Lanthana-Doped Ceria as Active Support for Oxygen Carriers in Chemical Looping Combustion

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Abstract:

The redox properties and oxygen buffering capacity of reducible oxides, such as ceria, make them interesting support materials for oxygen carriers in chemical looping combustion (CLC), an emerging clean combustion technology. However, the effectiveness of reducible oxides for redox applications depends crucially on oxygen mobility in the oxide lattice. In the present work, we demonstrate that addition of an aliovalent dopant (La) strongly enhances oxygen mobility in ceria, resulting in multiple performance benefits. A series of La-doped ceria ($\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$, $0 < x < 0.3$) were investigated as supports for low-cost Fe-based oxygen carrier materials. Combining carrier synthesis and characterization with reactive tests, we demonstrate that La doping of ceria not only results in a drastic improvements in carrier reactivity and oxygen carrying capacity, but also strongly improved carrier stability during redox cycling. This is consistent with the creation of oxygen defects, which stabilize the supported Fe particles and facilitate oxygen transport in the ceria lattice. A balance between enhancement of oxygen mobility and lowered reducibility upon formation of a lanthana phase results in a strongly nonlinear dependence of carrier reactivity on the dopant concentration and gives rise to an

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23 optimum at low dopant concentrations. Overall, the results suggest that doping of reducible
24 supports constitutes a highly attractive, effective, and low-cost way to strongly enhance the
25 performance of oxygen carriers in chemical looping applications.

26

27 **Keywords:** Chemical looping combustion, CO₂ capture, iron, ceria, lanthana, doping.

1. Introduction:

Increasing supply of energy is imperative for continued growth of modern society, particularly in the so-called developing world. The International Energy Agency (IEA) predicts that global primary energy demand will increase by almost 20% over the next 15 years alone. Although the share of fossil fuels is predicted to decrease slightly from 82% now to 76% by 2035, energy-related CO₂ emissions are expected to rise by 20% over the same time-frame^{1, 2}. As the source of two-thirds of the global greenhouse-gas emissions, technological advances in the energy sector will be pivotal in abating CO₂ emissions. Given our dependence on fossil fuels, alternative technology solutions for clean combustion of fossil fuels with simultaneous CO₂ capture should hence have high priority in our energy R&D landscape.

Chemical Looping Combustion (CLC) has emerged over the past decade as a particularly promising technology in this context, offering a highly efficient route for clean combustion of fossil fuels with inherent CO₂ capture³⁻⁵. In CLC, an oxygen carrier (typically a metal oxide) is contacted with fuel in a first reactor (fuel reactor), undergoing reduction while providing the necessary oxygen for combustion of fuel (Figure 1). After combustion, the reduced metal is transferred to the second reactor (air reactor) where it is re-oxidized in contact with air. The oxidized metal is then circulated back to the fuel reactor, closing the material ‘loop’. In the fuel reactor, ideally, a pure mixture of CO₂ and H₂O is formed as combustion gases, from which high-concentration, sequestration ready CO₂ streams can be readily obtained via condensation of steam. Thus, CLC offers a unique and efficient route for NO_x-lean, flameless combustion of fossil fuels with inherent CO₂ capture at minimal efficiency penalty for CO₂ capture, making it rather unique among current and emerging CO₂ capture technologies⁶⁻⁹.

Figure 1: Schematic for CLC using CH_4 as fuel

Although the concept of CLC has been demonstrated widely¹⁰⁻¹⁷, there is still need for improvement in the design of efficient oxygen carriers, with sufficient carrier stability and fast redox kinetics as key issues. Depending on the reactor configuration used for CLC, continuous cycling of particles between reduced and oxidized states subjects the oxygen carriers to chemical, thermal and mechanical stress in transport reactor configurations. Consequently, vast efforts have been dedicated to developing efficient oxygen carriers that can cope with the harsh environment of CLC. Most of the oxygen carriers reported in the literature are synthetic carrier materials. Cu-, Ni-, Fe-, Mn-, and Co-based oxygen carriers have been investigated for their thermal stability and reactivity¹⁸⁻²², with their thermal stability typically improved by supporting the active metal on inert oxide supports such as Al₂O₃, SiO₂, ZrO₂, and MgAl₂O₄^{10, 23-27}. Although these inert oxides can be quite effective in rendering the supported metal thermally stable, they contribute neither to the oxygen carrying capacity nor the redox kinetics for the composite carrier. Instead, the significant mass fraction of an oxygen carrier represented by a non-reducible support results in additional energy demand required in handling such carrier materials during looping operations. Recent work by our own group²⁸⁻³⁰ and others³¹⁻³³ has shown that such inert support materials can be replaced by “active” reducible support materials, such as ceria or perovskites⁶⁰⁻⁶². In our previous work, we observed that use of reducible oxides as supports is highly advantageous since it i) facilitates complete utilization of the supported metal, ii) results in faster redox kinetics, and iii) stabilizes the metal phase in bimetallic carriers without resulting in the formation of undesired spinel structures (which are typically inactive in redox processes)^{29, 30}. Although the use of reducible oxides as supports is a recent concept in CLC, use of “active” supports is well established in the field of heterogeneous catalysis where reducible oxides, in

particular ceria, are widely used as support for metal nanoparticles in various catalytic redox reactions³⁴, including automotive exhaust clean-up (catalytic convertor)³⁵, water gas shift reaction^{36, 37} and catalytic methane oxidation³⁸⁻⁴⁰. In those applications, the promotional effects of ceria as support can be traced back to strong metal-support interactions⁴¹ and oxygen buffering, i.e, the facile and reversible release of lattice oxygen via the $\text{Ce}^{4+} \rightleftharpoons \text{Ce}^{3+}$ transformation⁴². Ceria also finds applications as a solid electrolyte in high temperature electrochemical devices such as solid oxide fuel cells (SOFCs), due to its excellent electronic conductivity^{43, 44}. The overall performance of ceria in these applications is further improved by creation of oxygen vacancies or defects, typically achieved via doping, which influences both oxygen as well as electron transport in the ceria lattice. In particular, doping ceria with cations with significantly different cationic radii than Ce (such as zirconia, Zr^{4+} ,^{38, 45}) or with aliovalent dopants such as La^{3+} ^{39, 46} has been shown to promote redox properties by facilitating oxygen transport in the ceria lattice, where a strong relation between concentration of oxygen defects and oxygen carrying capacity exists^{36, 47}. Such doping is also known to improve the thermal stability/textural properties of the support oxides^{38, 39, 45, 46, 48}. Finally, addition of rare earth dopants (Sm^{3+} , Gd^{3+} , Y^{3+}) to CeO_2 has been reported to result in improved overall ionic conductivity and reducibility^{49, 50}, with optimal concentrations depending on the kind of dopant⁵¹⁻⁵³.

