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# Isothermal reverse water gas shift chemical looping on $La_{0.75}Sr_{0.25}Co_{(1-Y)}Fe_YO_3$ perovskite-type oxides

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ABSTRACT

The RWGS-CL is a two-step process for the conversion of $CO_2$ to CO using a redox cycle of a parent metal oxide. Previously, this process was demonstrated using $La_{0.75}Sr_{0.25}CoO_3$ perovskite, but this material required different oxidation and reduction temperatures. In this study, oxidation and reduction were achieved at the same temperature. $La_{0.75}Sr_{0.25}Co_{(1-Y)}Fe_YO_3$ ($Y = 0$, 0.5, 0.75 and 1) perovskite-type oxides were synthesized by the Pechini method and were tested by X-ray diffraction (XRD), temperature-programmed reduction ($H_2$-TPR) and oxidation with carbon dioxide ($CO_2$-TPO). Results demonstrated that the $LaFeO_3$ ($Y = 1$) sample showed structure stability when reduced at 550 °C, the lowest CO formation onset temperature (450 °C) and high selectivity toward CO. Five isothermal RWGS-CL cycles were performed at 550 °C on the $Y = 1$ sample. The stability of the crystalline structure throughout the cycles was demonstrated by XRD. CO formation rates increased during the first cycles and stabilized at the third cycle due to the increased accumulated amount of oxygen vacancies ($\delta$) on the perovskite surface, which is consistent with the findings from the density functional theory studies that directly correlate the $CO_2$ binding strength to the amount of oxygen vacancies. The high CO formation rates and the repeatability of the process make RWGS-CL a promising technology for $CO_2$ conversion, if a renewable hydrogen source is available.

## 1. Introduction

In 2011, the total $CO_2$ emissions exceeded 30,000 Mt [1], but less than 1% of the $CO_2$ produced is re-purposed in industrial processes [2]. Since late 2010, the EPA began contemplating setting restrictions to $CO_2$ emissions from stationary sources [3]. In particular, the EPA has promoted the use of alternative technology by carbon and coal plants to reduce $CO_2$ emissions. Current efforts to decrease $CO_2$ emissions are dominated by carbon capture and storage (CCS), also called carbon sequestration. CCS is considered a potential $CO_2$ mitigation technique, but even at the top of its estimated storage capacity (120 Mt per year [4]), CCS will not be able to mitigate more than 1% of the global $CO_2$ emissions. In addition, $CO_2$ emissions are expected to increase due to population and economic growth. Here, an alternative to CCS is proposed, where $CO_2$ can be transformed to high-value chemicals needed to close a synthetic carbon cycle.

A potentially sustainable way to close a $CO_2$-hydrocarbon cycle is to convert $CO_2$ to CO, as an intermediate step to synthesize liquid fuels [5]. Recently, Mallapragada et al. [6] performed a techno-economic analysis on the conversion of $CO_2$ to fuels by different approaches including using algae, photosynthesis and the reverse water gas shift reaction (RWGS). The study determined the RWGS process, operated at 976 °C and 30 atm, as the method with the highest estimated current and future efficiency. In this process, solar energy was used to heat the reactor to this temperature and to power electrolyzers, which provided the $H_2$ for the process. In analyzing the solar energy use in the overall process, the dominant need was to generate $H_2$ for the RWGS and CO hydrogenation reactions. Assuming only the stoichiometric amount of $H_2$ and cost of $6.5/kg of renewable hydrogen, we estimate the cost contribution of hydrogen to a gallon of gasoline as $3.80 [7]. Thus, improvements in the efficiency of $H_2$ use would aid in making the process more economically feasible, though advances in the production of renewable hydrogen that allow cost reduction are also instrumental.

Previously, we have developed the reverse water gas shift chemical looping (RWGS-CL) process on Co-based perovskites [7]. The RWGS-CL is a two-step process for the conversion of $CO_2$ to CO

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using a redox cycle of a parent metal oxide. The first step of the process is the reduction by $H_2$ of the parent metal oxide and the second step is the oxidation of the reduced material by $CO_2$ with CO forming. By performing the RWGS-CL rather than RWGS catalysis, $H_2$ use can be minimized by conducting stoichiometric reactions without the need of excess $H_2$ for kinetic and thermodynamic reasons and avoiding the side methanation reaction by inherently keeping the $H_2$ and CO separated. In our original report [7], Co stabilized on a layered perovskite oxide support was the active phase for $CO_2$ conversion and was formed by $H_2$ reduction at 500 °C. The use of hydrogen allows for the generation of the active phases in the perovskite, at temperatures ~500 °C lower than thermochemical studies with active phases generated by extensive heating performed on similar oxides [8–12], but causes the Co-based perovskite to change crystalline phases. The second step is a $CO_2$ re-oxidation of the material, which yielded increasing CO generation rates with rising temperature. The obtained rates for CO formation on metallic cobalt supported on layered perovskite were competitive with RWGS [13–15], and significantly improved in comparison to photochemical reactions [16–18]. But still, the minimum temperature for generation of CO was 650 °C and the highest rate was obtained at the highest temperature tested (850 °C).

Although this initial study with Co-based materials showed promise, there is a desire to lower the temperatures in the process and to use the same temperature (referred to as an isothermal cycle) for both steps in the process. Operation at lower temperatures allows for use of less expensive materials (i.e. stainless steel) in the reactor and reduces the potential heat losses in the system. Isothermal operation would decrease process inefficiencies caused by cycling between temperatures. Iron use is popular in oxygen carrier materials for chemical looping because of its non-toxic nature, low carbon formation, low cost and low tendency toward agglomeration [19,20]. In addition, there is both experimental [21–24] and computational [25] evidence that the use of Fe or an Fe–Co mixture in the perovskite phase would aid in lowering the temperatures in the RWGS-CL process.

