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Supported Perovskite-type Oxides: Establishing a Foundation for CO$_2$ Conversion through Reverse Water-gas Shift Chemical Looping

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Supported Perovskite-type Oxides: Establishing a Foundation for CO₂ Conversion through Reverse Water-Gas Shift Chemical Looping

by

Bryan J. Hare

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering Department of Chemical and Biomedical Engineering College of Engineering University of South Florida

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ABSTRACT

Perovskite-type oxides show irrefutable potential for feasible thermochemical solar-driven CO$_2$ conversion. These materials exhibit the exact characteristics required by the low temperature reverse water-gas shift chemical looping process. These properties include structural endurance and high oxygen redox capacity, which results in the formation of numerous oxygen vacancies, or active sites for CO$_2$ conversion. A major drawback is the decrease in oxygen self-diffusion with increasing perovskite particle size. In this study, the La$_{0.75}$Sr$_{0.25}$FeO$_3$ (LSF) perovskite oxide was combined with various supports including popular redox materials CeO$_2$ and ZrO$_2$ along with more abundant alternatives such as Al$_2$O$_3$, SiO$_2$, and TiO$_2$, in view of its potential application at industrial scale. Supporting LSF on SiO$_2$ by 25% mass resulted in the largest increase of 150% in CO yields after reduction at 600 °C. This result was a repercussion of significantly reduced perovskite particle size confirmed by SEM/TEM imaging and Scherrer analyses of XRD patterns. Minor secondary phases were observed during the solid-state reactions at the interface of SiO$_2$ and TiO$_2$. Density functional theory-based calculations, coupled with experiments, revealed oxygen vacancy formation only on the perovskite phase at these low temperatures of 600 °C. The role of each metal oxide support towards suppressing or enhancing the CO$_2$ conversion has been elucidated. Through utilization of SiO$_2$, the reverse water-gas shift chemical looping process using perovskite-based composites was significantly improved.
CHAPTER 1: INTRODUCTION

Throughout preceding decades, global environmental concerns instigated a major shift of research focus and investment in renewable energy generation. However, the need for fossil fuels remains on the rise due to demand for transportation fuels and electricity, resulting in vast emissions of carbon dioxide, a major greenhouse gas. Carbon capture and storage (CCS) is aimed at mitigating this CO₂ emission problem and promote carbon neutrality. However, annual emissions (~35 GT in 2015) continue to relentlessly outweigh the scale of reutilization (estimated ~35 MT in early 2017). This scenario demands several processes that are capable of

Figure 1. Reverse water-gas shift chemical looping (RWGS-CL) process
converting CO₂ to CO to valuable hydrocarbons.² The extreme conditions required for natural
CO₂ dissociation, over 2000 °C in vacuum,³ underscore the need for catalytic reinforcements and
more energy-efficient processes. Amongst the proposed techniques, solar thermochemical
approach (STC), for instance, is particularly attractive.⁴⁻¹⁰ It presents the novelty of harvesting
solar energy towards repurposing waste CO₂ emissions to hydrocarbons. Corresponding CO
selectivity and CO₂ conversion rates are much higher than those of photocatalytic methodologies
which struggle to achieve even 1 μmol g_{cat}⁻¹ min⁻¹.¹¹ However, STC processes are typically
accompanied by extreme operation temperatures (≥ 1000 °C),⁷⁻⁸ thereby limiting implementation
due to a narrow range of stable materials. A feasible alternative, reverse water gas shift chemical
looping (RWGS-CL), is capable of converting CO₂ to CO at much lower temperatures (450 –
700 °C).

The RWGS-CL process (Figure 1) is a 2-step process, previously demonstrated by our
group,¹² whereby metal oxides (MOX) are used for generation of 100% selective CO from CO₂.
In comparison to general CO₂ splitting,⁵, ¹³ CO formation rates in the RWGS-CL process are
much higher in a much lower operation temperature of about 450-750 °C depending on the oxide
used.¹⁴ The first step involves partial reduction of the perovskite oxides to their oxygen deficient
forms (MOX-δ) under exposure to hydrogen. The second step is the platform for converting CO₂
to CO over these oxygen vacant perovskites, allowing the oxides to regain their original
stoichiometric forms (MOX). This cyclic operation converts CO₂ to CO, which can be
subsequently converted to hydrocarbons via Fischer-Tropsch synthesis. The overall process for
producing and using these fuels can be CO₂-neutral to the environmental if solar (or other non-
fossil fuel derived energy source) is used for hydrogen generation (i.e., water splitting). Low and
moderate temperature thermochemical processes permit higher sun-to-fuel efficiencies compared
to current and future technologies, making RWGS-CL appropriate for large-scale implementation.\textsuperscript{15-16} Wenzel et al. investigated the solar-to-fuels efficiencies of the isothermal chemical looping process and determined a reactor system with separation may consume up to 54\% less energy than the conventional reverse water gas shift reaction.\textsuperscript{16} Given the promising potential of the RWGS-CL process, it is thus imperative to identify and optimize a suitable catalytic material.
CHAPTER 2: MATERIAL BACKGROUND

2.1 Perovskite Oxides

Perovskite oxides (ABO$_3$) are key materials that support and enable this operation due to their consistent and intrinsic stability in both stoichiometric and non-stoichiometric forms, fitting the criteria for generating vast quantities of CO. With the ability to tailor the lattice and synthesize an infinite array of metal combinations, scientists can fine-tune the properties of these materials to maximize redox abilities. The A-site typically consists of lanthanides and alkaline Earth metals while the B-site if most often occupied by transition metals and semi metals. Perovskites of diverse compositions, such as La$_{0.75}$Sr$_{0.25}$FeO$_3$ (LSF) and La$_{0.6}$Ca$_{0.4}$MnO$_3$ (LCM), have been shown to match and even surpass the redox activity of popular redox materials such as CeO$_2$ in the thermochemical conversion of both CO$_2$ and H$_2$O. The utilization of perovskites in redox applications is advantageous due to the formation of an oxygen diffusion network throughout the bulk lattice. In the instance of C-O bond cleavage during CO$_2$ reduction on the catalyst surface, the resulting oxygen atom diffuses into the bulk and reopens the active site. Stable nonstoichiometric perovskites with high concentrations of vacancies typically exhibit higher rates of oxygen self-diffusion as well as stronger CO$_2$ affinity. The ability for these materials to repeatedly produce and replenish vacancies while retaining structural stability in chemical looping processes therefore provides a stable foundation for feasible CO$_2$ conversion over long periods.
2.2 Oxygen Self-Diffusion

