Increased nickel exsolution from LaFeNiO₃ perovskite-derived CO₂ methanation catalysts through strontium doping

Patrick Steiger,^{a,b} Oliver Kröcher^{a,b} and Davide Ferri^{a*}

^a Paul Scherrer Institut, Forschungsstrasse 111, CH-5232 Villigen, Switzerland

^b École polytechnique fédérale de Lausanne (EPFL), Institute of Chemical Sciences and Engineering, CH-1015 Lausanne, Switzerland

* Corresponding author

E-mail: davide.ferri@psi.ch

Phone: +41 56 310 27 81

Graphical abstract

Highlights

- A-site of LaFe_{0.8}Ni_{0.2}O₃ prepared by the amorphous citric acid method is modified by Sr
- A-site Sr promotes the segregation of Ni
- The self-regeneration of Ni in LaFe_{0.8}Ni_{0.2}O₃ is maintained upon substitution of La by Sr
- An optimum value of Sr substitution (5 mol%) provides maximum CH₄ production during CO₂ hydrogenation

Abstract

Perovskite-derived Ni catalysts offer the remarkable benefit of redox stability that allows their regeneration after deactivation through poisoning or Ni particle growth. Here, the catalytic activity of $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ towards CO_2 methanation was improved by increasing Ni reducibility and segregation to the perovskite surface through partial substitution of La by Sr ($\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$, $0 \leq x \leq 0.1$). Temperature programmed reduction, X-ray diffraction, scanning electron microscopy and X-ray absorption spectroscopy were used to characterize the materials, their stability against severe reduction at high temperatures and to quantify Ni segregation. It is shown that Ni reducibility was significantly increased (up to 50%) upon introduction of Sr, because more Ni was exsolved during catalyst pre-reduction. Nickel reincorporation into the perovskite-type oxide lattice during reoxidation was not affected at these Sr levels and complete redox stability could be demonstrated for all compositions investigated in this work.

Keywords: CO_2 hydrogenation; perovskite-type oxide; Nickel; $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$; self-regeneration

Introduction

Metal catalysts derived from perovskite-type metal oxides (PMO) have attracted great attention due to their high stability towards catalyst deactivation through metal particle sintering and coke deposition. In these materials catalytically active metals can be preferentially reduced and segregated from the host PMO lattice to produce the active material [1-3]. It was demonstrated that this metal segregation results in strong metal particle-support interactions due to the segregation process compared to a metal deposition type process such as wet impregnation and hence high sintering stability

and resistance towards coke formation at the particle-support interface [4]. Furthermore, application of PMO potentially allows the exploitation of their structural reversibility that is the reversible segregation of metals from the PMO lattice during reduction and reincorporation of these elements under oxidizing atmospheres and at sufficiently high temperatures [1, 5]. This property induces catalyst redox stability and can be exploited for catalyst regeneration [6, 7]. In recent years this property has been investigated for Ni in PMOs such as $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_3$ (LFNO) [7-9]. Nickel is widely applied in industrially relevant catalytic reactions including hydrogenation of carbon oxides [10-15], water gas shift [16], Fischer-Tropsch reaction [17], dry and wet reforming of hydrocarbons [16, 18-20], dry reforming of methane and carbon dioxide [21] and the production of methanol from methane [22]. In these processes nickel is used at a large scale because of its high activity and relatively low cost compared to precious metals. However, Ni catalysts can deactivate severely as a result of the deposition of carbon [19, 23-25], which requires oxidative regeneration at high temperatures [26]. Despite the advantages in terms of catalyst redox stability induced by the reversible segregation of Ni from LFNO perovskite-type catalysts, the major drawback of this approach is probably the difficulty to obtain complete Ni reduction and segregation from the bulk PMO. This results in the inefficient use of the active metal compared to conventional supported Ni-based catalysts [3, 7, 8]. Because the mixed metal oxide produces selectively CO and selectivity to CH_4 is highly dependent on the amount of Ni dispersed on the LFNO surface [7], improving the extent of Ni reduction and segregation in PMO materials is anticipated to be beneficial to achieve higher CH_4 yields. Since Ni reducibility is highly dependent on the composition of the host PMO lattice [27], it is likely that tuning the PMO composition through doping will affect both Ni reduction and segregation. Substitution of lanthanum by strontium in LaFeO_3 was

