Extent of oxygen
vacancies (δ)

More Cu, more problems: Decreased CO₂ conversion ability by Cu-doped La_{0.75}Sr_{0.25}FeO₃ perovskite oxides

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Abstract

The effect of Cu-doping on the conversion of CO₂ to CO was investigated on H₂-reduced La_{0.75}Sr_{0.25}FeO₃ perovskite oxides. Six La_{0.75}Sr_{0.25}Fe_{1-Y}Cu_YO₃ perovskites, labeled Cu100*Y (with Y=0, 0.10, 0.25, 0.50, 0.75 and 1) were synthesized and characterized through X-ray diffraction (XRD), temperature-programmed oxygen vacancy formation, and temperature-programmed reduction (TPR). Incorporation of Cu facilitates the formation of oxygen vacancies at lower temperatures but also increased the instability of the perovskite. DFT simulations suggested that the Cu10 sample is favored to produce oxygen vacancies compared to Cu0 and Cu25 samples, which was consistent with experimental oxygen vacancy formation results. For the Cu0, Cu10 and Cu25 samples, temperature programmed CO₂ conversion (TPO-CO₂) after isothermal H₂-reduction at 450 °C and post-reduction XRD were performed to evaluate the ability of the materials to convert CO₂ at low temperatures and to identify the crystalline phases active in the reaction. Peak conversion of CO₂ to CO was achieved 30 °C lower on the Cu10 sample versus the Cu0, but less CO was produced, due to a decreased re-oxidation activity of the Cu-doped samples. CO production was inhibited in the Cu25 sample, likely due to a combined effect of poor CO₂ dissociative chemisorption energies on metallic Cu and increased thermodynamic stability of the oxygen vacant perovskites. Control experiments (Cu deposited onto La_{0.75}Sr_{0.25}FeO₃) indicated the stability of the copper-containing perovskite oxides phases was the primary limiting factor preventing CO formation from CO₂.

Keywords

carbon dioxide conversion; carbon monoxide production; reverse water gas shift; perovskite oxides; copper-doping; chemical looping

Abbreviations

Cu0	$\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$
Cu10	$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cu}_{0.10}\text{Fe}_{0.90}\text{O}_3$
Cu25	$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cu}_{0.25}\text{Fe}_{0.75}\text{O}_3$
Cu50	$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cu}_{0.50}\text{Fe}_{0.50}\text{O}_3$
Cu75	$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cu}_{0.75}\text{Fe}_{0.25}\text{O}_3$
Cu100	$\text{La}_{0.75}\text{Sr}_{0.25}\text{CuO}_3$

1. Introduction

In 2013, the atmospheric concentration of carbon dioxide reached 400 ppm [1], and emissions are expected to increase at least 20% by 2030 [2]. The world dependency on fossil fuels is steadily leading to their depletion while consumption trends are bound to increase, particularly because the development of technologies that can produce green fuels is still ongoing. An alternative to ensure a continuous supply of liquid fuels is to close a synthetic carbon cycle by transforming the highly available carbon dioxide to fuels.

The most popular technology for CO₂ mitigation is Carbon capture and storage (CCS). With around 14 operational plants worldwide, the projected capacity for the large scale processes is 0.106 Gt per year [3]. The main drawback of this process is the availability of sequestration sites, which are also a source of concern due to potential leakage [4-6]. Carbon capture and utilization (CCU) is an alternative to simultaneously decrease CO₂ emissions and ensure a continuous supply of carbon-based products including liquid fuels and chemicals [7, 8], while avoiding the drawbacks of CCS. But, with such an excessive amount of CO₂ available, only strategies that achieve high-volume products such as fuels would potentially impact CO₂ emissions noticeably. For example, use of CO₂ for methanol production would decrease CO₂ emissions by 0.26% at most, even though methanol is among the top ten commodity chemicals produced [9]. The

challenge is that CO₂ conversion requires hydrogen atoms, which directly or indirectly comes from water or methane. Since, as an example, methane steam reforming produces at least 9 t of CO₂ per t of H₂ produced [10], implementation of carbon-free hydrogen sources is required to impact CO₂ emission amounts. As a result, the cost of renewable hydrogen is key economic parameter in many CO₂ conversion processes [11].

The most energy efficient way to convert CO₂ using solar-assisted processes is reducing it to CO for liquid fuels synthesis [12]. Previously, we developed the Reverse Water Gas Shift Chemical Looping (RWGS-CL) process for the conversion of CO₂ to CO using mixed metal oxides as the redox material. Being a looping cycle process, the RWGS-CL inherently separates the reaction products (CO and H₂O), decreasing potential deactivation of the material and the possibility of side reactions [13, 14]. Additionally, because the reactions taking place are stoichiometric, excess H₂ is not required. In the first step of the process, a stream of hydrogen reduces the metal oxides. In the second step, CO₂ is flowed to the reactor where it is converted to CO while one O atom is incorporated into the metal oxide structure. Perovskites oxides (ABO₃) have been the material of focus due to their ability to accommodate oxygen vacancies in their structures. Oxygen vacancy formation depends on gas environment, temperature, and the metals on the A and B site of the oxide material [15-18].