The true potential of many perovskites remains unrecognized due a considerable lack of specific surface area.\textsuperscript{17} With emerging reactor technology for water-gas shift reactions and thermochemical splitting,\textsuperscript{28-30} it is crucial to design novel perovskite-based materials that maintain high surface area over long-term use at elevated temperatures. Industrial-scale pellets are often shaped as spheres, Raschig rings, and other common variations with an extruded substrate serving as a catalyst support.\textsuperscript{31-33} As opposed to using bulk single-phase catalyst pellets, the inclusion of supporting material is necessary to improve perovskite surface area and accelerate oxygen self-diffusion. The speed at which oxygen is recovered by nonstoichiometric oxides may be modeled with the one-dimensional equation

\[
\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp\left(-\frac{b_n^2 D t}{l^2}\right)}{b_n^2 (b_n^2 + l^2 + L)} \quad \ldots \ldots (1)
\]

where \(M_t\) is the sample mass at time \(t\), \(M_\infty\) is the sample mass at the experiment conclusion, and \(l\) is the radius. \(D\) represents the effective diffusivity of the oxygen vacancy which in this case will depend on the perovskite metallic composition and a thermodynamic proportionality factor.\textsuperscript{35-36} An effective diffusivity coefficient (\(D\)) of \(2 \times 10^{-7}\) cm\(^2\)/s was obtained for LSF at 600 °C through the interpolation of data obtained by Armstrong et. al \textsuperscript{37}. \(L\) is the dimensionless ratio \(lk/D\) where \(k\) is the surface exchange coefficient, given as \(10^{-5}\) cm/s.\textsuperscript{38} \(b_n\) is the \(n^{th}\) positive root of \(b \tan(b) = L.\textsuperscript{34}\) Figure 2a illustrates this phenomena with LSF and foreshadows low CO yields and long cycle times if pellets are designed without supporting material. Therefore, the identification of an optimal material that is proficient in maintaining small catalyst particle sizes and, as a result, enhance the CO\(_2\) convertibility of LSF and other perovskite oxides. Powders synthesized by gel-based citrate methods often result in particle sizes ranging from 30 to 80 nm.\textsuperscript{27,39-40} Others have
achieved below 10 nm by utilizing alternative chelating agents or low calcination temperatures.\textsuperscript{41-42} However, using LCM as an example, Figure 2b shows a decline in the stability of perovskites calcined at lower temperatures after converting H\textsubscript{2} and CO\textsubscript{2} in temperature-programmed oxidation experiments. This lack of stability is denoted by the presence of binary oxide impurities. Therefore, the search for a supporting material that can reverse the sintering of perovskite particles synthesized at higher temperatures remains imperative. This would result in smaller perovskite nanoparticles, accelerated oxygen self-diffusion, and enhanced CO production yields.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Self-diffusion and stability properties. a) Change in nonstoichiometric LSF mass over time with different particle sizes. The time required for vacancies to replenish decreases with particle size as calculated by Eqn 1 (D = 2 \times 10^{-7} \text{ cm}^2/\text{s}). b) Structural stability of post-reaction La\textsubscript{0.75}Ca\textsubscript{0.25}MnO\textsubscript{3} calcined at different temperatures (1200 and 950 °C).}
\end{figure}

\section*{2.3 Material Overview}

The ideal support should further enhance the capabilities of perovskites already popular in applications that rely on oxygen vacancy formation. LSF in particular has shown great promise in RWGS-CL process due to the low energy barrier for oxidation state transitions (Fe$^{3+}$...
– Fe$^{2+}$) during redox cycles. CO$_2$ also exhibits affinity for the material due to the slight basicity of La, while moderate Sr doping results in slight oxygen deficiency to promote a greater extent of oxygen self-diffusion throughout the lattice. Our group previously demonstrated indispensable characteristics of LSF such as the perovskite’s willingness to retain nonstoichiometry and endure numerous cycles of RWGS-CL at low temperatures. Due to its stability and superior CO$_2$ conversion rates, LSF is a suitable candidate for RWGS-CL processes.

By focusing strictly on oxide supports, there lies the potential to expand the perovskite oxygen network. CeO$_2$ for instance is a popular material for its high extent of oxygen vacancy formation and replenishment in various redox applications. ZrO$_2$ has also sufficed as both an active catalyst and efficient catalyst support and may even introduce additional oxygen vacancies when Zr is doped into the active phase. While catalyst size reduction was already demonstrated using these supports, large-scale CO$_2$ utilization will nonetheless require a lower cost alternative. A few earth-abundant examples include Al$_2$O$_3$, SiO$_2$, and TiO$_2$, each of which have been previously tested as supports for assorted types of catalysts.

This study concentrated on the use of various catalyst supports for reducing complex oxide particle size, and therefore, increasing CO formation in the RWGS-CL process. While focus was given to LSF, the ideal support should suffice for any thermodynamically stable perovskite capable of sustaining vacancies without deterioration. LSF was supported on popular materials such as CeO$_2$ and ZrO$_2$ along with more abundant alternatives including Al$_2$O$_3$, SiO$_2$, and TiO$_2$. These composites were tested in temperature-programed experiments with H$_2$ and CO$_2$ to observe distinctions in redox activity. These findings were backed by density-functional theory (DFT) based calculations regarding vacancy formation energies. Samples were intensively characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM),
and transmission electron microscopy (TEM) to decipher the crystallographic reasoning behind improved or curtailed CO$_2$ conversion by perovskites in the RWGS-CL process.
3.1 Composite Synthesis

A sol gel-based Pechini method was used to synthesize the La$_{0.75}$Sr$_{0.25}$FeO$_3$ (LSF) perovskite oxide similar to that proposed by Popa and Kakihana\textsuperscript{40} Using citric acid (CA) (Aldrich >99.5%) as a chelating agent, a 2 M aqueous solution was made with deionized water. Metal precursors La(NO$_3$)$_3$ (Aldrich 99.9%), SrCO$_3$ (Aesar 99.994%), and Fe(NO$_3$)$_3$ (Aldrich ACS grade +98%) were each dissolved into the CA solution followed by 2 hr of stirring (200 rpm) at 60°C to minimize mixture variations. Ethylene glycol (EG) (Aldrich >99%) was then added to induce polyesterification as the solution was stirred for 7 hr at 90°C. All reagents were measured to achieve a La : Sr : Fe : CA : EG molar ratio of 0.75 : 0.25 : 1.0 : 10 : 40.\textsuperscript{69} The resulting dark red viscous gel (Figure 3a) was immediately charred at 450°C (25°C/min) for 2 hr. The solidified residue (Figure 3b) was crushed into powder and further calcined in air at 950°C (25°C/min) for 6 hr to finalize LSF crystallization (Figure 3c).

Figure 3. Perovskite synthesis stages. a) the red viscous gel following polyesterification, b) the solidified residue after charring, and c) the final perovskite powder after calcination at 950 °C
The resulting catalyst was then combined with CeO₂, ZrO₂, Al₂O₃ (Sigma-Aldrich puriss corundum), SiO₂ (Sigma-Aldrich purum quartz), TiO₂ (Alfa Aesar 99.5% rutile) 25% by mass. CeO₂ and ZrO₂ in particular were acquired by thermolysis of Ce(NO₃)₃ (Alfa Aesar 99.5%) and ZrO(NO₃)₂ respectively at 600 °C. Black silicon carbide 70 grit (Panadyne Abrasives) was also included as a support and but was first subjected to thermal pretreatment at 1000°C for 2 hr to achieve crystalline phases that would remain stable throughout high-temperature TPO-CO₂ experiments. LSF and the aforementioned materials were grinded together by hand in a mortar and pestle for about 15 min and then heated in air at 950°C for 10 hr to achieve aggregation of constituents.