demonstrated to promote the formation of oxygen vacancies, which increase oxygen conductivity through the bulk of the PMO lattice, resulting in increased bulk reducibility [28-31]. This effect may be exploited to increase the catalytic activity of PMOs towards oxidation reactions, which rely on oxygen release from the lattice [32-34]. Its excellent ionic conductivity makes $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ a suitable cathode material for solid oxide fuel cells [30]. Deng et al.[35] reported increased Ni reducibility in LFNO upon doping the A-site by Ca, Sr, Mg, Ba, Pr and Ce. Ca, Sr, Mg and Ba adopt an oxidation state of +2, thus reducing the nominal charge at the A-site, which is compensated by either oxygen vacancy formation or lower oxidation states of the B-site elements. Pr on the other hand also adopts the +3 oxidation state of La, whereas introduction of Ce^{4+} leads to the formation of additional interstitial lattice oxygen as well as lower oxidation states of B-site elements [36]. Doping by Pr appeared to increase perovskite reducibility the most; however, more commonly a similar increase in reducibility is achieved by A-site doping with divalent alkaline earth elements. Taylor et al.[37] used density functional theory calculations to determine the stability of solid solutions for A-site doping by Mg, Ca, Sr and Ba and demonstrated that solution energies decreased from Mg to Sr along group II before increasing again for Ba. Solution energies could be directly linked to ionic size and were found to be the lowest for Sr^{2+} ($r_i = 1.44 \text{ \AA}$) due to its similar ionic radius to La^{3+} ($r_i = 1.36 \text{ \AA}$) [38]. These results also confirm previous investigations on the solubility of A-site dopants in LaFeO_3 [39].

Because of the good solubility properties of Sr in LaFeO_3 as well as the fact that its behavior in PMOs is well-understood, this work focuses on the use of Sr doping to increase Ni reduction and segregation from $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ ($x \leq 0.1$). Despite the extensive studies on the effect of A-site doping on oxygen vacancy formation, ionic conductivity and perovskite reducibility, it is not clear whether increased Ni reduction

accordingly results in increased Ni segregation and what effect the destabilization of the PMO host has on potential Ni reincorporation. These issues are addressed in this work.

Experimental

$\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ (LFNO), $\text{La}_{0.95}\text{Sr}_{0.05}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ (LSFNO-5Sr) and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ (LSFNO-10Sr) were prepared via the amorphous citrate process [40]. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99.999% trace metals basis), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 99.95\%$ trace metals basis) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99.999% trace metals basis) were each dissolved in water and thoroughly mixed before being added to an aqueous solution of citric acid (Sigma-Aldrich, ACS reagent, $\geq 99.5\%$). The overall molar ratio of metal nitrates to citric acid was 1:1.05. The precursor solution was stirred at 70°C for 60 min before drying under low pressure at 70°C for 12 h. The resultant precursor foam was crushed to a fine powder and then subjected to calcination at 800°C for 5 h ($5^\circ\text{C} \cdot \text{min}^{-1}$ to 200°C ; then, $10^\circ\text{C} \cdot \text{min}^{-1}$ to 800°C) to obtain the calcined sample.

The specific surface area (SSA) of the calcined powder was determined from N_2 -adsorption isotherms at -196°C according to the Brunauer-Emmet-Teller (BET) model using a Quantachrome Autosorb I instrument. The samples were treated in vacuum at 300°C for 2 h prior to SSA measurements.

The crystal structure of the powder catalysts was investigated by powder X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer equipped with Ni-filtered Cu $\text{K}\alpha$ -radiation, variable slits and an energy-sensitive line detector (LynxEye). Diffractograms were collected at an acquisition time of 4 s and a step size of $\Delta 2\theta =$

0.03° between 2θ 15° and 80°. The Scherrer equation [41] was used to estimate the perovskite crystallite size (d) using peak parameters determined for the (121) and (202) reflections at 32.3° and 46.4° 2θ , respectively. Mean values calculated from results obtained for both reflections as well as standard errors are reported in the text.

In situ XRD measurements were conducted on the same instrument using a reactor chamber (XRK 900, Anton Paar). Reactive gases (10 vol% H_2/N_2 and 20 vol% O_2/N_2) were dosed to the chamber (100 mL·min⁻¹ at STP) using mass flow controllers (Bronkhorst) while the sample temperature was maintained at 600°C and monitored using a K-type thermocouple.

Temperature programmed reduction (TPR) experiments were conducted using a TPDRO-1100 (ThermoElectron) instrument equipped with mass flow controllers and a thermal conductivity detector. The samples (ca. 100 mg) were loaded into the quartz reactor tube and heated under constant flow of 20 vol% O_2/Ar to 500°C before cooling to room temperature. TPRs were recorded in 10 vol% H_2/Ar (20 mL·min⁻¹ at STP) and at a heating rate of 5°C·min⁻¹. The reoxidation temperature at which Ni is reversibly reincorporated into the perovskite lattice was estimated by TPR redox experiments. A TPR profile was recorded on the calcined sample up to 600°C followed by isothermal reduction for 1 h at the same temperature. After cooling to 25°C in Ar, the sample was heated to 400°C in 20 vol% O_2/N_2 and reoxidized at this temperature for 2 h. The sample was again cooled in Ar to 25°C before starting the second TPR. Such TPR-reduction-reoxidation-TPR cycles were repeated four times with increasing the reoxidation temperature (400°C, 500°C, 600°C and 700°C). The heating rate during reoxidation and cooling after all experiments was 10°C·min⁻¹.

