Reversible segregation of Ni in LaFe_{0.8}Ni_{0.2}O_{3±δ} during coke removal

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Abstract

The deactivation of supported nickel catalysts by coking is an important technological subject for many chemical processes, especially when high concentrations of unsaturated hydrocarbons are present in the feed gas. Here, the reversible segregation of Ni from a $\text{LaFeO}_{3\pm\delta}$ perovskite-type host lattice was exploited to completely recover a $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_{3\pm\delta}$ catalyst after it had been deliberately subjected to severe carbon deposition during CO_2 methanation in ethylene rich feed gas for several hours. Temperature programmed reduction, X-ray diffraction, electron microscopy, X-ray absorption spectroscopy and catalytic activity tests were used to follow the catalyst structure along the various steps of reduction, reaction, coking and subsequent regeneration, while Raman spectroscopy and electron microscopy were used to characterize the nature of the carbon deposits. It is shown that upon reduction Ni atoms segregate to the surface of the perovskite to form catalytic active Ni particles. Oxidation stimulates Ni atoms to readopt the coordination environment of Fe in the perovskite matrix. This property persisted after severe catalyst deactivation by filamentous, partially graphitic carbon. It is demonstrated that simple catalyst reoxidation can be applied to oxidize all carbon deposits while additionally reverting segregated Ni back into the host lattice, thus protecting Ni from particle growth and resultant long-term loss of catalyst activity over multiple regeneration cycles.

Introduction

Nickel-based catalysts are widely exploited in a variety of industrially relevant catalytic reactions including water gas shift,^[1] hydrogenation of carbon oxides,^[2-7] dry and wet reforming of hydrocarbons,^[1, 8-10] dry reforming of methane and carbon dioxide,^[11] conversion of methane to methanol^[12] and the Fischer-Tropsch reaction.^[13] Nickel is applied at a large scale because of its high activity and relatively low cost compared to precious metals. However, depending on reaction conditions, Ni catalysts can deactivate strongly as a result of the deposition of carbon,^[9, 14-16] which requires catalyst regeneration in oxidizing feeds at high temperatures.^[17] Especially graphitic forms of carbon require regeneration temperatures above 600°C. Such conditions, but also the exothermicity of hydrogenation reactions or the high operating temperatures needed for dry and wet reforming of methane, contribute to catalyst deactivation by promoting Ni particle growth.^[18] On conventional supported Ni catalysts sintering is an irreversible catalyst degradation process, which typically limits the number of oxidative regeneration cycles that can be applied to recover coked Ni catalysts.

Under these circumstances there is an impelling need to search for alternative routes to maintain high catalyst activity over prolonged periods of time. Strategies include the increase of catalyst coking resistance by careful choice of support material (e.g. increasing metal support interaction was found to be highly beneficial towards coking resistance),^[19, 20] by tuning the Ni loading as well as doping of the active Ni phase by other elements.^[21] Such measures target the reduction of the frequency of necessary oxidative regeneration cycles as the rate of catalyst coking is reduced. Catalyst deactivation through sintering may be reduced by similar means but also through advanced synthesis methods such as encapsulation of the active Ni phase.^[22-24] Careful selection of the operating conditions can also contribute to improve catalyst lifetime but is not always feasible in the case of highly exothermic reactions. The process of oxidative regeneration (i.e. the burning of coke residues) can also be tuned to minimize further catalyst degradation through Ni sintering.^[25, 26]

Irrespective of these efforts, supported Ni catalysts are eventually destined to degrade and catalyst regeneration is only successful for a limited number of times since particle growth cannot be completely eliminated.

One class of materials has the potential to overcome the problem of catalyst degradation by oxidative regeneration. Catalysts derived from a Ni-containing perovskite-type mixed oxide (ABO_3 , where A and B are metal ions)^[27] can preserve Ni particle size distribution over multiple redox cycles, thus potentially allowing the catalyst to be reoxidized over a higher number of regeneration cycles than conventional catalysts.^[28-30] In these catalysts, Ni can disperse at an atomic level inside a redox and temperature stable perovskite-type host lattice by adopting the coordination environment of the B-site cation. This Ni, which we term incorporated Ni^{n+} , is selectively reduced during either reductive catalyst pre-treatment or during catalyst operation in reducing feeds at elevated temperatures. The reduced Ni then segregates to the surface of the perovskite crystallites, where it forms catalytically active, metallic Ni particles, which excel by very strong Ni particle-support interactions that can mitigate the propensity for coking.^[20, 31, 32]^[20, 31, 32] During catalyst reoxidation at sufficiently high temperatures,^[28, 29] Ni can diffuse back and readopt the coordination of the host perovskite lattice, thus restoring the original perovskite catalyst precursor and preparing the material for a new reaction cycle. Such reduction-reoxidation cycles can be repeated many times without loss of catalytic activity. This self-regenerating property has been demonstrated for a number of metals (mainly precious group elements such as Pd, Pt, Rh),^[33-36] lately also for the most abundantly used Ni, in particular for $LaFe_{0.8}Ni_{0.2}O_{3\pm\delta}$.^[28] However, despite the use of perovskite-type oxides of La-Fe-Ni-O composition to produce redox stable Ni catalysts, this property has not yet been explored as a route to remove carbon deposits without impacting Ni particle size. In this work, we demonstrate the feasibility of exploiting the regenerability of perovskite-based Ni catalysts derived from $LaFe_{0.8}Ni_{0.2}O_{3\pm\delta}$, which have suffered from deactivation towards the methanation of CO_2 through severe coke deposition.