Previously, we used cobalt in the B site of the perovskites because it facilitates the generation of oxygen vacancies [16, 19] and stabilized metallic Co nanoparticles from the perovskite's decomposition were re-oxidized by CO₂ and CO was produced [13]. But, perovskite membranes with Co have proven unstable under demanding conditions [20-23], and particularly, Co-containing membranes suffer degradation due to contact with CO₂ [24]. To improve stability [17, 25], Fe was incorporated onto the B site which allowed for the two steps of the RWGS-CL process to be isothermal at 550 °C [14]. Other groups have also used Fe-based materials to achieve CO₂ conversion in a Chemical Looping process with H₂ as a demonstration fuel, but the reduction and conversion temperatures used were at least 700 °C [7, 26]. In addition to stability imparted by Fe, the CO₂ conversion process may have also been improved by the increased CO₂ chemisorption energies on Fe surfaces [27, 28]. Even though an isothermal process is an important achievement for requiring lower energy consumption, a decrease in the process

temperature to the ranges of Fischer-Tropsch (220 to 350 °C [29]) and methanol synthesis (210 - 260 °C [30, 31]) is desired.

In the present study, the doping of Cu onto the B site of Fe-based perovskite oxides is evaluated. Incorporation of small amounts of Cu into a $\text{La}_{0.6}\text{Sr}_{0.8}(\text{Fe},\text{Co})\text{O}_3$ perovskite, has shown increased oxygen vacancy formation when compared to un-doped materials [18]. Also, copper surfaces and stabilized copper nanoparticles have been studied for their CO_2 conversion properties in electrochemistry and photocatalysis [32-35]. Moreover, in methanol dehydrogenation reactions, CO production has been observed as low as 200–260°C in Cu-doped perovskites [36] and high CO formation has been achieved from CO_2 hydrogenation on Cu oxides supported on zinc, aluminum or silicon oxides [37-39]. An added advantage of incorporating Cu on the B site of the perovskite is related to its availability. There is approximately 100 times more Cu than Co in the world [40, 41], which is necessary to guarantee the continuous conversion of CO_2 and ability to replace the perovskite material when needed.

$\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{1-Y}\text{Cu}_Y\text{O}_3$ perovskites, ($\text{Cu}100*Y$, with $Y=0, 0.10, 0.25, 0.50, 0.75$ and 1) were synthesized and characterized. Select reduced materials were then tested for their CO_2 conversion capabilities. Incorporation of Cu into the B site of the $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ perovskite inhibited the conversion of CO_2 when Cu is in high proportions. However, when Cu is doped in small amounts, CO formation occurred with a similar onset temperature as the Fe perovskite, which indicated negligible catalytic effect of the Cu doping. Moreover, the Cu doping decreased the total amount of CO formed and the stability of the perovskite. Complementary computational studies determined the oxygen vacancy formation energies as a consequence of A and B site composition and oxygen vacancy extent (δ) and correlated to experimental reducibility trends.

2. Materials and methods

2.1. Synthesis of oxide powders

The Pechini method [42] was used to synthesize six perovskites: $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{1-Y}\text{Cu}_Y\text{O}_3$ where $Y = 0, 0.1, 0.25, 0.5, 0.75, 1.0$. Citric acid (Aldrich >99.5%) was dissolved in deionized water to approximately a 2 M aqueous solution. $\text{La}(\text{NO}_3)_3$ (Aldrich 99.9%), SrCO_3 (Aesar 99.994%),

$\text{Fe}(\text{NO}_3)_3$ (Aldrich ACS, grade 98+%), $\text{Cu}(\text{NO}_3)_2$ (Aesar, 98%) were dissolved into the citric acid (CA) solution followed by a 2 h stirring period at 60 °C to ensure a homogenous mix. Ethylene glycol (Aldrich, >99%) was then added to initiate polyesterification and the mixture was stirred 7 h at 90 °C to decrease water content and form a viscous sol-gel. All reagents were measured to satisfy an La:Sr:B:Citric Acid:Ethylene Glycol mole ratio of 0.75:0.25:1:10:40 [43] with the corresponding Cu:Fe ratios varying to achieve each desired composition. Lanthanum nitrate and cobalt carbonate were 6 and 4% hydrated, respectively.

The gel was transferred into an alumina crucible and charred in air at 450 °C (at 25 °C/min) in a Vulcan 3-550 furnace for 2 h to evaporate any remaining water and produce an amorphous powder. The resulting powder was crushed and calcined in air at 950 °C (at 25 °C/min) for 6 h. The perovskites were labeled Cu0-100 with respect to their copper content.

2.2. XRD

Diffraction patterns were collected at room temperature in a Bruker X-Ray Diffractometer with Cu $K\alpha$ ($\lambda = 0.154$ nm) from 20 to 100 $2\theta^\circ$. A step size of 0.0102 $2\theta^\circ$ was used with 1.2 s per step.

2.3. Reaction experiments

Approximately 75 mg of perovskite packed between glass wool in an U-tube quartz reactor were used in each experiment. All experiments were performed under a constant total flow rate of 50 sccm and a heating rate of 10 °C/min unless otherwise stated. All gases were purchased from Airgas in ultra-high purity (UHP) grade. The experiments were monitored by an MKS Cirrus mass spectrometer (MS). The reactor system used and species quantification methods were previously described [13, 14].