However, the effect of ceria doping on redox kinetics and/or carrier stability has not found much attention to-date in the chemical looping community. A sole study from the Chalmer's group³¹ investigated the effect of using ceria and 10% Gd-doped ceria (in comparison to conventional non-reducible alumina support) for iron-, copper-, and manganese-based carriers. The authors report that doped ceria particles were more reactive than pure ceria. However, the effect of

dopant concentration on redox behavior, carrier stability, and oxygen carrying capacity of oxygen carriers in CLC was not investigated – and the role of such dopants in the redox mechanism at CLC conditions as well as the optimal concentration of (typically more expensive) dopants required to observe the enhancement effects remained hence unexplored.

Doped ceria has recently also found some application in concentrated solar power (CSP), a closely related technology in which thermal decomposition of the oxide replaces the chemical reduction step. For example, Haile and coworkers tested 15% samarium-doped ceria for solar-thermal H₂O and CO₂ splitting chemistry without, however, further investigating mechanisms and optimal dopant levels³³. Other CSP studies investigated the impact of dopant concentrations on overall support reducibility, but did not report their effect on redox kinetics⁵⁴⁻⁵⁶. However, the operating temperatures (1,000-1,500°C) are significantly higher than those in typical chemical looping processes (~800-1,000°C), limiting the transferability of the reported results. Several related studies emphasize phase stability of doped ceria as a limiting factor for the application of these materials, in particular for transition metal dopants (Fe, Cu, Ni, Mn), due to phase separation via bleed-out of the dopant^{57, 58 59}, reaffirming the need for careful dopant selection and thorough investigation of carrier stability. However, in all these applications, ceria or doped ceria serves as the sole oxygen carrier material, i.e. the redox chemistry is conducted in the absence of (supported) metals. Overall, while the existing work hence suggests that addition of dopants can improve the redox performance of ceria, it points towards a need for a systematic evaluation of the effect of dopant concentration on carrier stability, oxygen carrying capacity, and redox kinetics, in order to enable rational design of optimal oxygen carrier for large-scale CLC applications.

In the present work, we focus on tailoring the reducibility of ceria supports via La doping. La was chosen as a dopant due to the fact that ceria and lanthana have different valences, resulting in the formation of oxygen defect sites in Ce-La solid solutions, as well as due to the fact that we had previously shown that ceria-lanthana solid solutions can be synthesized in a straightforward way over the entire range of Ce:La ratios and show the expected synergistic effects on the oxide reducibility³⁶. Iron was chosen as the active (i.e. “oxygen carrying”) metal component due to its low toxicity, low cost, and earth abundance, as well as its low intrinsic reactivity which benefits greatly from the use of active support materials. Fe-La_xCe_{1-x}O_{2-x/2} carriers were synthesized, characterized, and subjected to redox cycles in a thermogravimetric analyzer and a fixed-bed reactor to establish the effect of doping on the stability, redox kinetics, and oxygen carrying capacity of the carrier.

2. Experimental Section:

2.1 Oxygen Carrier Synthesis:

The main focus in the synthesis of La-doped ceria was not only to attain solid solution of La-Ce but also on simplicity of the synthesis procedure to keep the cost of the resulting material low and hence realistic for industrial application. Oxygen carriers were synthesized using a simple and scalable two-step approach. First, La-doped ceria is synthesized, and then iron is subsequently deposited on the La_xCe_{1-x}O_{2-x/2} support by deposition-precipitation.

La_xCe_{1-x}O_{2-x/2} supports with varying La concentration ($0 < x < 0.3$) were prepared via a facile hydrothermal synthesis procedure previously adapted in our research group³⁶. For example, La_{0.1}Ce_{0.9}O_{1.95} was synthesized by dissolving 0.675 g of Ce(NO₃)₃·6H₂O (99+%, Sigma-Aldrich) and 0.075 g of La(NO₃)₃·6H₂O (99+%, Sigma-Aldrich) in 8 ml DI water. 30 ml of NaOH (98+%,

Sigma-Aldrich) solution (7 M) was rapidly added under vigorous stirring. After 30 min of stirring, the slurry was transferred into a 50 ml autoclave, heated to 100°C under autogenous pressure for 72 h, and then allowed to cool to room temperature. The product was washed with DI water and collected via centrifugation to remove any ionic remnants until the pH of the solution was 7. Finally, the resulting powder was dried at 100°C overnight and calcined at 450°C for 2 h.

Next, Fe-based carriers were synthesized by deposition-precipitation. Briefly, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99+%, Sigma-Aldrich) was dissolved in DI water, and 40 mL of the 0.06M precursor solution was precipitated by 0.5M NaOH at pH of 9 – 9.5 on 200 mg of the desired support powder suspended in 100 mL DI water. After aging for 2 h, the resulting precipitate was centrifuged, vacuum dried at 100°C, crushed and finally calcined in air at 900°C for 2 h in air.