3.2 Reaction Experiments

Mass spectrometry is a laboratory technique capable of detecting gases during a reaction. Relevant molecules such as H₂, H₂O, CO₂, and CO are ionized before fragmentation species are sorted based on mass-to-charge ratios. A Faraday detector at its highest accuracy was used for all experiments. A MKS Cirrus mass spectrometer was used to monitor H₂O and CO production by perovskites in a variety of experiments. This system was preceded by a Alicat mass flow controller manifold that consisted of ultra-high purity gases supplied by Airgas along with a Thermo Scientific furnace. The central line consisted of He, the carrier gas, and was joined by those of various others gases that were required for this study. Mixed gas flows were directed into a quartz U-tube microreactor that was positioned in the center of the furnace before entering the mass spectrometer. For every experiment, the total flow rate was maintained at 50 sccm while the microreactor consisted of about 75 mg of sample positioned between pieces of inert quartz wool. An additional piece was added to the subsequent side for filtering volatile oxides may result from perovskite decomposition. The entire experiment set up is shown in Figure 4.
3.2.1 Temperature-programmed Reduction (TPR)

Temperature-programmed reduction (TPR) experiments were conducted to assay the reducibility of each sample using H₂ as a reducing agent. The He signal was permitted to stabilize for about 15 min at ambient temperature before adjusting the flow to 10% H₂ in He (v/v). The temperature was then increased to 950°C (10 °C/min) and held constant until the m/z = 18 signal, representing H₂O, was steady. Juxtaposed TPR profiles revealed a generalized peak reduction temperature for the material set.

3.2.2 Temperature-programmed Oxidation with CO₂ (TPO-CO₂)

For temperature-programmed oxidations (TPO-CO₂), each sample was heated under He flow to the desired reduction temperature. Once the He signal stabilized after about 15 min, 10% H₂ in He (v/v) was flowed for 30 min to reduce the perovskite phase and create oxygen vacancies, the active sites for CO₂ conversion. The oxygen-deficient material was allowed to cool naturally under He to about 100°C to maintain these vacancies. Each sample was then exposed to a 10% CO₂ in He (v/v) flow and heated to 950°C (10 °C/min). and CO generation
was represented by peak formation in the m/z = 28 signal. Quantitative analysis of the resulting data followed procedures previously described.12

3.2.3 Reverse Water-Gas Shift Chemical Looping (RWGS-CL)

Several samples were tested in eight consecutive isothermal cycles of RWGS-CL. These experiments were conducted to prepare samples for microscopy and to quantify production yields and rates of select samples. Following He signal stabilization at the chosen reduction temperature, the process began with a 20 min period of 10% H₂ in He (v/v) to instigate oxygen vacancy formation. He was flowed again for 20 min before changing the flow to 10% CO₂ in He (v/v) to re-oxidize the perovskite material and generate CO. H₂O and CO production was quantified for each cycle using the same procedures for TPO-CO₂ to test reaction capability and durability over elongated use.

3.3 Characterization

3.3.1 X-ray Diffraction (XRD)

X-ray diffraction was used to probe fresh and post-experimental samples. Main interests included changes in crystalline structure or secondary phases concomitant with solid-state reactions. A Bruker X-Ray Diffractometer with Cu Kα (λ = 0.154 nm) provided patterns at ambient conditions from 20 to 80° (2θ°) with a step size of 0.0102 (2θ°) and 1.2 seconds per step. Raw data and literature patterns from X’Pert Highscore Plus software were juxtaposed for reference when calculating the LSF orthorhombic lattice parameters of each sample. This assay consisted of indexing using Bragg’s Law and a unique geometrical formula relating interplanar distance to lattice parameters,71 represented as Equations 2 and 3. The exact lattice parameters of LSF in this study were calculated by minimizing the squared error. The orthorhombic cell volume was calculated using Equation 4. Library reference codes are provided where necessary.
\[ 2d \sin(\theta) = n\lambda \ldots \ldots (2) \]

\[ \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \ldots \ldots (3) \]

\[ V = abc \ldots \ldots (4) \]

Interplanar distance between atomic planes is represented by \( d \) while \( \theta \) denotes the angle, in degrees, at which a facet is probed. As aforementioned, the X-ray wavelength, \( \lambda \), is maintained constant at 1.54 nm. The \( n \) term is a positive integer assumed to be 1. Individual miller index components are represented by \( h, k, \) and \( l \) while \( a, b, a \) represent lattice parameters. \( V \) is the final orthorhombic cell volume.

A Scherrer analysis was also done with a shape factor of 0.9, an acceptable approximation for near spherical particles,\(^7\) across the width of the primary LSF (020) diffraction line. Using Equation 5, this permitted the comparison of crystalline sizes and surface areas of supported and unsupported LSF.

\[ \tau = \frac{K\lambda}{\beta \cos(\theta)} \ldots \ldots (5) \]

\( K \) represents the 0.9 shape factor. Similar to the previous equations, \( \lambda \) is the X-ray wavelength and \( \theta \) is the angle of interest. \( \beta \) represents angle width of the (020) diffraction line at full width half maximum. These variables result in \( \tau \), the crystallite size in Å.

### 3.3.2 Microscopy

A Field Emission Scanning electron microscope (SEM), accompanied with energy-dispersive spectroscopy (EDS), was used for precise imaging and elemental analysis of the post-calcination and post-experiment perovskite phases. The Hitachi S800 SEM with EDAX attachment was operated with 2 nm resolution at a working distance of 5 mm. High resolution transmission electron microscopy (HRTEM) was carried out using a Tecnai F20 microscope.
operated at 200 kV. Using a line resolution of 0.102 nm and 26° diffraction angle, the dominant LSF facet was revealed along with that of the supporting material.

3.3.3 Physisorption

Specific surface areas were obtained using Quantachrome Autosorb IQ analyzer. After degassing at 300 °C. Adsorption-desorption isotherms were obtained by measuring volume adsorbed by the sample at a set interval of partial pressures (P/P₀) using N₂ as the adsorbate at 77 K. Specific surface area was calculated using Brunauer-Emmet-Teller (BET) method using adsorption data points inside the P/P₀ range of 0.05 to 0.3.

3.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy (attenuated total reflectance (ATR)) was performed on all the perovskite-support samples in the Nicolet IS50 instrument from Thermo-Scientific. All the spectra comprised of 50 scans, taken at a resolution of 0.241 cm⁻¹ having a data spacing of 0.482 cm⁻¹.