2.3.1. Temperature-programmed oxygen vacancy formation

Upon the stabilization of the signals in the MS, the samples were heated to 950 °C in He. The temperature was maintained until stabilization of the signals. The generation of oxygen vacancies was monitored via the $m/z = 32$ (O_2) signal.

2.3.2. Temperature-programmed reduction (TPR)

Upon the stabilization of the signals in the MS, the environment was changed from He to 10% H₂/He. Again, after stabilization of the signals, the samples were heated to 950 °C. The heating was maintained at this temperature until the signals remained stable. Water formation was monitored via the $m/z = 18$ (H₂O) signal.

2.3.3. Temperature-programmed oxidation with CO₂ (TPO-CO₂)

Upon reduction at 450 °C for 30 min under 10% H₂/He, the samples were cooled under He to <100 °C. After stabilization of the signals, 10% CO₂/He was flowed to the samples for at least 15 min (or until the signals remained stable). Next, the samples were heated to 950 °C and the temperature was held until the MS signals remained stable.

2.4. Computational methods

Computationally, the perovskite oxides were investigated for their ability to form oxygen vacancies. Oxygen vacancy formation energy was calculated using density functional theory [44, 45] approach in Vienna ab-initio Simulation Package (VASP - 5.2.8) [46-48]. The electron densities were approximated by generalized gradient approximation (GGA). All the calculations were based on the projector augmented wave (PAW) potentials and Perdew-Burke-Ernzerhof (PBE) variant of exchange and correlation. Default PAW potentials as recommended by VASP were used for the purpose. Only the cubic phase of the perovskite oxides were investigated as these materials were often reported to exhibit cubic phases at high temperature reaction conditions [25]. Thus for comparison, all the materials have been studied in a body-centered-cubic super cell with 40 atoms. A 4×4×4 k point mesh generated by an automatic scheme having Monkhorst Pack grid was used for the purpose. A constant energy cut off of 500eV was used throughout the calculation with the ionic relaxation convergence criterion being 1×10^{-4} .

The cubic lattice constants (a) for each of the materials were obtained through a series of calculations having different cell volume. Different possible atomic distributions in the super cell leading to various configurations were also accounted for the La_{0.75}Sr_{0.25}BO₃ oxides. The most stable configuration of each material was subsequently studied for oxygen vacancy formation energy keeping the cell volume fixed as per the calculated lattice constants. The energy of oxygen vacancy formation (E_v) was calculated as following:

$E_v = E_{ABO_{3-\delta}} + \frac{1}{2}E_{O_2} - E_{ABO_3}$, where $E_{ABO_{3-\delta}}$ and E_{ABO_3} represent the DFT calculated energies of oxygen vacant perovskite and fully stoichiometric perovskite respectively. E_{O_2} is the energy of the gaseous oxygen molecule along with the correction factor of 1.36eV/O₂ to address the overbinding error [49]. The value of δ was varied between 0.125 and 0.250 as obtained by the removal of one or two oxygen atoms respectively from a 40 atom super cell comprising of 8 unit cells of ABO₃. The samples modeled were La_{0.75}Sr_{0.25}Fe_{1-Y}Cu_YO₃, with Y = 0, 0.125 and 0.250.

3. Results

Thermodynamic properties of oxygen vacant metal oxides depend on the constituent metals and extent of oxygen vacancies (δ) formed during the reduction period [50]. Therefore, multiple studies have chosen oxygen vacancy formation energies, amongst others, as descriptors to predict the feasibility and potential efficiency of H₂O and CO₂ thermochemical splitting to H₂ and CO respectively, on different metal oxides [50-52].

Deml et al. [52, 53] claim the existence of an ideal range of oxygen vacancy formation energies for which perovskites are thermodynamically favored to re-fill their vacancies with CO₂. Figure 1 shows the oxygen vacancy formation trends across La_(1-X)Sr_XBO₃ (X=0, 0.25, 1 and B=Cu or Fe). To avoid the extreme oxygen vacancy formation energies of X=0 and X=1, La³⁺ was partially substituted by Sr²⁺ ions. High Sr-substitution on the A site is undesired because it increases the oxygen non-stoichiometry of the perovskite [54-57] and therefore only low Sr²⁺ substitution was studied. This substitution induced changes in the oxidation state of the B site metal; as a consequence, the oxygen vacancy formation energies were enhanced [16, 18, 54, 58]. Substitution of the B site metal was still necessary to optimize the oxygen vacancy formation energy. The presence of copper in the B sites favored the formation of oxygen vacancies when compared to Fe perovskites (Figure 1). These oxygen vacancy formation trends are similar to the work done by Curnan et al. [59]. High Cu-substitution, however, lead to the decomposition of the perovskite, which is described in detail next.

Figure 1. Oxygen vacancy formation energy across $\text{La}_{(1-X)}\text{Sr}_X\text{BO}_3$ ($X=0, 0.5, 1$ and $B=\text{Cu}$ or Fe).