Changes in the microstructure of the samples were studied using scanning electron microscopy (field emission SEM, Zeiss ULTRA 55) on calcined samples as well as samples subjected to five catalytic tests alternated to five redox cycles. Nickel particle size distributions were obtained on the samples after catalytic testing using the ImageJ open source software package [42] by measuring and counting at least 650 particles. The minimum area analyzed on each sample was $2.5 \mu\text{m}^2$. The particle density was obtained by dividing the number of counted particles by the analyzed area. Particle density is used here instead of dispersion because we were not able to measure Ni dispersion by chemisorption likely as a result of the mean Ni particle size obtained after reduction, the low fraction of reduced Ni and the low specific surface area of the materials.

Catalytic activity tests towards CO_2 methanation were carried out on a homemade test setup in a quartz reactor of plug flow geometry (6 mm ID). Mass flow controllers (Brooks) were used to dose the reactant gases and a K-type thermocouple, which was placed in the middle of the catalyst bed, was used to monitor catalyst bed temperature. To avoid back pressure, all calcined powders were pelletized (4 MPa), crushed and sieved to 100-150 μm before use. The catalyst (100 mg) was diluted with cordierite powder (200 mg, 75-100 μm) to achieve a thoroughly mixed catalyst bed of ca. 15 mm in length. The reactant gas containing 8 vol% CO_2 , 32 vol% H_2 (rest Ar) was fed at a total flow rate of $50 \text{ mL} \cdot \text{min}^{-1}$ at STP resulting in a weight hourly space velocity (WHSV) of $30,000 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$. Prior to the catalytic tests, the sample was subjected to pre-reduction (20 vol% H_2/Ar , 600°C , 1 h). The experiment was then started at 600°C under reaction conditions and the reactor cooled to 300°C at $5^\circ\text{C} \cdot \text{min}^{-1}$ while recording catalytic activity. The reactor was then heated to 650°C in constant flow of Ar before conducting catalyst reoxidation (20 vol% O_2/Ar , 650°C , 2 h) and subsequent reduction

(20 vol% H₂, 600°C, 1 h). After the redox treatment catalyst activity was again recorded between 600°C and 300°C. This sequence was repeated four times. All gas lines were made of stainless steel and heated to 120°C to avoid condensation. A Pfeiffer OmniStar GSD 320 quadrupole mass spectrometer equipped with a heated stainless steel capillary was used for compositional analysis of the exhaust gas. CO₂ conversion (X_{CO_2}) and CH₄ yield (Y_{CH_4}) were calculated using equations 1 and 2, respectively,

$$X_{CO_2} = \frac{[CO_2]^{in} - [CO_2]^{out}}{[CO_2]^{in}} \times 100\% \quad (1)$$

$$Y_{CH_4} = \frac{[CH_4]^{out}}{[CO_2]^{in}} \times 100\% \quad (2)$$

where $[CO_2]^{in}$ is the initial concentration of CO₂ and $[CH_4]^{out}$ and $[CO_2]^{out}$ are the concentrations of CH₄ and CO₂ at the reactor outlet, respectively.

Ni K-edge (8.333 keV) X-ray absorption spectroscopy (XAS) data were collected on calcined and pre-reduced samples (10 vol% H₂/Ar, 600°C, 1 h) at the beamline SuperXAS of the Swiss Light Source (SLS, Villigen, Switzerland). The beam current and beam energy within the storage ring were 400 mA and 2.4 GeV, respectively. XAS spectra were collected in fluorescence mode using an ionization chamber filled with N₂ to measure incoming beam intensity and a Passivated Implanted Planar Silicon (PIPS) detector mounted at 90° to the incoming X-ray beam. Fluorescence mode was selected due to the high absorption cross section of the host perovskite at the Ni K-edge. The X-ray beam was collimated using a Si coated mirror, which was also used for the reduction of higher harmonic contributions while the X-ray energy was continuously scanned around the Ni absorption edge using a Si(111) channel-cut monochromator [43][43]. The beam was focused to a spot size of 1.0 mm x 0.2 mm (height x width) using a Rh-coated toroidal mirror. Measurements were performed on

pelletized samples after pretreatment and cooling in Ar. Reference spectra of metallic Ni (Ni^0) and NiO (Ni^{2+}) were collected in transmission mode using Ni foil and diluted NiO (Sigma-Aldrich, 99.99%), respectively. The Demeter software package (version 0.9.24) [44] was used for data reduction and linear combination fitting within the energy range 8.313 - 8.363 keV.

Results and discussion

X-ray diffraction (XRD) patterns of the calcined $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ (LFNO; tolerance factor $t = 1.04$), $\text{La}_{0.95}\text{Sr}_{0.05}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ (LSFNO-5Sr; $t = 0.808$) and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ (LSFNO-10Sr; $t = 0.808$) are displayed in Figure 1a. All powder samples exhibited similar patterns corresponding to the orthorhombic perovskite-type unit cell also observed for undoped LaFeO_3 [8, 27].