2.2 Oxygen Carrier Characterization:

To understand the effect of redox cycling, the carriers were carefully characterized after synthesis, reactive tests in TGA, and after fixed-bed reactor tests. The specific surface area of the oxygen carriers was obtained via nitrogen sorption in a Micromeritics ASAP 2020 gas adsorption analyzer using the BET method. Prior to the measurement, the samples were degassed for 2 h at 200°C under high vacuum. After calcination at 450°C for 2 h, all the support oxide materials were found to have total surface area between 70 – 90 m^2/g . Further calcination of the final $\text{Fe-La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ carriers calcined at 900°C reduced the surface area to $<7 \text{ m}^2/\text{g}$. The drop in surface area upon calcination is due to the well-known limitations in high-temperature stability of ceria supports^{38, 39, 45, 46}. X-ray diffraction (XRD) measurements were performed with

a powder X-ray diffractometer (Phillips PW1830) in line focus mode employing Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) with typical 2θ scans between 15° and 90° . Crystal phases were identified based on JCPDS cards. Average crystal lattice spacings were determined using Bragg's law.

2.3 CLC Reactive Tests:

2.3.1 Thermogravimetric Analyzer (TGA) Tests:

In first tests, pure H₂ was used as a model fuel to characterize carrier performance during redox cycles without the added complexity of carbon formation that often accompanies the use of methane as fuel. Kinetics and thermal stability of the carriers with H₂ as fuel were evaluated in thermogravimetric analyzer tests (TA instruments, SDTQ600). Subsequently, thermal stability and kinetic tests were conducted with CH₄ as fuel. Reduction half cycles were carefully timed to avoid carbon formation on the carrier material and possible undesired carbon carry-over from the reducer to the oxidizer.

In a typical run, up to 20 mg of oxygen carriers were heated inside the TGA cradle in an inert gas stream (Ar, Grade 5.0) to the desired reaction temperature (900°C). Then, H₂ (Grade 5.0) and air (Grade 0.1) were fed alternately at a flowrate of 20 sccm to simulate the periodic reduction–oxidation cycles of CLC. Between reduction and oxidation phases, the TGA was purged with Ar (20 sccm, Grade 5.0) to avoid formation of potentially flammable gas mixtures inside the instrument. In CLC with CH₄ as fuel (Grade 2.0, 5 sccm), suitable reduction times were determined by varying the duration of the reduction half cycle and the CH₄ flowrate while monitoring the occurrence of carbon burn-off in the oxidation half cycle. All other experimental conditions were identical as explained above for H₂. Up to 50 redox cycles were conducted in the

TGA experiments in order to identify trends in the stable operation or reveal any deactivation in the oxygen carrier performance and carrier conversion. All experiments were conducted at ambient pressure conditions.

2.3.2 Fixed-bed Reactor tests:

Oxygen carriers were evaluated in a fixed-bed reactor to investigate the effect of La-doping on carrier activity and selectivity in converting methane to steam and carbon dioxide. 100 mg of $\text{Fe-La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ powder was placed inside a quartz-glass tubular reactor ($\frac{1}{4}$ " ID), which was inserted into an electric oven (Thermo Electron Corporation – Lindberg/Blue M). The bed was equipped with a coke-resistant high temperature stable thermocouple to measure the actual bed temperature. The oven was heated to 900°C and CH_4 (1 sccm, Grade 2.0, $y_{\text{CH}_4} = 16.7\%$ in Ar) and 20% O_2 in balance He (20 sccm) were flown alternately to simulate the periodic reduction and oxidation in CLC. In between reduction and oxidation of the carrier, the reactor was purged with argon (Grade 5.0) to avoid formation of explosive mixtures of air and CH_4 inside the reactor and facilitate evaluation of distinct oxidation and reduction phases. After condensation of moisture, the effluent gases were recorded using a mass spectrometer (Pfeiffer Omnistar QMS 200) and the data was converted to molar flowrates (n_i) for all species observed during the reaction. A carbon balance was performed to assure the accuracy of the analysis and closed within 5 – 10 % error for all reported experiments.

Carbon Balance:

$$n_{\text{CH}_4, \text{in}} = n_{\text{CH}_4, \text{out}} + n_{\text{CO}_2, \text{out}} + n_{\text{CO}, \text{out}} + 0.5 \times (n_{\text{H}_2, \text{out}} - 2n_{\text{CO}, \text{out}}) \quad \dots (1)$$

On-stream methane conversion (X_{CH_4}) and cumulative carrier ($X_{carrier}$) conversion were evaluated using:

$$X_{CH_4} = \frac{n_{CH_4,in} - n_{CH_4,out}}{n_{CH_4,in}}, \quad X_{carrier} = \frac{4 \sum n_{CO_2,out} + \sum n_{CO,out}}{Total \text{ mol of O in carrier}} \quad \dots (2, 3)$$

Selectivity of various species (S_i) viz. CO_2 , H_2 , CO and carbon (C) formation by methane pyrolysis were calculated by the following equations.

$$S_{CO_2} = \frac{n_{CO_2,out}}{(n_{CH_4,in} - n_{CH_4,out})}, \quad S_{CO} = \frac{n_{CO,out}}{(n_{CH_4,in} - n_{CH_4,out})} \quad \dots (4, 5)$$

$$S_{H_2} = \frac{0.5 n_{H_2,out}}{(n_{CH_4,in} - n_{CH_4,out})}, \quad S_{Carbon} = \frac{0.5(n_{H_2,out} - 2n_{CO,out})}{(n_{CH_4,in} - n_{CH_4,out})} \quad \dots (6, 7)$$

As expected, total oxidation, partial oxidation and catalytic pyrolysis of methane were found to be the dominant reactions occurring in the system, illustrated schematically in the following reactions where “MeO” is a metal oxide and “Me” the corresponding reduced metal:

3. Results and Discussion:

3.1 Stability of lanthana-ceria solid solutions

226 Since understanding the effect of lanthana doping on carrier reactivity is the primary aim of the
227 present study, it is quite essential to first confirm the successful formation and stability of the
228 desired mixed oxides of $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ upon heat treatment and deposition of iron. Therefore,
229 Ce/La oxides calcined at 450°C were first subjected to X-ray diffraction to test for possible co-
230 existence of separate ceria and lanthana phases which would indicate incomplete incorporation
231 of La into the ceria lattice. Figure 2 shows the diffractograms of various $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ oxides
232 with the dotted vertical lines representing the standard X-ray diffraction angles for pure CeO_2 (as
233 obtained from JCPDS PDF #: 04-0593). One can observe good agreement between reference
234 pattern and XRD of pure CeO_2 . Upon doping ceria with lanthana, no separate peaks
235 corresponding to lanthana oxide (or La carbonates, which are known to form rapidly at ambient
236 conditions⁶³) are observed. Close observation of the diffraction pattern reveals that the
237 diffraction peaks shift to lower angles of reflection with increasing La concentration.