3.1. Effect of Cu addition in the crystalline structure, oxygen vacancies formation and reducibility of the samples

The effect of Cu doping on the diffraction patterns and perovskite crystalline structure are shown in Figure 2 and Table 1. The Cu0 sample only exhibited a single-phase orthorhombic (O) perovskite with a cell volume of $238.34 \text{ \AA}^3$. Small dopings of Cu (Cu10), decreased the orthorhombic unit cell volume to $237.84 \text{ \AA}^3$, as expected due to the smaller size of Cu [60] compared to Fe. This effect was also observed when comparing the main diffraction line of the orthorhombic phases (020), which increased from $32.33 2\theta^\circ$ for Cu0 to $32.43 2\theta^\circ$ for Cu10, due to unit cell size decrease. A small amount of cubic CuO was detected at 35.56 and $38.74 2\theta^\circ$, with ~1% relative intensity lines in the Cu10 sample.

In the Cu25 sample, the main diffraction line at $32.37 2\theta^\circ$ was attributed to an orthorhombic (O) phase rich in Fe (cell volume $237.99 \text{ \AA}^3$). A secondary phase (88.6% relative intensity) appeared at $32.48 2\theta^\circ$, possibly due to a tetragonal Cu-rich oxygen deficient phase, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{1-Y}\text{Cu}_Y\text{O}_{3-\delta}$ (T1) with a cell volume $454.13 \text{ \AA}^3$ (Figure 2 (b)). CuO was visible in higher proportions (~5% relative intensity) than on the Cu10 sample. The formation of the Cu-rich T1, and CuO, was presumably due to the difference in ionic radii of Fe and Cu and the preference of

Cu to exist in lower oxidation states than Fe inside the perovskite. In consequence, the O phase tolerated only small substitutions of Cu.

The diffraction profile of Cu50 exhibited two secondary phases and CuO as impurity. The three main intensity lines are shown in the range $32.2 - 32.8$ $2\theta^\circ$ (Figure 2 (b)). The main diffraction line (32.71 $2\theta^\circ$) was attributed to a tetragonal oxygen deficient $A_8B_8O_{20}$ (T2) structure [61]. The orthorhombic, Fe-rich phase (92.2% relative intensity) is seen at 32.34 $2\theta^\circ$, a 0.01 $2\theta^\circ$ difference with respect to the Cu0 sample, suggesting that the incorporation of Cu into the structure is minimal, and the copper content in the structure was less than in the O phase of the Cu10 sample. The T1 phase (82.4% relative intensity) was also detected, with a main diffraction line at 32.55 $2\theta^\circ$ and a cell volume of $453.82 \text{ \AA}^3$. The decrease in its cell volume and the higher $2\theta^\circ$ values for its main diffraction line, suggested that the Cu50_T1 phase was richer in Cu than the Cu25_T1.

The XRD profile of the Cu75 sample was similar to that of the Cu25. The main diffraction line (32.35 $2\theta^\circ$) was attributed to the O phase with a unit cell volume of $238.25 \text{ \AA}^3$. The Cu75_O phase shifted to lower $2\theta^\circ$ values and exhibited a smaller cell volume, suggesting that this phase was richer in Fe than the Cu25_O phase. The T1 phase was also evident at 32.38 $2\theta^\circ$ (94.5 % relative intensity) with a cell volume of $460.61 \text{ \AA}^3$. The Cu75_T1 phase was likely richer in Fe than the Cu25_T1 phase, as suggested by the T1 cell volume increase, and the shift in the diffraction pattern to lower $2\theta^\circ$ values. The CuO lines had a relative intensity of ~6%, similar to the Cu25 sample. This finding was counterintuitive because the T1 and O crystalline phases on the Cu75 were richer in Fe than the phases found in the Cu25 sample. However, due to the favored thermodynamics for the inclusion of Fe vs. Cu on the B site, the similarity in the profiles for Cu25 and Cu75 suggested that in the Cu75 sample, a large proportion of Cu was in an amorphous phase, undetected by XRD.

In the Cu100 sample, the structure returned to a single-phase profile with a main diffraction line at ~ 32.91 $2\theta^\circ$, characteristic of a tetragonal structure similar to T1 but without Fe on the B site. The diffraction profile shifted to higher $2\theta^\circ$ values and decreased its cell volume to $453.49 \text{ \AA}^3$. The Cu100 also had multiple unidentified diffraction lines. The most intense line (13% at 37.89

20 °) was observed in a similar position to the most intense diffraction line of the highly unstable tetragonal SrCu_2O_2 structure (reference 00-38-1178). The next most intense unidentified diffraction lines on the Cu25 XRD profile correspond to 31.18, 31.26 and 38.73 20 ° with 6.8, 6.3 and 5.3% intensity respectively. These peaks could be attributed to an orthorhombic $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ structure, which is formed from the reaction of SrCu_2O_2 with O_2 at temperatures higher than 300 °C [62]. The rest of the unidentified diffraction lines had relative intensities lower than 5%.

