of processes unified by the use of metal oxide redox cycles as enabling process engineering tools.

Due to the advent of hydraulic fracturing, immense quantities of natural gas in tight gas formations have become available for utilization in the past two decades. However, many tight gas formations are geographically isolated, imposing a large cost in transporting the produced natural gas for sale or use. This cost is so high that frequently this natural gas is flared rather than being shipped to refineries or power plants. There is potential for overcoming this barrier by converting natural gas directly to cheap-to-ship value-added liquid products at extraction sites, however effective hydrocarbon or oxygenate production from methane is thermodynamically difficult. Formation of hydrocarbons is thermodynamically unfavorable, as C-H bonds in CH₄ are the most stable among all hydrocarbons. Partial oxidation of methane to oxygenates is similarly difficult as complete oxidation to CO and CO₂ is far more favorable than the production of any valuable oxygenates. Methane dehydroaromatization is unique among methane upgrading reactions due to the increased stability of C-H bonds in aromatics, which allows a comparatively low thermodynamic barrier of the reaction. Despite this, the dehydroaromatization reaction is still generally thermodynamically limited at reaction conditions (700 °C and 1 atm). To shift this limitation, we utilize reactive separation of hydrogen via chemical looping. In this coupling a metal oxide redox pair is reduced via hydrogen oxidation and oxidized by steam, allowing the formation of a
readily removed product (water) and reproducing hydrogen as a secondary product. We evaluate this potential coupled process via detailed reactivity studies of the state-of-the-art methane dehydroaromatization catalyst when subjected to hydrogen removal, tests of the ability of an iron oxide based oxygen carrier to remove hydrogen via chemical looping, the construction and operation of an integrated reactor system, and a detailed technoeconomic analysis of a potential mobile chemical plant design for utilization of this coupled process at petroleum extraction sites.

Advances in CO$_2$ capture technologies are imperative to slow or reverse the effects of anthropogenic climate change to ensure the continued prosperity of human society. While several commercialized and profitable technologies for removal of CO$_2$ from point sources exist, capturing CO$_2$ from the atmosphere is far more challenging. Current technologies based on amine adsorbents suffer from low adsorbent stability in oxidizing environment and current hydroxide adsorbent based systems suffer from low thermal efficiencies and particle growth during cycling. We develop an integrated process for coupled thermochemical water splitting and direct air capture of CO$_2$ based on the previously developed Mn-Na- CO$_2$ thermochemical water splitting cycle. We validate this integrated process via the design, construction, testing of a novel reactor design that is capable of one-vessel operation of the complex chemistry of the cycle for five cycles, demonstration of the ability of our process to capture atmospheric CO$_2$ with similar efficacy to other technologies via CO$_2$ adsorption studies, and evaluation of the economic favorability of our approach via a preliminary technoeconomic analysis.

Combustion based auxiliary power units in the aeronautic industry are limited in their thermodynamic efficiencies by the inherent limitations of heat engines. Several proposals for replacing current auxiliary power systems with solid oxide fuel cell systems exist. However, several factors must be addressed before these systems can be fully realized. Standard aviation kerosenes (JP-8, Jet A) have very lax sulfur restrictions, occasionally containing up to 3000 ppm sulfur in the form of organosulfur compounds. While these compounds have little effect on the operation of combustion based auxiliary power systems, sulfur based catalyst deactivation of both solid oxide fuel cell electrocatalysts and the steam reforming catalysts required for proton exchange solid oxide fuel cells is often quite severe. Thus, it is of the utmost importance to develop new catalysts that are resilient to sulfur poisoning in both steam reforming of aviation fuels and act as effective hydrogen oxidation electrocatalysts. We develop a nickel based multi-component catalyst, based on selective sulfur scavenging by a secondary material, which exhibits substantial improvements in stability in sulfur containing environments. We establish the effectiveness of this strategy using detailed catalyst deactivation studies using both model and real sulfur containing fuels and detailed post reaction characterization of our deactivated catalysts.