All reflections slightly shifted to higher angles, which reflects a decrease in unit cell volume with increasing Sr content. This is best represented by the small difference in the position of the main (121) reflection, which shifted from 32.33° to 32.39° 2θ with increasing Sr content (Figure 1b). Because the ionic radius of twelve-fold coordinated Sr^{2+} is larger than that of La^{3+} in the same coordination (1.44 Å vs. 1.36 Å) [38] unit cell contraction is not likely to be caused directly by the introduction of A-site cations of different sizes. Charge compensation could be also achieved through an increase in oxidation state of the B-site elements, which would however lead to increased B-site ion radii and eventually to lattice expansion. It is more likely that the observed unit cell contraction is a result of the more prominent effect of the formation of oxygen vacancies induced by the decreased charge at the A-site to maintain charge neutrality. The absence of further phases, for example Sr-containing and the shift of the PMO

reflections with increasing Sr content confirm that the samples were phase pure. Besides shifts, also significant peak broadening was observed for Sr-containing samples. The crystallite sizes estimated using the Scherrer equation [41] were 41 ± 1 nm, 22 ± 2 nm and 19 ± 2 nm for LFNO, LSFNO-5Sr and LSFNO-10Sr, respectively. The decrease in crystallite size with increasing Sr content was accompanied by an increase in specific surface area from $6.2 \pm 0.5 \text{ m}^2\cdot\text{g}^{-1}$ (LFNO) to $7.5 \pm 0.5 \text{ m}^2\cdot\text{g}^{-1}$ (LSFNO-5Sr) and to $9.4 \pm 0.5 \text{ m}^2\cdot\text{g}^{-1}$ (LSFNO-10Sr).

Reducibility and stability of the perovskite host during high-temperature reduction was assessed by recording in situ XRD patterns during isothermal reduction experiments (10 vol% H_2/N_2 , 600°C) using a lab source. Contour plots summarizing these experiments are shown in Figure 2. While LFNO did not exhibit phase changes due to reduction and a La_2O_3 phase did not form over 40 h of the experiment (Figure 2a), both Sr-containing samples showed appearance and growth of the characteristic reflections of a metallic Ni/Fe phase, starting after 7 h (LSFNO-5Sr, Figure 2b) and 3 h (LSFNO-10Sr, Figure 2c) into the experiment. This is a strong indication that the increasing Sr content increasingly destabilizes the LFNO perovskite-type oxide, thus promoting the reduction of B-site elements. Whether this reflects increased Ni reducibility and segregation and thus catalytic activity has to be demonstrated.

The element specific X-ray absorption near edge structure (XANES) analysis of the Ni K-edge (8.333 keV) was used to investigate the effect of Sr on Ni reduction. The spectra of both calcined and reduced (10 vol% H_2/Ar , 600°C , 1 h) LFNO, LSFNO-5Sr and LSFNO-10Sr are presented together with the spectra of Ni^0 (Ni foil) and NiO references in Figure 3. The spectra of all calcined samples were very similar, indicating both similar oxidation states as well as coordination geometry. This is not surprising since Sr substitution of La was kept at a low level and Ni K-edge XANES may be only

significantly influenced for higher degrees of A-site substitution. The spectra can be assigned to Ni in octahedral coordination ($\text{Ni}^{n+}_{\text{oct}}$, $n > 2$).⁸

The spectra of the reduced samples exhibited decreased whiteline intensity and resembled a linear combination of the spectrum of $\text{Ni}^{n+}_{\text{oct}}$, obtained for calcined LFNO, and of the Ni^0 reference. This indicated partial reduction of Ni in all samples. Linear combination fit (LCF) was used to quantify the contribution of Ni^0 to the spectra of the reduced materials. Corresponding fitted spectra as well as contributions of individual spectra to the final fit are displayed in Figure S1. An increased contribution of Ni^0 was observed with increasing Sr content. Ni^0 concentration increased from $29 \pm 3\%$ for LFNO to $31 \pm 3\%$ for LSFNO-5Sr and to $38 \pm 3\%$ for LSFNO-10Sr. The increase in the extent of Ni reducibility may be a direct consequence of the decreased stability of the host perovskite towards reduction of the B-site elements as observed in Figure 2.

Analysis of the extended X-ray absorption fine structure (EXAFS) spectra was used to follow Ni-Ni bond formation during reduction, which is indicative of Ni particle formation. Plots of k^3 -weighted $\chi(k)$ functions of all samples and of Ni^0 and NiO references are presented in Figure S2. The corresponding Fourier transforms are displayed in Figure 4. All reduced samples presented the contribution at $2.1 \text{ \AA}$ that is also present in the Ni^0 reference and is characteristic of the first Ni coordination shell in Ni metal, thus providing evidence for Ni-Ni bond and Ni particle formation. While this feature was weak in reduced LFNO (Figure 4b), its intensity increased in reduced LSFNO-5Sr (Figure 4c) and LSFNO-10Sr (Figure 4d). This is readily interpreted with the increase in the fraction of metallic Ni that is present in the form of Ni particles after reduction with increasing Sr content. This effect may be beneficial for catalyst activity because Sr-containing samples could exhibit higher Ni metal level at the perovskite surface. However, catalyst activity towards CH_4 formation in CO_2 methanation is eventually

determined by Ni metal specific surface area and is thus also dependent on Ni particle size.