3.3.5 Density Functional Theory (DFT)

The oxygen vacancy formation energy of the perovskite oxide and the metal oxide supports (CeO₂, TiO₂, SiO₂, ZrO₂, and Al₂O₃) was obtained through DFT-based calculations using Vienna ab initio Simulation Package (VASP – 5.3.3). Plane wave basis sets were considered throughout the calculations along with generalized gradient approach (GGA) for electron densities. Perdew-Burke-Ernzerhof (PBE) variant of exchange correlation was used. A consistent energy cut off of 600 eV was maintained throughout the calculations. The crystal structures of these materials were based on the experimental results as obtained from XRD patterns. The atomic distribution within the crystal lattice was based on the minimum energy configuration as per DFT-calculations. Pure bulk LSF perovskite oxide was modeled by a 2×2×2
supercell comprising of 40 atoms. Monkhorst Pack grid based 4×4×4 k-point mesh was used for the calculations of LSF. For the metal oxides, the k-point mesh was generated according the supercell size in order to maintain a similar k-point grid spacing. The convergence criterion of 0.001 eV/atom was used for the ionic relaxations. Once the initial ground state configurations of these materials were obtained through varying cell volume calculations, these were used for subsequent oxygen vacancy calculations. Oxygen atoms were removed to create a consistent oxygen vacancy extent (δ) of 0.125. The resulting oxygen vacancy formation energies as calculated according to the following equation were used to gain insights on the materials’ tendency to form oxygen vacancies.

$$E_{\text{vac}} = E_{\text{MO}(x-\delta)} + \delta \times \frac{n}{2} E_{O_2} - E_{\text{MO}_x} \quad \ldots \ldots (6)$$

$E_{\text{MO}_x}$ is the total energy of the pure stoichiometric materials (LSF and the metal oxides), $n$ is the number of unit cells in a one supercell, while $E_{\text{MO}(x-\delta)}$ is that of the oxygen vacant material and $E_{O_2}$ is the molecular energy of oxygen. The correction factor for oxygen over-binding error (for PBE functionals) by Wang et al. was considered as well.\textsuperscript{73}
CHAPTER 4: SUPPORT SCREENING RESULTS

4.1 Temperature-programmed Experiments

Successful RWGS-CL is contingent on generation of oxygen vacant active sites throughout the perovskite surface and bulk during the reduction step. These active sites are then repurposed for CO₂ to CO conversion in the subsequent oxidation step. Under H₂ flow and increasing temperature, H₂O formation indicates the generation of oxygen vacancies by removal of oxygen installed in the bulk and strongly adsorbed to the surface. Consecutive disintegration of the perovskite phase into simpler, unary and oxides is also observed. These reactions are depicted in Figure 5a by H₂O formation (m/z = 18) below 700 °C and over 750 °C respectively. For the majority of samples, the perovskite reduction temperature remains the same as the unsupported control (550 °C). Others, notably LSF₂₅/SiO₂ and LSF₂₅/TiO₂, exhibit higher peak

![Image](image_url)

**Figure 5.** Support screening reaction spectra. a) Temperature-programmed reductions with H₂ and b) temperature-programmed oxidations with CO₂ for LSF and affiliated composites.
temperatures around 600 °C. This phenomenon may be related to the formation of cationic vacancies during the sintering of LSF and SiO2. A previous study done by Maiti et. al delineated the increase in oxygen vacancy formation energy as the extent of vacancies in the lattice increases.74 Therefore, the slight but permanent removal of Fe and La from the perovskite lattice results in the formation of FeSiO3 and La2SiO5 respectively along with the shift in the perovskite reduction temperature.

Table 1. Quantified TPR and TPO-CO2 results for support screening.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H2O yield (μmol/gLSF)</th>
<th>CO yield (μmol/gLSF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSF</td>
<td>2210</td>
<td>690</td>
</tr>
<tr>
<td>LSF25/CeO2</td>
<td>1720</td>
<td>1100</td>
</tr>
<tr>
<td>LSF25/ZrO2</td>
<td>2040</td>
<td>1350</td>
</tr>
<tr>
<td>LSF25/Al2O3</td>
<td>2920</td>
<td>490</td>
</tr>
<tr>
<td>LSF25/SiO2</td>
<td>3690</td>
<td>1700</td>
</tr>
<tr>
<td>LSF25/TiO2</td>
<td>2180</td>
<td>850</td>
</tr>
</tbody>
</table>

Total H2O and CO yields (Table 1) were obtained from numerical integration. Most notably, LSF25/SiO2 resulted in the highest H2O and CO yields of 3690 and 1700 μmol/gLSF respectively. This significant 150% increase in CO production by LSF25/SiO2 even surpassed those of LSF25/CeO2 and LSF25/ZrO2. Due to the similarity between LSF and LSF25/CeO2 TPR profiles below 600 °C along with the CeO2 reduction peak witnessed at about 800 °C, it was highly unlikely that this support participated in the reactions. This catalytic hindering may be alleviated by using higher redox temperatures, which contradicts the incentives for feasible CO2 utilization due to a higher energy input. While TiO2 appeared to have no consequential effect on
the reaction, the use of Al₂O₃ is evidently detrimental to the redox properties of LSF given the 29% decrease in CO production. Nonetheless, LSF₂₅/SiO₂ remains the top composite candidate for perovskite-based syngas production.

4.2 XRD

XRD patterns were examined for changes in crystalline phases and the presence of secondary phases due to solid state reactions between the perovskite and support. As illustrated by Figure 6, the overall stability of orthorhombic LSF (Ref. Code 00-035-1480) on each support is assured while (020) remains the dominant perovskite facet throughout the sample lifetime from particle sintering to the conclusion of TPO-CO₂ experiments. The crystal structures of CeO₂, ZrO₂, Al₂O₃, SiO₂, and Al₂O₃ were cubic, monolithic, hexagonal, hexagonal, and tetragonal respectively. Close examination revealed the minute presence of orthorhombic FeSiO₃ (Ref. Code 01-076-0886) and monoclinic La₂SiO₅ (Ref. Code 00-040-0234) at the LSF:SiO₂ interface following composite sintering at high temperatures. These phases have been witnessed before in iron oxide:silica composites yet are not expected to exercise notable presences as reflected by current difficulties in synthesizing bulk single-phase quantities of FeSiO₃. In addition, cubic Fe₂.₅Ti₀.₅O₄ (Ref. Code 00-051-1587) was detected at 35.6 2θ as a result from solid state reactions during either the reduction or oxidation of LSF. These phases do not initially appear detrimental to the catalytic activity but may pose consequences of interest during the manufacturing of large-scale pellets and monoliths.

By utilizing the geometrical characteristics of the (020) diffraction line, LSF crystallite size was estimated before and after 8 cycles of RWGS-CL through a Scherrer analysis (Table 2). These values demonstrate the effect of each support on perovskite particles. By utilizing silica, the average LSF crystallite size decreases by 21% as opposed to an increase with every other
support. These results compliment the expected increase in catalytic performance predicted with Equation 1. Although the majority of the supports resulted in further sintering of the perovskite particles, they each induced strain on the perovskite lattice and enlarged the LSF cell volume.