Figure 2: Typical X-ray diffraction pattern of $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ carriers calcined at 450°C in air for 2 h. X-ray diffraction confirm peaks corresponding to CeO_2 with fluorite structure shifted to higher angle with increasing lanthana concentration, while no lanthanum containing secondary phase are detected.

The peak position for each La/Ce oxide allows calculation of the lattice parameters of these support oxides. Figure 3a shows the average lattice parameters for $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ as a function of La-doping ($x = \text{mol La}/(\text{mol La} + \text{mol Ce})$). The calculated lattice parameter for pure CeO_2 synthesized via the hydrothermal technique (0.5415 nm) is in close agreement with that of bulk ceria (0.5411 nm, JCPDS PDF #: 04-0593). Overall, the lattice parameter of the mixed oxides increases with increasing lanthana content due to the larger ionic radius of $^{\text{VIII}}\text{La}^{3+}$ (1.16 Å) compared to $^{\text{VIII}}\text{Ce}^{4+}$ (0.97 Å)⁶⁴. (Note that due to the relatively large standard deviation of the lattice parameter for pure CeO_2 , the value for the 2% La-doped carrier is statistically unchanged, i.e. the apparent dip is within the error margin of the measurement). Overall, the absence of a separate La-containing phase and the shift of X-ray reflections to a lower angle, i.e. the expansion of ceria lattice upon increasing lanthana concentration, thus confirm successful incorporation of lanthana into the ceria crystal structure.

Figure 3: Lattice parameter of $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ oxides after subjecting it to a) air calcination at 450°C , b) deposition of iron and subsequent calcination in air at 900°C , c) TGA redox stability tests of $\text{Fe-La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ at 900°C using H_2 as fuel.

Upon confirmation of the formation of homogeneous solid solutions of ceria and lanthana for all samples, iron was deposited onto the support powders via deposition-precipitation, and the obtained materials were calcined at 900°C. Figure 4 shows typical X-ray diffraction patterns for all Fe-La_xCe_{1-x}O_{2-x/2} carriers after calcination at 900°C. Up to 10% La, only Fe₂O₃ and CeO₂ are detected (figure 4a-d). Again, no signs for the presence of a separate La-containing phase are apparent and the shift of all the support oxide peaks towards a lower diffraction angle remains unchanged from the Fe-free doped ceria samples, indicating the stability of La in the ceria structure in presence of iron oxide. However, starting at 10% La doping (figure 4d), XRD shows the appearance of low intensity peaks which indicate formation of LaFeO₃. Hence, at higher doping, signatures of lanthana bleed-out from the support structure are observed, although detection of only a few low-intensity X-ray reflections in the XRD pattern of LaFeO₃ suggests that the lanthana iron oxide is only a minor phase in the Fe-La_{0.1}Ce_{0.9}O_{1.95} materials. Further increase in the lanthana concentration gives rise to distinct peaks for LaFeO₃ as well as some unassigned peaks in the vicinity of the ceria diffractions at lower diffraction angle (marked by downward arrows in figure 4f). Apparently, once lanthana starts bleeding out of the support structure, the samples contain two ceria phases: ceria that has lost most of the La dopant (which hence shows peaks corresponding to pure ceria), and ceria with some remnant La doping resulting in XRD peaks at lower angle. Overall, these observations indicate that beyond a threshold concentration of ~10%, it is difficult to stabilize La in the ceria structure in the presence of iron oxide. It is likely that strong interactions between lanthana and iron provide a strong driving force for bleed-out of lanthana which was stable in the ceria structure prior to iron loading.

275 This is further supported by the average lattice parameters for the support oxides in $\text{Fe-La}_x\text{Ce}_{1-x}$
276 $\text{O}_{2-x/2}$ calculated from XRD (figure 3b). After iron deposition, the lattice parameter for all
277 $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ oxides decreases. However, the decrease in lattice parameter is small up to 10%
278 La-doping, above which a strong decrease in the lattice parameter is observed, consistent with a
279 significant bleed-out of La in parallel with the formation of LaFeO_3 , as confirmed in XRD.
280 (Note that the large standard deviation in the lattice parameters at high La-containing oxides is
281 due to the poorly defined peaks, again suggesting a rather disorganized bleed-out process due to
282 the “scattered” presence of Fe on the support surface, and a much restricted sample space for
283 statistical averaging.

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Figure 4: Typical X-ray diffraction pattern of $\text{Fe-La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ carriers, with $x =$ a) 0, b) 0.02, c) 0.05, d) 0.1, e) 0.2 and f) 0.3, calcined at 900°C in air for 2 h. XRD patterns show that a minimum threshold concentration of lanthana is required to observe lanthana bleed-out and significant formation of lanthana iron oxide (LaFeO_3).

3.2 Reactive tests in TGA using H₂:

3.2.1 Redox cycles at 900°C:

After establishing the thermal stability of the oxygen carriers at non-reactive conditions, all carrier materials were subjected to redox cycling in a thermogravimetric analyzer (TGA) at 900°C. CLC operation was simulated by periodically switching between fuel (carrier reduction) and air (oxidation), separated by a purge phase to avoid direct contact of fuel and oxidizing gas. The aim of these studies was to understand thermal stability and redox kinetics of the carriers as a function of La doping into the support. Therefore, H₂ was again first used as model fuel to avoid complications arising due to multiple parallel and sequential reaction pathways in the oxidation of methane, including carbon deposition due to fuel pyrolysis.