Figure 2. (a) X-ray diffraction patterns of the Cu-doped samples. Cu0 to Cu75 exhibit predominantly orthorhombic (O) crystalline structures (reference 00-035-1480). From Cu10 until Cu100, cubic CuO (■) was also found (reference 00-001-0428). The Cu100 sample exhibited a tetragonal pattern with at least one unidentified crystalline structure (●). (b) Main diffraction lines from 31 to 34 20 °. The Cu25 and Cu75 samples exhibit the O phase and a secondary phase (T₁), possibly a tetragonal $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{1-y}\text{Cu}_y\text{O}_{3-\delta}$. The Cu50 sample exhibits three main phases: O, T₁ and a tetragonal $\text{A}_8\text{B}_8\text{O}_{20}$ structure (T₂, reference 01-083-0366). The Cu100 sample exhibits a tetragonal $\text{La}_{0.75}\text{Sr}_{0.25}\text{CuO}_{2.44}$ (T₃, reference 00-046-0653). Profiles are normalized to most intense line.

Table 1. Unit cell parameters of the perovskite phases for the fresh $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{1-y}\text{Cu}_y\text{O}_3$ samples as calculated from X-ray diffraction data.

Sample	Main diffraction line (2θ °) and intensity (%)	Phase	a (Å)	b (Å)	c (Å)	Cell volume (Å ³)
Cu0	32.33 (100%)	Orthorhombic	5.53	5.53	7.80	238.34
Cu10	32.43 (100%)	Orthorhombic	5.53	5.50	7.82	237.84
Cu25	32.37 (100%)	Orthorhombic	5.52	5.52	7.81	237.99
	32.48 (88.6%)	Tetragonal_1	10.94	10.64	3.90	454.13
Cu50	32.71 (100%)	Tetragonal_2	10.79	10.79	3.90	454.28
	32.34 (92.2%)	Orthorhombic	5.50	5.54	7.85	239.48
	32.55 (82.4%)	Tetragonal_1	10.81	10.78	3.89	453.82
Cu75	32.35 (100%)	Orthorhombic	5.50	5.53	7.82	238.25
	32.38 (94.5%)	Tetragonal_1	10.85	10.85	3.91	460.61
Cu100	32.91 (100%)	Tetragonal_3	10.84	10.85	3.86	453.49

The oxygen vacancy formation profiles of the perovskites (Figure 3(a)) and the oxygen vacancies formed, δ (Figure 3(b)) were used to compare the samples in terms of reducibility. Overall, incorporation of Cu decreased the stability of the perovskite. The Cu0 sample exhibited enhanced stability when compared to the Cu-doped samples due to its less favored oxygen vacancy formation energy (Figure 1). Desorption of surface oxygen likely contributed to the profiles to a small extent. The profile of Cu10 demonstrated only one O₂ formation area from 810 to 870 °C (peak at 860 °C) consistent with having only one perovskite phase (Figure 2). The Cu25 sample, which initially possessed two main crystalline phases, produced 2.5 times more oxygen vacancies than the Cu10 sample, possibly due to oxygen vacancy formation and subsequent partial decomposition of the T1 structure, as suggested by post-reduction XRD (shown later). Decomposition of the samples to Cu₂O was detected via red stains left on the reactors subsequent to the experiments, particularly in the samples with high Cu substitution. Even though, intuitively, the Cu25 sample was expected to initiate the formation of oxygen vacancies at lower temperatures than Cu10, the oxygen vacancies formation on the Cu25 sample

occurred in the range of 810 to 900 °C (peak at 890 °C). This phenomenon was studied with DFT and will be discussed in section 3.3.

The two areas in the profiles of the Cu50, Cu75 and Cu100 samples, correlate with the co-existence of multiple crystalline phases. Likely, for the Cu50 and Cu75 samples, the two most predominant phases (O and T1) formed oxygen vacancies and decomposed to other phases at higher temperatures. The T2 structure, is known to be stable in its oxygen deficient state [63]. The first oxygen vacancy formation area in the Cu50 and Cu75 samples peaked at approximately the same temperature (870 °C) and formed almost the same amount of oxygen vacancies, which is consistent with the presence of similar crystalline phases. The second oxygen vacancy formation area was larger in Cu75 than in Cu50, as it is expected due to its increased Cu doping. The Cu100 sample also exhibited two oxygen vacancy formation areas, which could be attributed to decomposition of either the T3 or the unidentified phases.

Figure 3. (a) Temperature-programmed oxygen vacancy formation. The $m/z=32$ signal was normalized with respect to He. (b) Quantification of the oxygen vacancies formed $((\text{mol of O}_2 / 2) / \text{initial mol P})$. For Cu50, Cu75 and Cu100, the solid bars represent the oxygen vacancies formed from 750 to ~900 °C and translucent bars represent the oxygen vacancies formed from 900 °C until the stabilization of the $m/z=32$ signal. The Cu10 oxygen vacancy formation experiment was performed three times and the standard deviation was 1.5×10^{-3} mol of $\text{O}_2/2 / \text{mol P}$.