Typically, chemical looping studies use $O_2$ from air as an oxidant to recuperate the oxygen mobile material [26,27], and recent studies have also used steam [28]. Because of the poorer oxidative nature of $CO_2$ when compared to these two oxidants, maintaining the phase stability of the oxygen carrier is desired because less energy is required to re-oxidize an oxygen vacant material as opposed to recovering its crystalline phase. Experimentally, two groups have studied conversion of $CO_2$ to CO by oxidizing a hydrogen reduced Fe-containing material. Bhavsar et al. [21,22] studied $CO_2$ conversion on a three-step Chemical Looping Dry Reforming (CLDR) process using Fe-based oxides and supported Fe particles at 800 °C with either $H_2$ [22] or $CH_4$ [21] as the reducing agent. The three-step nature of the process is due to the poor oxidizing nature of $CO_2$, when compared to $O_2$, which led to incorporation of a second oxidant (oxygen from air) to recuperate the original structure of the oxygen carrier. Similarly, Nordhei et al. [23] demonstrated $CO_2$ conversion to CO and C(s) at 300 °C, by incorporating Co, Zn and Ni into Fe-based spinels. The same group showed that by reducing Co-substituted Fe-spinels at 500 °C, a Co–Fe alloy was formed and both metals participate in the conversion of $CO_2$ to CO and C(s). Furthermore, a mixture of Co and Fe enhances $CO_2$ conversion when compared with the base material (Fe-spinel) [24]. It is unclear if the CO production rates obtained from these studies on reduced spinels are comparable to the rates obtained on reduced perovskites. In a DFT study made by Bligaard et al. [25], the dissociative chemisorption of carbon dioxide was found to be more favorable on metallic iron than on metallic cobalt. Transition metals with lower energies for $CO_2$ dissociative chemisorption could lower the temperature for $CO_2$ conversion. However, it is not expected that the Fe perovskite phase will decompose to the base metal and metal oxides as Co-based materials did in the previous study on the RGWS-CL process. Incorporating Fe into the $La_{0.75}Sr_{0.25}CoO_3$ perovskite improves its crystalline structure stability under a reducing agent until ~850 °C [29,30].

In addition to reactivity considerations that have been based on operation temperatures, product selectivity of the $CO_2$ conversion process may also prove significant. This is especially important as the work described above indicated C(s) may form when reacting $CO_2$ with Fe-containing oxide systems. The desired reaction pathway in the RWGS-CL process is described in reactions (I) and (II). In the first step, hydrogen is flowed and oxygen vacancies and water are formed. When $CO_2$ is flowed (second step), one O regenerates the perovskite to its initial fully oxidized state, while forming CO. This pathway intensifies our previous work because the first reaction (I) does not decompose the perovskite phase into its base and metallic oxides.

Pathway 1

$$ABO_3 + \delta H_2 \rightarrow ABO_{3-\delta} + \delta H_2O \tag{I}$$

$$ABO_{3-\delta} + \delta CO_2 \rightarrow ABO_3 + \delta CO \tag{II}$$

In addition to the desired pathway (Pathway 1), a competing pathway (Pathway 2, reactions (III) and (IV)) involving $CO_2$ decomposition to C(s) and $O_2$ may also be possible. In Pathway 2, C(s) could be deposited on the perovskite surface while $O_2$ could be oxidizing the oxygen deficient perovskite or leaving the system as gaseous $O_2$.

Pathway 2

$$ABO_3 + \delta H_2 \rightarrow ABO_{3-\delta} + \delta H_2O \tag{III}$$

$$ABO_{3-\delta} + \delta CO_2 \rightarrow ABO_3 + \delta C + \delta/2O_2 \tag{IV}$$

In this study, the RWGS-CL has been intensified to work isothermally at 550 °C without phase change by incorporating Fe into the B site of the perovskite. Being a two-step process, the RWGS-CL avoids the need for additional set ups to further oxidize the oxygen carriers. Using Fe-based perovskites allows for an isothermal RWGS-CL at a temperature 300 °C lower than the process developed on Co-based perovskites. Structure stability and CO production rates throughout five RWGS-CL cycles on an Fe-rich ($La_{0.75}Sr_{0.25}Co_{(1-Y)}Fe_YO_3$) perovskite were studied. CO production rates were found to be of the same order as our previous study. The enhanced structural stability caused by the incorporation of Fe in the perovskite is maintained throughout the reaction cycles. Furthermore, the selectivity of the process was determined as 30 times more favorable toward Pathway 1 when compared to Pathway 2. Additionally, a computational investigation using density functional theory correlated carbon dioxide adsorption strength, generally a strong barrier in $CO_2$ conversion, on the (1 0 0) crystal facets on $La_{0.75}Sr_{0.25}FeO_{(3-\delta)}$ to increasing surface oxygen vacancies.

## 2. Experimental procedure

### 2.1. Synthesis of oxide powders

A Pechini synthesis as described by Popa and Kakihana [31] was followed to synthesize the $La_{0.75}Sr_{0.25}Co_{(1-Y)}Fe_YO_3$ powders. First, citric acid (Aldrich, ACS grade ≥99.5%) was dissolved in water at 60 °C while stirring. Then, the precursors $La(NO_3)_3$ (Aldrich, 99.9%), $SrCO_3$ (Alfa Aesar, 99.994%), $CoCO_3$ (Aldrich, Co 43–47%) and $Fe(NO_3)_3$ (Aldrich, 98+%) were added to the solution and were stirred at the same temperature for 2 h. Next, the solution temperature was raised to 90 °C and ethylene glycol (Aldrich, Reagent Plus ≥99%) was added. The solution was kept at this temperature for 7 h while stirring. The resulting resin was transferred to a crucible and