Figure 5a shows 10 redox cycles for Fe-La_{0.1}Ce_{0.9}O_{1.95} during cyclic operation with H₂ and air at 900°C. One can see that the carrier shows stable operation over the duration of the experiment as indicated by the unchanged sample weight in the reduced and oxidized state of the carrier over multiple cycles. Similar experiments were performed to confirm the thermal stability of all carriers investigated in this study (not shown). Although some of the carriers had shown bleed-out of lanthana in the calcined state, all carriers were found to show stable operation up to 10 cycles, suggesting that—following the initial La bleed—the carrier attains a stable state. Figure 5b shows a single cycle in detail for a Fe-La_{0.1}Ce_{0.9}O_{1.95} carrier. The carrier shows rapid loss of oxygen (i.e. reduction) upon exposure to hydrogen. Interestingly, the sample weight obtained in the reduced state of the carrier is much lower than the expected weight due to full reduction of the iron phase in the carrier (depicted by the bottom-most dotted line in figure 5b), indicating a fractional reduction of the doped ceria of up to 2% of the total sample weight.

Figure 5: a) Multiple redox cycle and b) a single redox cycle during CLC operation of $Fe-La_{0.1}Ce_{0.9}O_{1.95}$ in TGA at $900^{\circ}C$ with reduction in H_2 , argon purge, and air oxidation (20 sccm). Dotted lines in the panel b show the sample weight that corresponds to various oxidation states of the carrier during redox operation.

Figure 6: Rate of carrier conversion with respect to time for $\text{Fe-La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ carriers as a function of carrier conversion (X) during reduction half cycle in TGA at 900°C using H_2 as fuel. Numbers next to the arrows indicate the %La doping in the lanthana-ceria mixed oxide supports. For better visibility, the inset shows the minimum conversion (i.e. highest degree of reduction) of the carrier as a function of La doping. Low La doping ($0 < \% \text{La} < 10$) results in deeper carrier reduction than a further increased doping, as indicated by the “more negative” X .

Previously, we had observed that the use of (undoped) reducible supports yields very limited contribution to the oxygen carrying capacity; however, the oxygen mobility in the support structure resulted in fast redox kinetics and facilitated complete utilization of the supported metal^{29, 30}. Therefore, the impact of La-doping on the redox kinetics of the overall carrier was evaluated by calculating the rate of reduction of the oxygen carriers. Figure 6 shows the reduction rate (dX/dt) as a function of the degree of carrier reduction (X) for all carriers, where X is defined as: $X = (W(t) - W_{\text{red}})/(W_{\text{ox}} - W_{\text{red}})$, with $W(t)$ denoting the momentary weight of the carrier, W_{ox} the carrier weight in the fully oxidized state, and W_{red} the carrier weight in the fully reduced state. Importantly, all values are calculated based on the complete reduction of the metal only, thus keeping a consistent reference for the differently doped carriers (which allow reduction of the support to different degrees). Thus, $X = 1$ represents the carrier in its fully oxidized state, while $X = 0$ indicates that the active metal in the oxygen carrier is fully reduced (without any contribution of the reducibility from support). Measurable contributions of the reducibility of the support beyond the full reduction of the metal phase hence result in $X < 0$ due to the additional decrease in the carrier weight.

Overall, all carriers show similar trends for the rate of carrier conversion: A strong maximum in the rate of reduction is observed during the initial stage of carrier reduction ($1 > X > \sim 0.7$). The boundaries of this rapid reduction regime correspond well with the reduction of Fe_2O_3 ($X = 1$) to FeO ($X = 0.67$), indicating that the initial reduction of the fully oxidized iron oxide phase proceeds very rapidly and without a detectable transition in the rate corresponding to the formation of a magnetite phase. Subsequent reduction of carrier below FeO is slow and hence characterized by a broad and low rate profile. Finally, the rate of carrier conversion drops almost to zero as the oxygen reservoir is depleted. Although the metal is completely reduced, however, a

measurable, non-zero rate of oxygen consumption is observed which indicates continued loss of oxygen from the reducible support. Close inspection of the dX/dt profile in the final stages of carrier reduction (see inset in figure 6) reveals that small amount of lanthana doping ($0 < \%La < 10$) results in deeper carrier reduction, i.e. enhanced oxygen availability compared to undoped ceria. Although the oxygen contribution from the support is overall small (~14% of the total oxygen utilization for Fe-La_{0.1}Ce_{0.9}O_{1.95}), low La doping results in almost doubling of the reducibility of the ceria support. Further increase in the lanthana doping is actually counterproductive and reduces the contribution of support. Furthermore, the rate dX/dt during the initial rapid reduction phase ($Fe_2O_3 \rightarrow FeO$) shows similar dependence on lanthana doping concentration, with an initial increase in rate, a maximum at 10 wt.%, followed by a decrease at higher doping concentrations.

Following the CLC tests, all carriers were characterized via XRD to test if exposure to the harsh environment of redox cycling affected their phase stability (figure 3c). One can see that up to 10% La doping there is no significant change in the lattice parameters of the supports after calcination at 900°C (figure 3b) and after subsequent exposure to redox cycling using H₂/air at 900°C (figure 3c). Furthermore, XRD of these carriers confirms presence of only Fe₂O₃ and CeO₂ as significant phases (not shown here). Both observations thus confirm good stability of the doped ceria structures at low dopant concentrations. As expected, further increasing the concentration of lanthana doping exacerbates the lanthana bleed-out seen in the unreactive stability tests before, and presence of LaFeO₃ is confirmed in XRD.