Despite the apparent stability of all samples against complete reduction to the single metal and metal oxides components for at least 3 h (Figure 2), XRD may be not sensitive to the formation of only few and small crystallites of Ni metal or Ni/Fe alloy as well as the La_2O_3 phase especially at the beginning of the reduction. The potential partial decomposition, which was likely present on Sr-containing samples, may hinder complete Ni reincorporation and the structural reversibility over repeated regeneration cycles. It was shown previously that LFNO calcined at 700°C exhibited complete structural reversibility after reoxidation (20 vol% O_2/N_2 , 650°C , 2 h) [7, 8].

TPR was used to determine Ni speciation on the samples after redox cycles. Ni speciation through TPR is feasible as the reduction temperature of oxidized Ni species differs depending on the Ni coordination environment. Under the selected TPR conditions NiO species reduce at higher temperatures (ca. $300\text{--}400^\circ\text{C}$) than Ni in the coordination environment of the B-site of PMO (ca. $150\text{--}300^\circ\text{C}$, $\text{Ni}^{n+}_{\text{oct}}$) [27]. Figure 5 shows the results of TPR-redox cycles with increasing reoxidation temperatures. Whenever Ni was incorporated within the perovskite lattice in the form of $\text{Ni}^{n+}_{\text{oct}}$ ($n > 2$) during reoxidation, the subsequent TPR exhibited only a low temperature reduction event starting at 150°C and peaking at 273°C for LFNO (Figure 5a), 271°C for LSFNO-5Sr (Figure 5b) and 252°C for LSFNO-10Sr (Figure 5c). These values are lower than the temperature required to reduce bulk NiO (Figure 5a) and NiO deposited on LaFeO_3 by impregnation [8]. Whenever the reoxidation temperature between the TPR cycles was not high enough to completely restore all $\text{Ni}^{n+}_{\text{oct}}$, Ni was oxidized to NiO at the surface of the perovskite, thus producing an additional reduction feature at higher temperature in the following TPR run. The intensity of the feature distinctive of NiO

decreased with increasing oxidation temperature from 400°C to 700°C for all compositions and vanished at 700°C. This suggests that complete Ni reincorporation occurs at temperatures between 600°C and 700°C in all samples.

All samples were further subjected to five consecutive TPR-TPO redox cycles at constant reoxidation temperature (650°C). This allowed to refine the temperature of Ni reincorporation and to emphasize subtle differences between samples. Figure 6 shows the TPR profiles collected during these redox experiments. Appearance of a reduction event at ca. 330°C due to reduction of NiO could be regarded as a sign of structural irreversibility. LFNO did not display such feature in all redox cycles (Figure 6a). While it was observed in LSFNO-5Sr (Figure 6b) and LSFNO-10Sr (Figure 6c), this feature did not grow indicating that the redox experiment did not affect further the existing fraction of NiO. On the contrary, redox cycles involving reoxidation at 600°C for 2 h evoked the growth of such a feature in all three samples (Figure 6d, LFNO; Figure 6e, LFSNO-5Sr; Figure 6f, LSFNO-10Sr) and thus an increasing fraction of NiO. While this phenomenon was hardly visible in LFNO, it was significant in the LSFNO-type materials suggesting that Ni reincorporation was more difficult on the latter. The decreased stability of the perovskite lattice due to Sr introduction likely caused a reduction of the thermodynamic driving force for Ni reincorporation. Hence, higher temperatures are required to restore $\text{Ni}^{\text{n+}}_{\text{oct}}$ in the presence of Sr.

CO_2 methanation activity and CH_4 yield were measured on pre-reduced samples (20 vol% H_2/Ar , 600°C, 1 h) after each of five redox cycles. A redox cycle was composed of a reduction segment, reaction and an oxidation segment. This sequence was repeated five times. Since the PMO surface is highly selective towards the reverse water gas shift reaction and thus to CO production [8], CH_4 production can be anticipated to occur only on Ni metal surfaces. Therefore, CH_4 yield can be used to

assess changes in Ni specific surface area along the redox cycles, which is dependent on both the quantity of segregated Ni as well as the Ni particle size. Figure 7 shows the CO₂ conversion data of LFNO (Figure 7a), LSFNO-5Sr (Figure 7b) and LSFNO-10Sr (Figure 7c) measured after each redox cycle. The CH₄ yields on these materials are low likely as a result of a combination of low specific surface area and low amount of exposed Ni. On all samples CO₂ conversion improved significantly with increasing number of redox cycles as indicated by the shift of the conversion curves towards lower reaction temperatures. It is also apparent that while CO₂ conversion appeared to have reached the maximum already after a single redox cycle on LSFNO-10Sr, LSFNO-5Sr showed an increase in activity towards CO₂ conversion after three redox cycles while catalytic activity of LFNO stabilized only after four redox cycles. The corresponding CH₄ yields reflect the same behavior (Figure 7d-f) indicating that the accessible Ni surface area stabilized only after four and three redox cycles on LFNO and LSFNO-5Sr, respectively. Furthermore, LSFNO-5Sr exhibited highest CH₄ yields of around 20% at 470°C, whereas maximum CH₄ yield was 16% (at 480°C) and 13% (480°C) for LFNO and LSFNO-10Sr, respectively.