The reduction profiles of the samples, in the presence of a reducing agent (H_2), changed with Cu content (Figure 4 (a)). The O atoms removed from each perovskite during the reduction period (Figure 4 (b)), correspond to the mol of H_2O formed per mol of perovskite [14]. The Cu0 sample exhibited two reduction areas. The first one started at 350 °C and peaked at 550 °C. The smallest initial peak is likely formed during the reduction of the Fe^{4+} ions to Fe^{3+} , while the second one (onset at ~500 °C) was formed due to reduction of Fe^{3+} ions. In the samples with both metals on the B site, the onset reduction and peak reduction on the first area decreased by 100 and 300 °C, respectively.

The Cu10 sample had two low-temperature areas, the first from 250 to 350 °C potentially due to the reduction of Cu^{3+} and Fe^{4+} ions. The second reduction area (350 to 450 °C) was attributed to the reduction of the Fe^{3+} ions. The high temperature reduction area was larger in Cu0 than in Cu10 due to higher Fe content on the Cu0 sample, when compared to the Cu10 sample. In general, the low and high-temperature reduction areas had a direct and inverse relation to Cu content, respectively (Figure 4(b)). The Cu75 and Cu100 samples reduce almost completely below 650 °C. The $m/z=18$ peak observed at ~850 °C on the Cu75 sample, was attributed to the reverse water gas shift reaction between previously adsorbed carbon dioxide and hydrogen.

The samples with both Cu and Fe on the B site (Cu10, Cu25, Cu50, Cu75), exhibited lower onset reduction temperatures than the Cu100 and Cu0. This effect was a consequence of the combined stability of Fe with the reducibility of Cu. The TPR profile for Cu100 seemed to undergo a lumped reduction below 550 °C. A characteristic that makes an oxide material ideal for RWGS-CL or thermochemical cycles, is to have tunable oxygen vacancies as a function of temperature. A lumped reduction such as the one suffered by Cu100 is difficult to control. More discrete profiles such as the Cu0 and Cu10 are desired due to the multiple reduction areas with different onset and peak temperatures.

Figure 4. (a) Temperature-programmed reduction of the samples under 10% H₂/He. (b) Quantification of moles of water produced during the reduction normalized by the initial moles of perovskites. The solid bars represent water formation below 450 °C, the translucent bars represent the reduction above 450 °C. The solid bars increase in size with Cu, showing that Cu addition increases the reducibility of the samples at lower temperatures.

3.2. Effect of Cu doping in the CO formation profiles of La_{0.75}Sr_{0.25}Fe_{1-y}Cu_yO₃ perovskites

The effects of Cu doping on CO₂ conversion characteristics for the Fe-based perovskite were investigated on samples with low doping of Cu (Cu10, Cu25). These samples were chosen due to their enhanced stability, as opposed to the high Cu-doped samples. The Cu0 sample was tested for comparison purposes. Prior to the temperature-programmed CO₂ conversion, the samples were reduced at 450 °C under 10% H₂/He for 30 min. This temperature was chosen because it was at the end of the low-temperature reduction area for the samples containing both Cu and Fe, and inside that area for the Cu0 sample.

During the isothermal reduction period, water was formed, which was quantified as mol of H₂O formed per mol of perovskite. The reduction increased with copper content. The Cu0, Cu10 and Cu25 samples formed 0.38, 0.44 and 0.65 mol of H₂O per mol of perovskite, respectively (Table 2). These values suggested that the main phases of the Cu0, Cu10 and Cu25 samples only

underwent minor reductions. Post-reduction XRD (Figure 5) confirmed that the samples retained their main crystalline structure. The reduced Cu10 and Cu25 samples exhibited increased crystallinity, as evident by the disappearance of the amorphous shoulder at low 2θ ° values, and the narrower main diffraction lines. The T1 phase was still present although the main diffraction line decreased in relative intensity to 63.3%. Both phases were oxygen deficient, evident from the shift of XRD profiles to lower 2θ ° values. CuO was reduced to Cu⁰ on the Cu10 and Cu25 samples. The Cu0 sample also underwent a reduction, as noted by the appearance of metallic Fe at ~ 45 2θ °.

The onset CO production temperature was ~ 450 °C for Cu0 and Cu10 (Figure 6) and the peak CO production occurs at 540 and 570 °C for Cu10 and Cu0, respectively. The similar onset temperatures suggested that Cu did not contribute to a catalytic effect. CO formation was not detected on the Cu25 sample. Expressly, the amount of O removed from the perovskites increased with Cu doping, and the CO production decreased with Cu. Also, the Cu10 sample only re-oxidized 13.6% of its oxygen vacancies, while the Cu0 sample re-oxidized 23.7% of the oxygen vacancies formed during the isothermal reduction (Table 2). These findings are not consistent with previous results, which showed that oxygen vacancies are the primary driving force for the CO₂ bond breaking in La_{0.75}Sr_{0.25}FeO₃ samples [14] and will be discussed in section 4. The decreased CO production on the Cu doped samples and the lower percentage of re-oxidized vacancies indicated that the RGWS-CL would be less favored than on the Cu0 sample, therefore, repeated cycle studies were not performed.

It is important to mention that in CO hydrogenation experiments, others have shown that introducing Cu ions into the LaMnO₃ perovskite promotes the formation of methanol from CO hydrogenation [64]. This suggested that Cu doping could promote the conversion of CO to other methanol on the La_{0.75}Sr_{0.25}FeO₃ perovskite. However, $m/z = 31$ was tracked during the temperature-programmed CO₂ experiments and no formation of methanol was detected, this is due to the H₂ and CO₂ remaining separated during the looping-type experiment.