3.2.2 Redox cycles at 600°C:

From the above comparison of the carriers during redox cycling at 900°C it is evident that carrier capacity, reactivity, and stability (i.e. likelihood of LaFeO_3 formation) show a strong dependence on the extent of La doping. However, to further elucidate the difference in intrinsic carrier reactivity, additional tests were conducted at low temperature (600°C) in order to slow down the redox kinetics and hence enhance any intrinsic reactivity differences between the carriers due to oxygen mobility. Figure 7a and b shows the carrier conversion profiles during reduction (figure 7a) and re-oxidation (figure 7b), where the numbers next to the curves indicate the respective %La doping. As observed before, low concentrations of La-doping (0 – 10%) strongly accelerate the carrier reduction but result in only marginal improvements in the amount of oxygen available for fuel oxidation. Further increase in the La-doping does not further improve the kinetics but adversely affects the amount of oxygen available for the reduction.

The loss in oxygen carrying capacity upon increasing La doping beyond 10% can be traced back to two effects: On one hand, the reduced amount of ceria available for reduction (lanthana is essentially irreducible at these conditions), and on the other hand the formation of LaFeO_3 (which is similarly difficult to reduce). We have previously shown that lanthana is significantly less reducible than ceria⁴⁷, and additional TGA redox cycles using Fe- La_2O_3 (where LaFeO_3 is a major phase) at various temperature (400 – 1000°C; not shown here) showed that LaFeO_3 can be reduced to Fe and La_2O_3 only at sufficiently high temperatures (>700 – 1000°C), while it is stable and shows poor reactivity during reduction at low temperature. Therefore, the superposition of the beneficial formation of oxygen vacancies upon doping with these detrimental effects on reducibility result in the observed optimum in the amount of La doping.

Figure 7: Integral carrier conversion (a, b) and rate of carrier conversion (c, d) during reduction (a, c) and re-oxidation (b, d) of Fe-La_xCe_{1-x}O_{2-x/2} carriers during redox cycling in TGA at 600°C using H₂ and air (20 sccm). Numbers next to the curves indicate the %La-doping in ceria.

Unlike reduction, the oxidation kinetics do not show a maximum at an optimal La concentration: Figure 7b and d show that the integral carrier conversion and conversion rate during air re-oxidation show increasing trends up to 10% La, beyond which very little detectable change occurs. All carriers with at least 10%La-doping show very rapid and complete re-oxidation, while carriers with lower dopant levels show extremely slow re-oxidation which hence remains incomplete even over ~2 hrs of re-oxidation. Despite the absence of a kinetic maximum, 10%La doping again emerges as the optimum as it is the lowest doping level which is sufficient to dramatically accelerate the oxidation rate and achieve complete re-oxidation. Similar fast re-oxidation of carriers was seen with Ni-La₂O₃ at 350°C²⁹, and Fe-La₂O₃ at 600°C (not shown here), confirming that La is the key component for re-oxidation of the carrier.

Overall, TGA tests with hydrogen demonstrate that the extent of La doping has significant impact on the stability of the supported metal, its effective oxygen carrying capacity, and on redox kinetics.

3.3 Reactive tests with CH₄ as fuel:

Ultimately, oxygen carriers will be used in the combustion of carbonaceous fuels. We hence extended the studies onto investigation of the redox performance of these carriers with methane as fuel. Based on the trends observed in the hydrogen-fueled redox cycles (discussed above), 0, 2, 10, and 30% La-doped carriers were down-selected to further corroborate the observation that an optimal concentration of La exists for optimal carrier performance.

3.3.1 Reactivity tests in TGA:

The down-selected carriers were evaluated in multi-cycle CLC tests at 900°C with CH₄ as fuel for 6 – 8 cycles. All carriers showed stable operation over the duration of the experiment (~7 – 8 h). Figure 8 shows a direct comparison of carrier conversion vs time during the reduction half cycle with CH₄ for the selected carriers with four different %La-doping (0, 2, 10, and 30%). Undoped Fe-CeO₂ takes the longest time for complete reduction of the carrier, while 2% and 10% La doping results in a significant acceleration of the reduction i.e. shorter time for complete reduction of the carrier. Furthermore, close observation of the carrier reduction values at the end of the reduction half cycle reveal that 2 and 10% La-doped carriers supply more oxygen for the combustion of methane than undoped or 30% La doped carrier. Thus, irrespective of the fuel used, i.e. H₂ or CH₄, an excess concentration of La reduces the oxygen carrying capacity and yields less reactive carriers, i.e. in both cases an optimal doping level exists. X-ray diffraction after CLC cycling (not shown) again confirms the tendency of carriers with high La doping to form LaFeO₃. In agreement with the H₂ experiments, restricting the La-dopant below 10% is beneficial not only for carrier reactivity and oxygen carrying capacity but also for carrier stability.

Figure 8 : Comparison of carrier conversion profiles as a function of %La-doping for $\text{Fe-La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ carriers during CLC operation in TGA at 900°C with reduction in CH_4 (5 sccm), N_2 purge and air oxidation (20 sccm). Numbers next to the curves indicate the %La-doping in ceria

3.3.2 Reactivity tests in fixed-bed reactor:

Although redox cycles in TGA provide useful information about carrier reactivity and stability, TGA experiments are run with large excess of gas phase reactants and do not adequately represent gas-solid contacting patterns in a fixed bed or fluidized bed configuration. Hence, redox cycles in TGA cannot give meaningful insight into fuel conversion and product selectivity in the gas phase. Selective total oxidation of the fuel is important as CLC aims at (near-)complete carbon capture via total oxidation of fuel to CO₂ and steam, while products from undesired side-reactions such as partial oxidation and fuel cracking result in reduced carbon capture efficiency and can result in carrier deactivation. Therefore, Fe-La_xCe_{1-x}O_{2-x/2} carriers were next subjected to extended reduction in methane to understand the effect of La doping on fuel conversion and CO₂ selectivity.