A plausible reason for the improved activity of LSFNO-5Sr compared to LFNO and LSFNO-10Sr can be found by comparison of the scanning electron micrographs (SEM) of the calcined materials (LFNO, Figure 8a; LSFNO-5Sr, Figure 8d; LSFNO-10Sr, Figure 8g) and of the samples after the catalytic tests of Figure 7 (LFNO, Figure 8b; LSFNO-5Sr, Figure 8e; LSFNO-10Sr, Figure 8h). In the calcined state, none of the samples exhibited features other than what could be assigned to the perovskite phase. However, on the reduced materials after redox cycling and catalytic testing, small particles were clearly present on all three materials. Significant differences could be found for both the size distributions as well as the particle density. The median particle

size was lowest for LSFNO-5Sr (6 - 8 nm; Figure 8f), whereas it was significantly higher (10 - 12 nm) for both LFNO (Figure 8c) and LSFNO-10Sr (Figure 8i). Furthermore, particle density was also highest for LSFNO-5Sr (ca. 300 μm^{-2}) compared to LFNO (ca. 100 μm^{-2}) and LSFNO-10Sr (ca. 150 μm^{-2}). Thus, we attribute the increase in CH_4 yield on LSFNO-5Sr compared to undoped LFNO not only to a larger extent of Ni reduction observed by Ni K-edge XANES (Figure S1), but also to the improved morphology of the catalyst after reduction, i.e. lower median Ni particle size, higher particle density and thus higher Ni specific surface area. Despite the fact that the extent of Ni reduction was further increased, the observed decrease in CH_4 yield with further Sr addition to yield LSFNO-10Sr can be tentatively explained by Ni particle size and density as these did not seem to deviate significantly from the values obtained for LFNO. It should be noted that due to the increased reducibility of LSFNO-10Sr compared to the other two compositions, also Fe of the host PMO started to reduce, thus contributing to particle formation and likely increased Fe content in the Ni particles. It cannot be excluded that the presence of Fe in the Ni catalyst may modify catalytic activity as well as selectivity towards CH_4 production during CO_2 methanation [45]. We lack information on the detailed surface composition of the samples before and after Ni segregation with respect to the other elements that does not allow us to conclude on the role of the support material on CH_4 production in the presence of Ni particles. The surface composition could change under the reduction and oxidation conditions to which the samples are exposed.

Conclusions

Partial substitution of La by Sr on the A-site of $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ led to significant decrease in perovskite phase stability towards reduction. As a result increased amounts of B-site Ni could be segregated to the perovskite surface, forming Ni particles active towards the hydrogenation of CO_2 to CH_4 . The degree of Nickel reduction at 600°C was found to increase with Sr content and was highest for $\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$. However, despite the low levels of substitution, highest CH_4 yields were found for the intermediate composition $\text{La}_{0.95}\text{Sr}_{0.05}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$, which exhibited increased Ni reduction compared to Sr-free $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$, decreased median particle size of the segregated Ni particles as well as highest particle density. Therefore, La substitution on the perovskite A-site by Sr can be used to increase Ni segregation as well as catalytic activity. The observed changes in catalytic activity are attributed mainly to the presence of the Ni particles, but we cannot discard effects of the surface composition that have been produced upon reduction. The decreased stability of Sr-containing compositions towards reduction at elevated temperatures did not affect the structural reversibility of the materials over short redox cycles at 650°C . However, indications were found that Ni reincorporation was increasingly more difficult with increasing Sr content. Furthermore, Sr-doping may cause difficulties in the case of prolonged operation in the highly reducing atmospheres and at the constant elevated temperatures typically experienced by a CO_2 methanation catalyst due to decreased material stability towards reduction. Although limits of structural reversibility at 650°C were not observed throughout the experiments shown in this work, it is likely that high degrees of perovskite-decomposition after prolonged reduction would not allow for complete structural reversibility at similar reoxidation conditions as were applied here.

Acknowledgements

The authors are thankful for the financial support from the Swiss National Science Foundation (SNF, No. 200021_159568) and the Competence Center for Energy and Mobility (CCEM). The work was conducted in the context of the Swiss Competence Center for Energy Research (SCCER BIOSWEET) of the Swiss innovation agency Innosuisse. The X10DA (SuperXAS) beamline at the Swiss Light Source (SLS) in Villigen (Switzerland) and Dr. M. Nachtegaal are thanked for kindly providing the beam time and support during measurements.