Table 2. H₂O and CO formation on the La_{0.75}Sr_{0.25}Fe_{1-Y}Cu_YO₃ (Y=0, 0.10 and 0.25) samples during the temperature-programmed oxidation with CO₂ (CO formation) experiments.

Sample	(mol H ₂ O/mol P)	(mol CO/mol P)	% of vacancies re-oxidized
Cu0	0.38	0.09	23.7
Cu10	0.44	0.06	13.6
Cu25	0.65	--	--

Figure 5. XRD patterns after isothermal reduction at 450 °C in 10% H₂/He for 30 min. Fresh patterns are repeated from Figure 2. All samples exhibited mainly an orthorhombic (O) crystalline structure. Other phases found: metallic Fe (◄), metallic Cu (*) and CuO (■). The profiles are normalized to the most intense peak.

Figure 6. Temperature-programmed CO formation on Cu0, Cu10 and Cu25 (raw signals of $m/z=28$) after isothermal reduction at 450 °C in 10% H_2/He for 30 min.

3.3. Simulations studies

The effect of doping copper in the B site of $La_{0.75}Sr_{0.25}BO_3$ on their oxygen vacancy formation abilities is shown in Figure 7. The DFT calculated oxygen vacancy formation energies revealed that, for low concentrations of oxygen vacancies ($\delta = 0.125$), the Y=0.125 sample exhibited the lowest formation energy. For higher extent of oxygen vacancies ($\delta = 0.250$), which involves more atomic relaxations in the crystal lattice, the Y=0.250 sample had the lowest oxygen vacancy formation energy. Low oxygen vacancy formation energies specify that the materials are favored to generate oxygen vacancies.

Due to the extent of oxygen vacancies or reduction generated in the temperature-programmed experiments, the oxygen vacancy formation (Figure 3) and the reduction (Figure 4) of the samples can be correlated with the $\delta = 0.125$ and $\delta = 0.250$ DFT analyses. Experimentally, no oxygen vacancy formation was observed on the Cu0 sample (Figure 3), which is consistent with it having the highest oxygen vacancy formation energy on Figure 7. Furthermore, Cu10 exhibited a lower peak oxygen vacancy formation temperature than Cu25, which is agreed with favored oxygen vacancy formation capabilities on the theoretical sample Y=0.125 at $\delta=0.125$. The $\delta = 0.250$ data (Figure 7) indicated that the oxygen vacancy formation energy decreased with Cu content. Similarly, the amount of mol H_2O /mol P for the temperature range from 250 to 450 °C also increased with Cu (Figure 4).

Figure 7. Bulk oxygen vacancy formation energies of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{1-Y}\text{Cu}_Y\text{O}_3$ for $Y = 0, 0.125$ and 0.25 , for oxygen vacancy extent (δ) of 0.125 (left, black squares) and 0.25 (right, blue circles).

4. Discussion

The inhibition of CO formation during the temperature-programmed CO_2 oxidation experiments was directly proportional to Cu content. In the following sections, we investigate whether the effect was due to the changes in the Cu phase (Cu outside the perovskite) or due to the effect of B-site Cu substitution inside the perovskite structure.

4.1 Effect of Cu containing secondary phases

CuO was found on the XRD profiles of the Cu10 and Cu25 samples in 1 and 5% relative intensities, respectively. The detail that relative intensities was a factor of 5 different whereas the Cu amount in the sample was factor of 2.5 different suggested the fraction of Cu in secondary phases was increasing with Cu amount in the sample. An impurity rich in Cu initially points to the conclusion that the perovskite was B-site deficient, but B-site cationic vacancies are not

thermodynamically favored [16] and therefore, are rarely seen. Ge et al. [65] determined that high concentrations of B site vacancies on $(\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Co}_{0.8}\text{Fe}_{0.2})_y\text{O}_{3-\delta}$ membranes induced the appearance of A-metal oxides near the membrane surface, detected by FTIR but undetected by XRD. Previous efforts [17] found that, as Fe content decreased in $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$, the surface composition of the oxides was enriched in La and Sr. An increased La and Sr concentration near the surface, presumably in the form of base metal oxides, could highly favor the adsorption of CO_2 as carbonate [66, 67] as opposed to breaking the C-O bond on the oxygen vacancy site of the perovskite oxide. To investigate potential carbonate adsorption, FTIR was performed on the Cu25 sample with and without CO_2 adsorption. A sample was treated to an isothermal reduction in H_2/He for 20 min, He flushing for 20 min, and subsequent CO_2 flow for 20 min at 550 °C. Vibrations in the carbonate regions decreased in intensity (and some even disappeared) when compared to the same sample treated in He at 550 °C for the same period of time where some carbonates from the atmospherical adsorption were not removed. This comparison suggested that carbonate formation was not the issue.