During fixed-bed reactor tests, the oxygen carrier bed was brought to the reaction temperature (900°C) and then methane was flown over the pre-oxidized carriers until the carrier was completely reduced, i.e., until the selectivity for total or partial oxidation products (CO₂ or CO) disappeared and hydrogen (from methane cracking over the reduced metal) was the dominant product. Product gases were analyzed by mass spectrometry. The reactor was then purged with Ar and the carrier was regenerated in synthetic air (20% O₂ in He). During re-oxidation, the evolution of CO and CO₂ indicated carbon burn-off while breakthrough of oxygen indicated complete regeneration of the carrier.

Figure 9 compares various Fe-La_xCe_{1-x}O_{2-x/2} carriers with regard to total oxidation (i.e. CO₂) selectivity (figure 9a), rate of methane conversion (figure 9b) and CO₂ yield (figure 9c) as

function of relative carrier weight during reduction in the fixed bed reactor. Carrier weight is 100% at the start of the reduction half cycle, indicating that oxygen carrier was completely oxidized prior to reduction. Subsequent exposure to methane leads to loss of oxygen resulting in overall drop in the weight of the carriers. The vertical dotted lines in the graphs indicate the relative carrier weight corresponding to various oxidation states of iron in $\text{Fe-La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ with 40 wt.% Fe loading.

Methane oxidation transitions through various phases of activity and selectivity, which—for the undoped ceria support—can be directly correlated with the oxidation state of Fe. Figure 9a shows that reduction of Fe_2O_3 to Fe_3O_4 is most selective for total oxidation of methane, while further reduction of the carrier results in a drop in CO_2 selectivity with the sharp breaks in CO_2 selectivity closely matching the transition from Fe_3O_4 to FeO and FeO to Fe , respectively. As expected, reduction of undoped (0% La) Fe-CeO_2 stops in close vicinity of the calculated carrier weight for fully reduced metallic iron suggesting little to no contribution from the support material. Comparing this base case with 2%La-doped carrier, we observe that $\text{Fe-La}_{0.02}\text{Ce}_{0.95}\text{O}_{1.99}$ shows a qualitatively similar CO_2 selectivity profile. However, all the transitions in the CO_2 selectivity are strongly shifted towards lower carrier weights, i.e. towards higher oxygen consumption than stoichiometrically required for the transition between the respective iron oxidation states alone. At the end of the reduction half cycle, the oxygen contribution from $\text{Fe-La}_{0.02}\text{Ce}_{0.95}\text{O}_{1.99}$ is almost double that of Fe-CeO_2 . Clearly, La-doped ceria strongly contributes oxygen for the combustion of methane. Interestingly, the oxygen contribution from the support structure is quantitatively much higher than that expected for stoichiometric reduction of CeO_2 to (thermodynamically stable) Ce_2O_3 , suggesting that La doping enables non-stoichiometric reduction of ceria at the operating conditions, i.e. it significantly alters the

thermodynamic stability of ceria. It is furthermore remarkable that the shift of the selectivity “breaks” towards lower carrier weight (i.e. higher oxygen consumption) is already present for the very first transition, i.e. the transition from Fe_2O_3 to Fe_3O_4 . This indicates that the carrier support contributes oxygen to the methane combustion from the very onset of the reaction and not only after the oxygen in the Fe-phase has been depleted. This suggests that the oxygen exchange between the Fe-phase and the support proceeds in a very facile way and agrees with earlier observations that La doping results in the formation of oxygen vacancies which greatly facilitate oxygen transport inside the (doped) ceria lattice^{36, 47}.

The increased oxygen mobility in the support not only enhances oxygen availability but also assists in increasing the carrier reactivity during the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ transition that is of concern for CLC operation with Fe-based materials (figure 9b). Compared to undoped Fe-CeO₂, higher reactivity and a larger fraction of the carrier weight that can be used for total oxidation of methane combine to a doubling in both the CO₂ yield and the usable carrier weight for 2%La-doped carrier!

Figure 9: Comparison of a) CO₂ selectivity, b) rate of methane conversion and c) CO₂ yield as a function of overall carrier weight during reduction of 40wt.% Fe-La_xCe_{1-x}O_{2-x/2} in fixed bed reactor at 900°C using methane (16.7 vol.%, 1 sccm).

In agreement with the TGA studies, a further increase in lanthana doping is not favorable for oxygen carrying capacity and carrier overall performance. Increasing the dopant concentration from 2 to 10% already results in a significant loss in the overall amount of oxygen that can be extracted from the material, and upon a further increase in the La concentration to 30% any enhancement disappears and the CO₂ selectivity trace closely overlaps with that of Fe-CeO₂. Interestingly, however, the initial activity during the Fe₂O₃ → Fe₃O₄ transition remains strongly increased compared to the undoped carrier (see fig. 9b). In fact, all three doped carrier show similar initial rate enhancements, suggesting that the oxygen mobility enhancement due to La doping remains intact upon increasing the doping. While we have no conclusive evidence for the reasons behind the lower carrier utilization with increasing reactivity, previous work suggests that the low reducibility of lanthana compared to ceria may compensate for the increased oxygen mobility and hence limit overall oxygen availability^{36, 47}, although our observation of La bleed-out at higher doping levels (discussed above) offers a possible alternate explanation. Similar enhancement effects have been reported with doping low concentrations of gadolinium³¹ (10%) and samarium³³ (15%) into ceria, but the present results underscore that dopant effects cannot be linearly extrapolated and are non-trivial problems with strong dependence on the nature and/or concentration of dopant, operating conditions, etc.

3.4 Effect of La-doping on redox cyclic stability:

Finally, it can be expected that doping of the support may affect – beyond the reactivity – also the carrier stability during redox cycling. It has been previously reported that doping ceria helps

abate the deterioration of its textural properties which in turn helps preserve the oxygen defects in the support structure^{38, 39, 45, 46}. Therefore, multi-cycle TGA redox tests were used to investigate the effect of La-doping on the redox stability of the carriers at CLC conditions.