References

- [1] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, N. Hamada, *Nature*, 418 (2002) 164-167.
- [2] D. Neagu, G. Tsekouras, D.N. Miller, H. Menard, J.T.S. Irvine, *Nat. Chem.*, 5 (2013) 916-923.
- [3] D. Burnat, R. Kontic, L. Holzer, P. Steiger, D. Ferri, A. Heel, *J. Mater. Chem. A*, 4 (2016) 11939-11948.
- [4] D. Neagu, T.S. Oh, D.N. Miller, H. Ménard, S.M. Bukhari, S.R. Gamble, R.J. Gorte, J.M. Vohs, J.T.S. Irvine, *Nat. Commun.*, 6 (2015) 1-8.
- [5] H. Tanaka, M. Taniguchi, M. Uenishi, N. Kajita, I. Tan, Y. Nishihata, J. Mizuki, K. Narita, M. Kimura, K. Kaneko, *Angew. Chem. Int. Edit.*, 45 (2006) 5998-6002.
- [6] P. Steiger, D. Burnat, H. Madi, A. Mai, A. Holzer, J. Van Herle, O. Kröcher, A. Heel, D. Ferri, *Chem. Mater.*, (2019).
- [7] P. Steiger, M. Nachtegaal, O. Kröcher, D. Ferri, *ChemCatChem*, 10 (2018) 4456-4464.
- [8] P. Steiger, R. Delmelle, D. Foppiano, L. Holzer, A. Heel, M. Nachtegaal, O. Kröcher, D. Ferri, *ChemSusChem*, 10 (2017) 2505-2517.
- [9] J. Kuc, Y.C. Zhang, R. Erni, S. Yoon, L. Karvonen, A. Weidenkaff, S.K. Matam, *Phys. Status Solidi RRL*, 9 (2015) 282-287.
- [10] M. Araki, V. Ponec, *J. Catal.*, 44 (1976) 439-448.

- [11] P. Schoubye, *J. Catal.*, 14 (1969) 238-246.
- [12] J.L. Falconer, A.E. Zağli, *J. Catal.*, 62 (1980) 280-285.
- [13] G. Garbarino, D. Bellotti, P. Riani, L. Magistri, G. Busca, *Int. J. Hydrogen Energ.*, 40 (2015) 9171-9182.
- [14] G.A. Mills, F.W. Steffgen, *Catal. Rev.*, 8 (1973) 159-210.
- [15] C. Vogt, E. Groeneveld, G. Kamsma, M. Nachtegaal, L. Lu, C.J. Kiely, P.H. Berben, F. Meirer, B.M. Weckhuysen, *Nat. Catal.*, 1 (2018) 127-134.
- [16] J.G. Xu, G.F. Froment, *AIChE J.*, 35 (1989) 88-96.
- [17] B.C. Enger, A. Holmen, *Catal. Rev.*, 54 (2012) 437-488.
- [18] J.L. Rogers, M.C. Mangarella, A.D. D'Amico, J.R. Gallagher, M.R. Dutzer, E. Stavitski, J.T. Miller, C. Sievers, *ACS Catal.*, 6 (2016) 5873-5868.
- [19] P. Gronchi, D. Fumagalli, R. Del Rosso, P. Centola, *J. Therm. Anal.*, 47 (1996) 227-234.
- [20] J.R. Rostrup-Nielsen, *J. Catal.*, 31 (1973) 173-199.
- [21] S.R. Li, J.L. Gong, *Chem. Soc. Rev.*, 43 (2014) 7245-7256.
- [22] C. Okolie, Y.F. Belhseine, Y.M. Lyu, M.M. Yung, M.H. Engelhard, L. Kovarik, E. Stavitski, C. Sievers, *Angew. Chem. Int. Edit.*, 56 (2017) 13876-13881.
- [23] C.H. Bartholomew, *Catal. Rev.*, 24 (1982) 67-112.
- [24] A.D. Moeller, C.H. Bartholomew, *Ind. Eng. Chem. Prod. Res. Dev.*, 21 (1982) 390-397.
- [25] K.E. Wilson, Heterogeneous catalysts for converting renewable feedstocks to fuels and chemicals, in: L. Gucci, A. Erdôhelyi (Eds.) *Catalysis for Alternative Energy Generation*, Springer, New York, 2012.
- [26] J.R. Rostrup-Nielsen, *Catal. Today*, 37 (1997) 225-232.
- [27] P. Steiger, I. Alxneit, D. Ferri, *Acta Mater.*, 164 (2019) 568-576.
- [28] F. He, X.N. Li, K. Zhao, Z. Huang, G.Q. Wei, H.B. Li, *Fuel*, 108 (2013) 465-473.