**Figure 6.** Support screening XRD. Diffraction pattern of a) LSF and b) a close inspection of identified secondary phases witnessed in fresh LSF25/SiO2 (red, top) and post TPO-CO2 LSF25/TiO2 (green, bottom). Post heat treatment at 950 °C and post TPO-CO2 diffraction patterns of c) LSF25/CeO2, d) LSF25/ZrO2, e) LSF25/Al2O3 (with corundum), f) LSF25/SiO2 (with quartz), and g) LSF25/TiO2 (with rutile) which all demonstrate structural stability throughout material lifetime.
This slight expansion of interplanar distance between atoms decreases oxygen vacancy formation energy, making it easier for more oxygen to desorb from the lattice.\textsuperscript{39}

**Table 2.** LSF cell volume, secondary phases identified in perovskite composites, and crystallite size estimations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>LSF orthorhombic cell volume (Å(^3))</th>
<th>Post–calcination secondary phases</th>
<th>Post - TPO-CO(_2) secondary phases</th>
<th>Post - calcination LSF crystallite size (Å(^3)) (^a)</th>
<th>Post – 8 cycles RWGS-CL (600 °C) LSF crystallite size (Å(^3)) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSF</td>
<td>237.9</td>
<td>-</td>
<td>-</td>
<td>370</td>
<td>351</td>
</tr>
<tr>
<td>LSF(_{25})/CeO(_2)</td>
<td>240.5</td>
<td>-</td>
<td>-</td>
<td>384</td>
<td>526</td>
</tr>
<tr>
<td>LSF(_{25})/ZrO(_2)</td>
<td>239.8</td>
<td>-</td>
<td>-</td>
<td>367</td>
<td>448</td>
</tr>
<tr>
<td>LSF(_{25})/Al(_2)O(_3)</td>
<td>238.7</td>
<td>-</td>
<td>-</td>
<td>367</td>
<td>475</td>
</tr>
<tr>
<td>LSF(_{25})/SiO(_2)</td>
<td>238.5</td>
<td>FeSiO(_3), La(_2)SiO(_5)</td>
<td>FeSiO(_3), La(_2)SiO(_5)</td>
<td>351</td>
<td>278</td>
</tr>
<tr>
<td>LSF(_{25})/TiO(_2)</td>
<td>239.6</td>
<td>-</td>
<td>Fe(<em>{2.5})Ti(</em>{0.5})O(_4)</td>
<td>367</td>
<td>448</td>
</tr>
</tbody>
</table>

\(^a\) Calculated by Scherrer analysis of XRD data with a shape factor of 0.9

**4.3 DFT**

Oxygen vacancy formation energies (E\(_{\text{vac}}\)) serve as descriptors for the ability of an oxide material to convert CO\(_2\).\textsuperscript{14} If a material exhibits a high E\(_{\text{vac}}\), it will be unwilling to form vacancies, and therefore CO\(_2\) conversion active sites, at low RWGS-CL operating temperatures. On the other hand, a low E\(_{\text{vac}}\) will encourage numerous vacancies that are unlikely to be
replenished in an oxidation reaction. With an $E_{\text{vac}}$ of about 3.4 eV, calculated with Equation 6, LSF resides in the optimal regime for notable catalytic activity. Each of the supporting materials however, including CeO$_2$, possess $E_{\text{vac}}$ values greater than 4.0 eV as shown in Figure 7a. These results suggest that each support remained inactive during TPO-CO$_2$ experiments and that the perovskite was the only phase to produce vacancies after reduction at 600 °C. Given that popular redox materials such as CeO$_2$ and ZrO$_2$ themselves do not participate in the reaction, utilizing them in low temperature RWGS-CL would contradict the investigation for a more economically friendly and kinetically enhanced composite.

![Graph](image_url)

**Figure 7.** DFT calculations. a) Oxygen vacancy formation energies of LSF, supporting materials, and detected secondary phases. $\delta$ represents the extent of oxygen nonstoichiometry for each support. b) Variation of oxygen vacancy formation energy with lattice strain.

Secondary phases identified through XRD analysis share unidentified roles in CO$_2$ conversion. Figure 7a also includes DFT-calculated $E_{\text{vac}}$ values for FeSiO$_3$, La$_2$SiO$_5$, and Fe$_{2.5}$Ti$_{0.5}$O$_4$ to provide insight regarding their own abilities to form oxygen vacancies at the composite interface. In regards to LSF$_{25}$/SiO$_2$, FeSiO$_3$ possesses an $E_{\text{vac}}$ of about 5.3 eV while La$_2$SiO$_5$ resides in the much higher energy regime with an $E_{\text{vac}}$ of about 7.0 eV. Given that CeO$_2$, the oxide with the lowest $E_{\text{vac}}$ aside from LSF, did not form its own vacancies until about 700 °C
in the TPR experiments, it remains highly improbable that these secondary phases are active participants at these experimental temperatures. The same conclusion was reached for Fe$_{2.5}$Ti$_{0.5}$O$_4$ due to its relatively high $E_{\text{vac}}$ of about 6.0 eV.

Moreover, the increased cell volume of the LSF perovskite indicates the presence of a strained perovskite structure. As shown in Figure 7b, an expanded crystal lattice enables oxygen vacancy formation in LSF. Thus, these strained interfaces, suggested by cell volume calculations in Table 1, were found to promote oxygen vacancy creation and subsequently enhance CO$_2$ conversion. This is apparently associated with formation of secondary phases (FeSiO$_3$, La$_2$SiO$_5$, Fe$_{2.5}$Ti$_{0.5}$O$_4$) at the LSF:support interface. These secondary phases act as catalyst poisons, reducing the composites’ ability to accommodate oxygen vacancies and CO generation capacity. They are also believed to be the underlying cause of an increase in $E_{\text{vac}}$ due to additional cationic vacancies,$^7$ and therefore the reduction temperature observed in the TPR experiments; most notably for SiO$_2$ and TiO$_2$.

4.4 Microscopy

Detailed images of each composite following 8 cycles of RWGS-CL are arranged in Figure 8. TEM revealed a consistent interplanar spacing of 0.27 Å for the LSF (020) facet when combined with each support. Minor amounts of strain resulted at each perovskite:support site of contact due to both interfacial forces and cationic migration during solid state reactions at high temperatures. The interplanar spacings of the LSF (020) facet on CeO$_2$, ZrO$_2$, Al$_2$O$_3$, SiO$_2$, and TiO$_2$ are 2.86, 2.74, 2.74, 2.78, and 2.70 Å respectively. The repercussions of this expanded lattice include decreased oxygen vacancy formation energy by perovskites and increased cell volume in accordance with XRD data.
The SEM images however provided valuable insight to changes in CO\textsubscript{2} conversion by LSF. The CeO\textsubscript{2}, ZrO\textsubscript{2}, and SiO\textsubscript{2} supports form small particles which correspond to the high CO yields in the TPO-CO\textsubscript{2} experiments. SiO\textsubscript{2} in particular demonstrated the greatest reduction in perovskite particle size, especially in comparison to the abundant alternatives. Not only did LSF retain its size, but the hexagonal Al\textsubscript{2}O\textsubscript{3} plates and TiO\textsubscript{2} growth appeared to mask the perovskite