Figure 10 compares performance of Fe-La_{0.1}Ce_{0.9}O_{1.95} and undoped Fe-CeO₂ over 50 cycles using H₂ as model fuel at 900°C. The La-doped carrier shows stable operation, characterized by reproducible carrier weights in successive reduced and oxidized states, and is fully reduced and oxidized during the redox process (as indicated by the dotted lines representing the sample weights in various oxidation state of the metal). Furthermore, as discussed before (section 3.2), the carrier weight in the reduced state dips well below the reference line for metallic iron indicating oxygen contributions from the La-doped reducible support.

In contrast to that, while Fe-CeO₂ appears to be stable over the initial ~11 cycles, this carrier subsequently shows strong deactivation with incomplete re-oxidation of the carrier. This inability to re-oxidize completely suggests sintering/agglomeration, where the increasing particle size results in increasingly long pathways for solid state diffusion in order to access the oxygen contained in the carrier. This was confirmed upon removal of the sample from the TGA test chamber after the CLC multicycles: The originally finely powdered Fe-CeO₂ carrier was found to be agglomerated into pelletized form after the cyclic redox exposure. Interestingly, however, this agglomeration behavior was similarly observed for the La-doped carrier with both the doped and un-doped carrier showing a BET surface area of <5m²/g in all cases after multi-cycle exposure. Hence, despite the fact that La-doping does not stabilize a high surface area post redox cycling at 900°C, the absence of a significant change in the redox kinetics over 50 cycles for the La-doped carrier suggests that La-doping helps to maintain a high oxygen mobility in the support structure and hence keeps the iron oxide phases easily accessible—and hence active for CLC—

522 even for larger particle sizes. This suggests that such doped support materials might be of
523 particular interest for large-scale CLC application in fluidized bed configuration, where
524 identification of low porosity carriers (which typically show better mechanical stability and
525 attrition stability) with sufficient reactivity is a key concern.

526

Figure 10: Fifty cycles of CLC redox operation of a) $Fe-La_{0.1}Ce_{0.9}O_{1.95}$ and b) $Fe-CeO_2$ at $900^\circ C$ in TGA using H_2 as model fuel. (H_2 , Ar, air = 20 sccm, 15 min each).

528

529 **4.0 Summary**

530 The identification of low-cost, highly active and stable oxygen carrier materials is critical for
531 successful implementation of CLC technology in industrial practice. To-date, most studies have
532 focused on monometallic carriers supported on simple oxides. In the present report, the impact of
533 La doping on ceria supports for Fe-based oxygen carriers was investigated, with the aim to
534 identify the effect of doping reducible oxides with an aliovalent dopant to improve oxygen
535 mobility and hence oxygen carrying capacity and reactivity of the carrier in CLC.

536 La-doped ceria supports were synthesized using a straightforward hydrothermal synthesis
537 approach and Fe was deposited onto the support matrix via deposition-precipitation. X-ray
538 diffraction and lattice parameter calculations confirm the formation of a uniform solid solution of
539 lanthana in ceria, i.e. complete incorporation of La into the ceria cubic lattice. Upon deposition
540 of iron onto the La-doped ceria supports, carriers with up to 10% La showed good thermal
541 stability, while those with >10% La doping showed lanthana bleed-out, resulting in the formation
542 of a poorly reducible LaFeO_3 phase. During redox cycling, all La-doped carriers showed stable
543 operation over 10 cycles, and extended stability tests (50 cycles) for $\text{Fe-La}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ and
544 undoped Fe-CeO_2 confirmed that La-doping strongly improves the thermal stability of these
545 carriers.

546 Significantly, the redox kinetics of these carriers shows a strongly non-linear dependence on the
547 dopant concentration. Both oxidation and reduction kinetics are strongly accelerated for low La
548 doping, while for higher doping the oxidation rate remains constant and the carrier reduction rate
549 starts to slow down. The drastic enhancement in carrier oxidation kinetics—which becomes

almost instantaneous upon doping of small amounts of La—has so far been largely overlooked in the looping community and is a direct indication for the drastic effect of the dopant on oxygen mobility in the ceria lattice. The reduction behavior is similar for H_2 and CH_4 as fuel, although optimum doping levels for CH_4 are slightly lower than for H_2 (2% vs 10% La, respectively). Interestingly, despite the strong impact on the kinetics, La-doping does not change the CO_2 selectivity curve qualitatively but the increased availability of oxygen due to doping shifts the selectivity curve towards higher oxygen utilization and hence increases the weight fraction of the carrier usable for CLC. Remarkably, as little as 2% La doping almost doubles the oxygen carrying capacity of the carriers in CLC of methane. Finally, the oxygen defects/vacancies generated via doping not only accelerate the oxygen transport and increase oxygen utilization, but also create anchor sites for the supported metal and strongly enhance carrier stability over long-term high-temperature cycling.

From an application perspective, the present results suggest that doped carrier supports, which have to-date not found much attention in industrial research on chemical looping, offer a range of benefits in return for minimal added carrier cost (due to low dopant concentrations and straightforward synthesis of these carriers). The strong enhancement of both oxidation and reduction kinetics allows reduction of both the reducer reactor and the oxidizer (or further enhancement of reactor throughput), while the increase in accessible oxygen in the carrier allows reduction of the carrier circulation rate. At the same time, enhanced stability will allow utilization of the carrier over more cycles and hence reduction in carrier cost due to carrier replacement.

While our studies were limited to La-doped ceria, it seems likely that the results apply to other doped oxides as well, i.e. we expect that doping reducible oxides in order to enhance their

oxygen mobility will result in strong enhancements in carrier reactivity and oxygen carrying capacity, suggesting that doped oxides (and, generally, highly oxygen-conductive oxide supports) offer vast possibilities for improvement of existing oxygen carriers for CLC. Such carriers could hence offer some of the advantages of other emerging oxygen carriers with high oxygen mobility, such as perovskites, while being based on simple, well-established, and inexpensive synthesis procedures^{62, 65}. However, the strongly non-linear dependence of thermal stability, oxygen carrying capacity, and reactivity on the extent of doping also underscores the importance of thorough analysis of such doped carriers and the need for an improved fundamental understanding of the complex underlying gas-solid and solid-solid reactive processes.

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