In addition to surface enriched oxides of La and Sr, Cu phases must be present. In this study, the samples were reduced for 10 minutes more than in previous efforts [14], therefore, metallic Fe^0 was also noted on the reduced $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$. This Fe^0 could have enhanced CO formation, due to the enhanced dissociative chemisorption of CO_2 in Fe [28] surfaces. Dissociative chemisorption of CO_2 has been proven highly unfavorable on Cu surfaces [27, 28, 69, 70]. Therefore, higher amounts of metallic Cu present on the Cu25 sample could be inhibiting CO production due to highly electronegative localized CO_2 adsorption on Cu nanoparticles, which is more thermodynamically favored than CO_2 dissociation. But, CO_2 conversion to CO has been achieved on Cu vapor-deposited on TiC(001) [72]. In both Cu-containing samples (Cu10 and Cu25) tested for CO_2 conversion, the isothermal H_2 treatment reduced the CuO phase to metallic Cu^0 , which might be sintering upon reduction higher than 400 °C [68].

To investigate the effect of the reduced Cu^0 on CO formation, five consecutive cycles of RWGS-CL are studied (similar to previous studies [14]) on 5% Cu on $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ synthesized by wet impregnation. The rates of CO formation on 5% Cu / $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ were compared to those of $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ (Table 3). CO formation was not inhibited by additional Cu, and the

formation rates were very similar to those of $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$. Although the temperatures were much lower than the synthesis temperature (550 vs 950°C), it is possible that the decrease with the 5% Cu / $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ was associated to Cu migration into the perovskite oxide. Regardless, this comparison indicated that excess amount of Cu external to the perovskite oxide did not inhibit CO production.

Table 3. Rate of CO formation at $T = 550^\circ\text{C}$ on the RWGS-CL process on $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ and Cu-supported $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ perovskite oxides. Only data after the third cycle is shown because it represents the rates upon stabilization. The first two reductions/oxidation cycles on the 5%Cu/ $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ sample were used to reduce copper oxide to metallic Cu^0 . Data from these two cycles were not considered to be representative of accurate oxygen vacancies formation due to additional water production from oxygen in the copper oxides.

Sample	$\mu\text{mol CO/ gram of perovskite/min}$		
	Cycle 3	Cycle 4	Cycle 5
$\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ [14]	69.58	77.15	73.09
5% Cu/ $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$	69.23	62.36	61.65

4.2 Effects of B-site doping of Cu into the $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ perovskite

Experimental studies (Figures 2 and 3) showed that increasing Cu content increased the oxygen vacancies formation abilities of the $\text{La}_{0.75}\text{Sr}_{0.25}\text{Fe}_{1-y}\text{Cu}_y\text{O}_3$ materials. Even though the CuO and Cu-doped perovskites remained stable in the reduced state (Figure 5), the Cu-doped materials have a lower oxygen affinity than the CuO samples (Figure 7, right axis), which lowered the thermodynamic drive to re-fill the oxygen vacancies for the Cu_{10} and Cu_{25} samples, than in the Cu_0 sample, particularly with a poor oxidant (CO_2 [71]). Nakamura et. al [56, 57] studied similar materials ($\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$) and found that increasing the perovskites reducibility, decreases its ability to refill its oxygen vacancies. These results and findings contrasted significantly from results with a less reducible perovskite oxide. For the $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ sample (Cu_0), production of CO increased (0.02, 0.13, 0.15 mol CO/mol $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$) with increasing reduction in the perovskite structure (0.13, 0.36, 0.71 mol H_2O /mol ABO_3 respectively). In these experiments, various amounts of H_2O were formed during isothermal reduction (at 3, 13.6 and 30 min

respectively) under 10% H₂/He. This comparison, on conjunction with the Cu supported on La_{0.75}Sr_{0.25}FeO₃ (Table 3) confirms that the stability of the reduced material is center to the low levels of CO production from the Cu containing samples.

5. Conclusion

The effects of Cu doping in Fe-based perovskites on the conversion of carbon dioxide to carbon monoxide were investigated. Six materials La_{0.75}Sr_{0.25}Fe_{1-Y}Cu_YO₃ with Y = 0, 0.1, 0.25, 0.5, 0.75 and 1, (labeled Cu100*Y) were synthesized, characterized, and tested for their reduction and oxygen vacancies formation capabilities. Select reduced materials were tested for their ability to convert CO₂ to CO. Cu addition reduces the stability of the perovskite and promotes the formation of oxygen vacancies. DFT calculations confirmed that, for the Cu0, Cu10 and Cu25 samples, the oxygen vacancies formation energies depend on both the Cu content and the extent of oxygen vacancies formed (δ). Only the perovskites with lowest Cu substitution (Y=0.1) and no Cu (Y=0) were able to produce CO. Results indicated that incorporating Cu into the perovskite structure induced a loss of oxygen affinity and decreased the ability of the perovskite to re-oxidize.

Acknowledgements

The authors thank Professor Gabor A. Somorjai for his guidance, leadership, and contributions in many areas including surface science, materials chemistry, and heterogeneous catalysis. The authors would like to acknowledge NSF award 1335817 for financial support and USF Research Computing. YAD acknowledges the Florida Education Fund for the McKnight Dissertation Fellowship and the NASA Florida Space Grant Consortium for the Dissertation Improvement Fellowship.

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