**Figure 8.** Support screening microscopy. SEM and TEM images respectively of a-b) LSF\textsubscript{25}/CeO\textsubscript{2}, c-d) LSF\textsubscript{25}/ZrO\textsubscript{2}, e-f) LSF\textsubscript{25}/Al\textsubscript{2}O\textsubscript{3}, g-h) LSF\textsubscript{25}/SiO\textsubscript{2}, and i-j) LSF\textsubscript{25}/TiO\textsubscript{2} all after 8 cycles of the RWGS-CL process at 600 °C
as seen in Figure 8e and 8i respectively. This encapsulation explains the absence of kinetic enhancement when using Al₂O₃ and TiO₂ as supports with physical barriers hindering CO₂ adsorption to the perovskite surface.
CHAPTER 5: A SiO₂ FOUNDATION

Given the results from previous chapter, it is thus imperative to narrow the focus to SiO₂ and the reasoning behind its capability. The LSF perovskite and SiO₂ support were combined into a composite powder as a novel candidate material for efficient CO₂ conversion in RWGS-CL. Black silicon carbide, a popular non-oxide support76-77, was also tested as a non-oxide alternative. Different perovskite:silica mass ratios are included, resulting in varying magnitudes of secondary phase formation and surface wetting. Sample nomenclature is displayed in Table 3. Structural stability and long-term activity of top performing materials are demonstrated in 8 cycles of RWGS-CL. DFT was used to calculate the oxygen vacancy formation energies of each oxide present in the composite, thus measuring their contribution potentials to redox chemical looping. Crystallographic studies confirmed the structural stability of LSF and SiO₂ in recurrent applications and reveal an interfacial wettability effect that reverses sintering of the active phase as confirmed by visual examination through microscopy. In this chapter, the role of silica in enhancing the CO₂ conversion performance by perovskite-type oxides was unraveled.

5.1 XRD

XRD patterns of LSF and SiO₂ along with that of the LSF₂₅/SiO₂ amalgam (25% by weight of LSF) are reported in Figure 9a. The composite sample indicates the dominant presence of pure phase silica (hexagonal quartz [Ref. Code: 00-046-1045]) and LSF phases (orthorhombic structure [Ref. Code: 00-035-1480]). Closer inspection of the 25-40 2θ° (Figure 9b) range reveal formation of secondary phases FeSiO₃ and La₂SiO₅ in minor amounts. These became more prominent after H₂-reduction and subsequent temperature-programmed oxidation under CO₂
Table 3. Sample nomenclature for perovskite composites synthesized and tested in temperature-programmed experiments. The orthorhombic lattice parameters of LSF in fresh samples are calculated using Ref. Code: 00-035-1480 from the X’Pert Highscore Plus data library. The BET specific surface areas (SSA) are also included for certain samples.

<table>
<thead>
<tr>
<th>LSF/support (X% w/w)</th>
<th>Sample</th>
<th>LSF orthorhombic lattice parameters of fresh samples (Å)</th>
<th>LSF Cell Volume (Å³)</th>
<th>FeSiO₃ XRD R.I. a</th>
<th>La₂SiO₅ XRD R.I. a</th>
<th>BET SSA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>LSF</td>
<td>5.510 5.540 7.792</td>
<td>237.93</td>
<td>-</td>
<td>-</td>
<td>1.9</td>
</tr>
<tr>
<td>25% Quartz (silica)</td>
<td>LSF₂₅/SiO₂</td>
<td>5.518 5.532 7.813</td>
<td>238.53</td>
<td>1.35 %</td>
<td>0.76 %</td>
<td>1.1 c</td>
</tr>
<tr>
<td>50% Quartz (silica)</td>
<td>LSF₅₀/SiO₂</td>
<td>5.522 5.537 7.826</td>
<td>239.33</td>
<td>1.74 %</td>
<td>0.72 %</td>
<td>-</td>
</tr>
<tr>
<td>75% Quartz (silica)</td>
<td>LSF₇₅/SiO₂</td>
<td>5.532 5.526 7.825</td>
<td>239.30</td>
<td>0.71 %</td>
<td>0.50 %</td>
<td>-</td>
</tr>
<tr>
<td>Black Silicon carbide</td>
<td>LSF₂₅/SiC</td>
<td>5.527 5.531 7.822</td>
<td>239.18</td>
<td>n. d. b</td>
<td>n. d. b</td>
<td>-</td>
</tr>
</tbody>
</table>

a Relative intensities of secondary phase diffraction lines with respect to the dominant crystalline Miller index
b Nothing detected
c Quartz SSA (after heat treatment at 950 °C): 1.7 m² g⁻¹

(TPO-CO₂) experiments. The LSF-SiO₂ interface region of the composite material is the most vulnerable to solid state reactions. Yet FeSiO₃ and La₂SiO₅ are present as traces and exhibit no adverse effects on the long-term stability of the composite. SiC is used as non-oxygen based reference support to test the effect of Si on stability, secondary phase formation, and CO₂ conversion performance of perovskite:SiC mixtures. The diffraction pattern of the SiC-based
amalgam illustrates absence of any secondary phases, even after H2-reduction and subsequent TPO-CO2, as is evident from Figure 9c and Figure 9d.

The presence of secondary phases (FeSiO3 and La2SiO5) in the LSF/SiO2 composites can be consequential to perovskite grain characteristics and CO2 conversion performance. Therefore, different ratios of LSF and SiO2 are tested, resulting in varying concentrations of these phases as evident from the relative peak intensities (R.I) at 28.0, 30.6, and 35.5 2θ° (Figure 9e). The R.I. of the primary diffraction pattern affiliated with orthorhombic FeSiO3 (Ref. Code: 01-076-0886) changes from 1.35% to 1.74% to 0.71% with increasing LSF content (25% to 75%) as indicated in Table 3. The (-202) XRD peak of monoclinic La2SiO5 (Ref. Code: 00-040-0234) however,
remains relatively constant between 0.76% and 0.50% possibly due to high activation energies for La ion migration in perovskites with short O - Fe – O and O – O distances in the lattice.\textsuperscript{78} Silica phase transition from quartz to tridymite, a typically lethargic transformation even with alkali promoters,\textsuperscript{79} was negligible. Overall, apart from the minor formation of secondary phases, which remain stable over several CO$_2$ conversion cycles, orthorhombic LSF and hexagonal SiO$_2$ phases maintain dominancy. Fourier transform infrared spectroscopy (FTIR) results, shown in Figure 9f, confirms a consistent trend of decreasing silica peak at 1080 cm$^{-1}$ with increasing LSF in the composites. A notable trend observed in the LSF:SiO$_2$ amalgams is the change in orthorhombic cell volume with different ratios as reported in Table 3. This pattern is complementary with the formation of secondary phases as shown in Fig 9e. The generation of secondary phases along with surface wetness results in interfacial strain and a slight increase in the cell volume as previously witnessed in interfacial layers between SiO$_2$ and complex Sr oxides.\textsuperscript{80} Calculation of the LSF crystallite size via Scherrer analysis reveals the role of supports in restricting the perovskites from sintering during RWGS-CL experiments as documented in Table 3. This particular role of supports in tuning the LSF crystallite size and strain is fundamental for exploring the underlying mechanism of CO$_2$ conversion over these composites.