- [29] H. Ullmann, N. Trofimenko, *Solid State Ionics*, 119 (1999) 1-8.
- [30] K. Huang, H.Y. Lee, J.B. Goodenough, *J. Electrochem. Soc.*, 145 (1998) 3220-3227.
- [31] Y. Teraoka, H.M. Zhang, S. Furukawa, N. Yamazoe, *Chem. Lett.*, (1985) 1743-1746.
- [32] N.A. Merino, B.P. Barbero, P. Grange, L.E. Cadus, *J. Catal.*, 231 (2005) 232-244.
- [33] M.A. Peña, J.L.G. Fierro, *Chem. Rev.*, 101 (2001) 1981-2017.
- [34] S. Royer, D. Duprez, F. Can, X. Courtois, C. Batiot-Dupeyrat, S. Laassiri, H. Alamdari, *Chem. Rev.*, 114 (2014) 10292-10368.
- [35] J. Deng, M.D. Cai, W.J. Sun, X.M. Liao, W. Chu, X.S. Zhao, *ChemSusChem*, 6 (2013) 2061-2065.
- [36] S. Royer, H. Alamdari, D. Duprez, S. Kaliaguine, *Appl. Catal. B*, 58 (2005) 273-288.
- [37] F.H. Taylor, J. Buckeridge, C.R.A. Catlow, *Chem. Mater.*, 29 (2017) 8147-8157.
- [38] R.D. Shannon, C.T. Prewitt, *J. Inorg. Nucl. Chem.*, 32 (1970) 1427-1441.
- [39] M. Cherry, M.S. Islam, C.R.A. Catlow, *J. Solid State Chem.*, 118 (1995) 125-132.
- [40] C. Marcilly, P. Courty, B. Delmon, *J. Am. Ceram. Soc.*, 53 (1970) 56-57.
- [41] P. Scherrer, *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen*, 1918 (1918) 98-100.
- [42] J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J.Y. Tinevez, D.J. White, V. Hartenstein, K. Eliceiri, P. Tomancak, A. Cardona, *Nat. Methods*, 9 (2012) 676-682.
- [43] O. Müller, M. Nachtegaal, J. Just, D. Lützenkirchen-Hecht, R. Frahm, *J. Synchrotron Radiat.*, 23 (2016) 260-266.
- [44] B. Ravel, M. Newville, *J. Synchrotron Radiat.*, 12 (2005) 537-541.
- [45] D. Pandey, K. Ray, R. Bhardwaj, S. Bojja, K.V.R. Chary, G. Deo, *Int. J. Hydrogen Energ.*, 43 (2018) 4987-5000.

Figure 1 (a) Powder XRD patterns of LFNO, LSFNO-5Sr and LSFNO-10Sr after calcination. (b) Magnification around the perovskite (121) reflection.

Figure 2 Contour plots of XRD patterns during *in situ* reduction of (a) LFNO, (b) LSFNO-5Sr and (c) LSFNO-10Sr starting from calcined powders. The patterns of the materials after calcination (0 h) and at the end of the experiment (40 h, 37 h and 17 h) are shown. Markers indicate reflections of the perovskite-type host (blue), the decomposition product La_2O_3 (orange) and the Fe/Ni-containing metallic phase (green).

Figure 3 Normalized Ni K-edge (8.333 keV) XANES spectra of calcined and reduced (a) LFNO, (b) LSFNO-5Sr and (c) LSFNO-10Sr. The spectra of Ni foil and NiO reference materials are also included.

Figure 4 Fourier transformed k^3 -weighted Ni K-edge EXAFS data of (a) Ni foil (Ni^0) and NiO reference materials, (b) LFNO, (c) LSFNO-5Sr and (d) LSFNO-10Sr in their calcined states as well as after reduction (10 vol% H_2/Ar , 600°C, 1 h). Data are non-phase shift corrected. Features on the curves of the reduced material are labelled according to the underlying Ni-Ni scattering path for metallic Ni.

Figure 5 TPR reduction-reoxidation cycles for (a) LFNO, (b) LSFNO-5Sr and (c) LSFNO-10Sr. H_2 consumption values were normalized by the number of moles of sample used. Reoxidized samples were subjected to reduction (10 vol% H_2/Ar , 600°C, 1 h) before reoxidation at the given temperature (20 vol% O_2/N_2 , 2 h).

Figure 6 TPR reduction-reoxidation cycles with constant reoxidation temperature of 650°C for (a) LFNO, (b) LSFNO-5Sr and (c) LSFNO-10Sr and of 600°C in (d), (e) and (f), respectively. H_2 consumption values were normalized by the number of moles of sample used. Reoxidized samples were subjected to reduction (10 vol% H_2/Ar , 600°C, 1 h) before reoxidation at the given temperature (20 vol% O_2/N_2 , 2 h).

Figure 7 CO₂ conversion profiles of (a) LFNO, (b) LSFNO-5Sr and (c) LSFNO-10Sr measured between five consecutive redox cycles. The corresponding CH₄ yields are shown in (d), (e) and (f), respectively.

Figure 8 SEM images of calcined (a) LFNO, (d) LSFNO-5Sr and (g) LSFNO-10Sr and reduced samples after five redox cycles; (b) LFNO, (e) LSFNO-5Sr and (h) LSFNO-10Sr. Histograms representing particle size distributions of the freshly formed particles are shown in (c), (f) and (i) for LFNO, LSFNO-5Sr and LSFNO-10Sr, respectively. Scale bars on SEM images represent 200 nm.

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8