\textbf{5.2 Temperature-programmed Experiments}

Sustainable chemical looping with perovskite oxides requires the formation of oxygen deficient phases without decomposition to disparate species. The TPR profiles (Figure 10a) suggest 600 °C is still an adequate temperature for achieving numerous vacancies prior to CO$_2$ conversion while retaining material intactness. CO formation is indicated by the m/z = 28 peak as displayed in Figure 10b. Complementary to TPR experiments, CO generates over the LSF composites at about 50 °C higher than over pure LSF. Quantifications in Table 4 shows that H$_2$O
production surpasses that of CO due to a few crucial factors. The entirety of perovskite surface oxygen, for instance, contributes to immense H₂O formation during first-time reduction. Yet replenishment remains highly implausible due to the gradual buildup of kinetic stagnation during CO₂ conversion. Moreover, the activity of oxygen vacant sites towards CO formation is closely related to the net number of oxygen vacancies present at any time. CO₂ adsorption strength over a perovskite oxide increases with the extent of surface oxygen vacancies, reflecting higher probability of conversion.¹⁰ Thus, with progressive refilling of oxygen vacant sites via CO₂

**Figure 10.** Temperature-programmed experimental data for H₂O and CO production by LSF in Si-based composites. a) TPR spectrums show 600 °C is an adequate temperature for partial reduction of the materials. b) TPO-CO₂ reveals the changes in CO production with each support and mass ratio. c) H₂O and CO quantifications.
conversion to CO comes a gradual stagnation of surface exchange kinetics resulting in less CO production than that of H2O in the first cycle.

Capacities of 2.21 mmol H2O gLSF⁻¹ and 0.69 mmol CO gLSF⁻¹ are produced during the control experiment with unsupported LSF. While utilization of SiO2 as a supporting material with 25% LSF results in a 67% increase in H2O formation capacity at 3.69 mmol gLSF⁻¹, CO production experiences a greater magnitude of improvement of 150% for a total yield of 1.70 mmol gLSF⁻¹. LSF25/SiC also exhibits improved H2O (2.91 mmol gLSF⁻¹) and CO (1.20 mmol gLSF⁻¹) formation. The XRD patterns of LSF:SiO2 amalgams after the experiment show the presence of pure orthorhombic LSF and hexagonal SiO2 phases along with minor concentrations of secondary phases of FeSiO3 and La2SiO5. Density functional theory (DFT) based calculations from the previous chapter revealed that the LSF phase is the most favorable substrate to accommodate oxygen vacancies while all other phases (SiO2, FeSiO3 and La2SiO5) demand a higher energy input to create oxygen vacancies (Figure 7a). CO2 conversion results for LSF25/SiC validate this hypothesis, for this composite demonstrates enhanced H2O and CO formation without consisting of SiO2 or secondary phases. Thus, the reason for better CO2 conversion is attributed to more surface area of LSF exposed for gas interactions. This is

<table>
<thead>
<tr>
<th>Sample</th>
<th>H2O yield (μmol/gLSF)</th>
<th>CO yield (μmol/gLSF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSF</td>
<td>2210</td>
<td>690</td>
</tr>
<tr>
<td>LSF25/SiO2</td>
<td>3690</td>
<td>1700</td>
</tr>
<tr>
<td>LSF25/SiC</td>
<td>2910</td>
<td>1200</td>
</tr>
<tr>
<td>LSF50/SiO2</td>
<td>1250</td>
<td>380</td>
</tr>
<tr>
<td>LSF75/SiO2</td>
<td>1540</td>
<td>530</td>
</tr>
</tbody>
</table>

**Table 4.** Quantified TPR and TPO-CO2 results for LSF with Si-based supports.
corroborated by the decreased crystallite size of LSF in the composites compared to its pure phase catalyst.

Moreover, the increased cell volume of the LSF perovskite indicates the presence of a strained perovskite structure. As shown in Figure 7b, an expanded crystal lattice enables oxygen vacancy formation in LSF. Thus, these strained interfaces, suggested by cell volume calculations in Table 3, were found to promote oxygen vacancy creation and subsequently enhance CO₂ conversion. SiO₂ shows greater promise than SiC, as it manifests a wettability effect on the perovskite particles. Silica was previously shown to demonstrate affinity for transition metals and is capable of both reducing particle sizes⁸¹ and contact angles.⁸² However, there exists an optimum LSF:SiO₂ ratio as is evident from Figure 10b whereby LSF₅₀/SiO₂ and LSF₇₅/SiO₂ shows poor CO₂ conversion performance. This is associated with increased formation of FeSiO₃ and La₄SiO₅ at the LSF:SiO₂ interface. These secondary phases act as catalyst poisons, reducing the composites’ ability to accommodate oxygen vacancies and CO generation capacity. As aforementioned, they are also believed to be the underlying cause of an increase in E_vac due to additional cationic vacancies,⁷⁴ and therefore the reduction temperature observed in the TPR experiments. LSF₂₅/SiO₂ however, simultaneously demonstrates minimal secondary phase formation and maximum wettability making the material a suitable candidate for chemical looping.

5.3 RWGS-CL

The stability and activity of the materials are demonstrated across eight consecutive RWGS-CL cycles (Figure 11). LSF₂₅/SiO₂ achieves the highest H₂O and CO yields per perovskite mass basis. By the concluding cycle, the results for LSF₂₅/SiO₂ settle at about 3.10
mmol H₂O g₇SF⁻¹ per cycle and 2.60 mmol CO g₇SF⁻¹ per cycle. Overall, LSF₂₅/SiO₂ exhibits 8% and 12% decreases in H₂O and CO production, respectively, after 8 cycles. Unsupported LSF shows no decrease in H₂O production, which stabilizes at about 1.10 mmol H₂O g₇SF⁻¹, or CO production, which remain steady around 0.90 mmol CO g₇SF⁻¹. LSF₂₅/SiC demonstrates better performance than pure LSF but fell short of LSF₂₅/SiO₂. The extent of oxygen vacancy formation, δ (in ABO₃₋δ), for LSF is calculated to be 0.26. That of LSF₂₅/SiO₂ and LSF₂₅/SiC are 0.72 and 0.40 respectively. The CO production rate for pure LSF stabilizes over time at 0.93
mmol CO g\textsubscript{LSF}\textsuperscript{-1} min\textsuperscript{-1} in comparison to 0.80 and 0.38 for LSF\textsubscript{25}/SiO\textsubscript{2} and LSF/SiC respectively, restrictions potentially imputed to transport limitations exhibited by the supports.

**5.4 Microscopy**

Perhaps the greatest significance of the chemical looping data is attributed to the escalation in the H\textsubscript{2}O production rate using SiO\textsubscript{2}. As aforementioned, accelerated oxygen vacancy formation is concomitant with smaller average perovskite particle radii\textsuperscript{34, 36}. It is also possible that water spillover to the silica support may enable faster reduction rates, but this effect is anticipated to be minimal in comparison due to the limited water adsorption at these elevated temperatures. Crystallite size reduction, resulting in increased surface area of LSF, is established to be the primary governing criteria for enhanced CO\textsubscript{2} conversion by supported perovskites. Although the average crystallite size of unsupported LSF remains unchanged throughout the 8 cycles, that of the supported samples decreases (Table 5). More in particular, LSF supported on SiO\textsubscript{2} results in a 55% decrease in crystallite size and compliments the loss of bulk oxygen during the course of particle separation. This notable change is illustrated and confirmed by transmission electron microscopy (TEM; Figure 12). While the size of fresh LSF particles, unsupported and supported, remain in the micron threshold, small clusters of LSF nanoparticles formed during RWGS-CL. These nanoparticles are essentially a source of active sites for oxygen vacancy formation and CO\textsubscript{2} conversion. These nanoparticles are not seen to consist of any metallic (Fe, Sr or La) phases nor are they comprised of any binary oxides (Fe oxides, Sr oxides and La oxides). As is evident from figure 6h, the high-resolution image of the nanoparticle structure reveals the (020) crystal facet that matches that of the fresh samples (Figure 12c) and post reaction samples (Figure 12e). Moderate interaction between LSF nanoparticles and silica rafts restricts their agglomeration, thereby ensuring a surfeit of active sites for CO\textsubscript{2} conversion.
Table 5. Crystallite size estimations by Scherrer analysis for fresh and post RWGS-CL experiment samples. Spherical particles are assumed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fresh perovskite crystallite size (Å)</th>
<th>Post RWGS-CL perovskite crystallite size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSF</td>
<td>350.9</td>
<td>350.9</td>
</tr>
<tr>
<td>LSF_{25}/SiO₂</td>
<td>351.2</td>
<td>269.1</td>
</tr>
<tr>
<td>LSF_{25}/SiC</td>
<td>384.6</td>
<td>336.3</td>
</tr>
</tbody>
</table>

Although silicon carbide demonstrates the same effect according to the Scherrer analysis, it is assured that the particle size reduction magnitude remains much greater when utilizing silica to support perovskite-oxides. Because the black silicon carbide was not reduced, but rather pretreated at 1000 °C in air, there is expected to be a notable presence of oxygen due to a partially oxidized surface^{83-84} and iron oxide impurities. Anton et.al concluded that interactions between a support and active phase are much stronger when using a bulk oxide as opposed to an inert support consisting of a few surface oxide layers.^{85} Perovskite segregation likely occurred during the second reduction step when surface oxygen was previously removed and the increase in H₂O was noted. The high presence of metallic B-site metals on the perovskite surface during reduction^{86-87} is perhaps the driving force for particle size reduction on silica due to the spontaneity of metals to diffuse into the top layers of the oxide bulk. The kinetic inclination of these ions perhaps pulls apart the large particles to form nanoparticles. This phenomenon is accompanied by the strong surface energy of the reduced perovskite, i.e., oxygen vacant perovskites show strong affinity for species with high oxygen content, such as CO₂ or even potentially SiO₂ regardless of its inert behavior. This surface behavior was not observed in the post TPO-CO₂ samples where CO₂ flows over these samples up to 950 °C. It is thus evident that
perovskite particle aggregation is inevitable at high temperatures during synthesis and other STC processes, but may be reversed by subjection to the RWGS-CL process in the presence of appropriate supports at low thermochemical temperatures.

**Figure 12.** Microscopy of LSF on SiO$_2$. a) Visual schematic of LSF particle size modification by supporting materials during RWGS-CL. TEM images of LSF indicating b) particle size and c) interplanar spacing. Fresh LSF$_{25}$/SiO$_2$ d) interface and e) interplanar spacing. LSF$_{25}$/SiO$_2$ after 8 RWGS-CL cycles f-h) illustrating a significant decrease in LSF particle size and formation of nanoparticles.
CHAPTER 6: CONCLUSIONS AND FUTURE WORK

6.1 Main Contributions

This work demonstrated 200% enhancements for CO generation yields for RWGS-CL through the formation of composite materials. SiO₂, as opposed to all other supports tested, is identified as an appropriate supporting material for perovskite-type oxides, La₀.₇₅Sr₀.₂₅FeO₃ (LSF) in this case, due to its wetting influence, ability to reverse LSF particle aggregation resulting from calcination, and induction of lattice strain. Formation of inhibiting species (i.e., metal silicate phases, FeSiO₃ and La₂SiO₅) that may cause interfacial barriers are restricted by adjusting the perovskite:silica mass ratio and avoiding the high temperatures of other solar thermochemical processes. Long-term stability of the LSF:SiO₂ composite (25 wt% perovskite) is demonstrated over eight cycles of RWGS-CL. Perovskite reduction, the cycle limiting step, is significantly improved to a rate of 1.7 mmol H₂O g⁻¹ LSF⁻¹ min⁻¹ using the composite while CO generation rates remains stable at 0.8 mmol CO g⁻¹ LSF⁻¹ min⁻¹. This study presents a new materials platform towards enhanced reaction activity by oxygen deficient perovskite oxides and provides an avenue to increase earth abundancy of materials used in sustainable production of fuels and chemicals using CO₂ as a feedstock.

6.2 Future Work

Now that SiO₂ was identified as an efficient and abundant supporting material, future studies may allocate focus towards optimization of the supporting material. Referring back to Table 3, the surface area of the quartz was merely 1.10 m²/g. It may then be of utmost interest to study mesoporous forms of SiO₂ such as SBA-15 which has achieved a surface area of about 500
m²/g and a pore diameter of up to 30 nm.\textsuperscript{88} Scherrer analysis results suggest perovskite particle sizes ranging from about 27 to 53 nm; much too large for the SBA-15. Applying the same composite synthesis procedures would either result in pore clogging or limitation of perovskite supporting to the exterior support surface, leaving the pore network interior virtually untouched. This will require a material-based study that develops procedures for synthesizing perovskite oxides on mesoporous SiO₂. It is imperative to maintain high calcination temperatures required to ensure perovskite stability yet SBA-15 must be synthesized at low temperatures (< 600 °C) to maintain large pore sizes. Focus will be allocated towards the effects of combining perovskite and SBA-15 precursor gels or synthesizing one component completely before combining it with the other precursor gel. For instance, combining SBA-15 with the perovskite gel may allow the polymer complex to diffuse inside the pore network where it will reside during calcination. On the other hand, the perovskite powder should dissolve in the ethanol-based SBA-15 precursor solution and may potentially incorporate itself inside the pore network during the final heat treatment step. Synthesizing perovskites on SBA-15 is expected to result in the same phenomenon witnessed using simple quartz. However, a much greater surface area is expected to increase the amount of perovskite that may be combined with it. With quartz, a significant decrease in CO production was witnessed with perovskite mass percentages over 25%. While perhaps the quartz surface neared saturation by perovskites, SBA-15 may circumvent this issue with a higher magnitude of particle segregation and surface distribution.
REFERENCES

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