Experimental

LaFe_{0.8}Ni_{0.2}O_{3±δ} (LFNO) was prepared via the amorphous citrate process.^[37] La(NO₃)₃·6H₂O (Sigma-Aldrich, 99.999 % trace metals basis), Fe(NO₃)₃·9H₂O (Sigma-Aldrich, ≥99.95 % trace metals basis) and Ni(NO₃)₂·6H₂O (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, ≥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 700°C for 2 h (5°C/min to 200°C; then, 10°C/min to 700°C) to obtain the calcined sample. The specific surface area (SSA) of the calcined powder was determined from N₂-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 determination.

The catalyst was characterized with respect to its textural and microstructural properties over a series of consecutive treatments: in its calcined state, oxidized after five redox cycles (red: 600°C, 20 vol% H₂/Ar, 1 h; ox: 650°C, 20 vol% O₂/Ar, 2 h), after subsequent reduction (600°C, 20 vol% H₂/Ar, 1 h), after coking (430°C, 8 vol% CO₂ / 32 vol% H₂ / 3000 ppm C₂H₄ / rest Ar, 9 h), after temperature programmed oxidation (10°C/min, 30-650°C, 20 vol% O₂/Ar) followed by isothermal oxidation at 650°C for 2 h and after a final reductive treatment (600°C, 20 vol% H₂/Ar, 1 h). The samples after each step are denoted as calcined, 5x redox, reduced, coked, reoxidized and regenerated. The treatments and schematic representations of the state of LFNO after each step are summarized in Scheme 1 for clarification. All sample treatments were carried out in a heated, tubular quartz reactor (6 mm ID) at weight hourly space velocity (WHSV) of 6,000 cm³g⁻¹h⁻¹ at STP conditions (0°C and 1 bar absolute pressure). Mass flow controllers (BROOKS) were used to regulate the required gas flows.

The crystal structure of the powder catalyst was investigated by ex situ powder X-ray diffraction (XRD, Bruker D8 Advance) equipped with Ni-filtered Cu K α -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 $\Delta 2\theta = 0.03^\circ$ between 2θ 15° and 80° . Prior to XRD analysis all treatments were carried out separately or in a sequence in the same heated tubular quartz reactor used for the catalytic study and the samples were cooled down in Ar after the corresponding treatment at elevated temperatures.

Hydrogen temperature programmed reduction (TPR) experiments were conducted on calcined and reoxidized powder samples using a bench top TPDRO-1100 (ThermoElectron) instrument equipped with mass flow controllers and a thermal conductivity detector. The TPR was conducted in 20 mL/min 10 vol% H_2 /Ar at STP (0°C , 10^5 Pa) with a heating ramp of $5^\circ\text{C}/\text{min}$.

Changes in the microstructure of the samples were studied using scanning electron microscopy (field emission SEM, Zeiss ULTRA 55). Powder samples were spread on sticky carbon pads and mounted on aluminum stubs before analysis. The samples were analyzed using a 1.0 keV electron beam and the in-lens secondary electron detector at a working distance of 1.2 mm. Typical magnifications in the range of 50,000-100,000 allowed the analysis of Ni particles of minimum size of 5-10 nm. Particle size distributions were obtained through visual analysis of the SEM images and by measuring the size of detected Ni particles using the ImageJ open source software package.^[38] The minimum sample area analyzed was $6\ \mu\text{m}^2$ and at least 500 particles were counted and measured.

Transmission electron microscopy (TEM) images were recorded with a JEOL JEM 2010 microscope equipped with a LaB_6 filament and a slow scan CCD camera (Gatan Inc.) at an acceleration voltage of 200 kV. Samples were prepared by depositing a droplet of an isopropanol suspension on a copper grid coated with lacey carbon.

Catalytic activity tests towards CO_2 hydrogenation 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 15 mm in length. The reactant gas containing 8 vol% CO₂, 32 vol% H₂ (rest Ar) was fed at a total flow rate of 50 mL/min at STP resulting in a weight hourly space velocity (WHSV) of 30,000 cm³g⁻¹h⁻¹. Prior to the catalytic tests the sample was in its reduced state (after five redox cycles). The experiment was then started at 430°C under reaction conditions. 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}) as well as CH₄ and CO yields (Y_{CH_4} and Y_{CO}) were calculated using equations 1, 2 and 3 respectively,

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

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

$$Y_{CO} = \frac{[CO]^{out}}{[CO_2]^{in}} \times 100 \% \quad (3)$$

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

Turn over frequencies (TOF) for CO₂ to CH₄ conversion were calculated under the assumption of ideal gas behavior of the reaction gas mixture. Furthermore it was assumed that only metallic Ni participates in CH₄ production and that all Ni surface atoms contribute equally to the observed activity. To calculate the number of available Ni sites it was assumed that all Ni⁰ (determined by linear combination analysis of X-ray absorption spectra) was present at the LFNO surface in form of spherical Ni particles with an average diameter of 12.3 nm found by SEM and submerged by 50% in the perovskite host crystallite (only 50% of Ni surface available for reaction).

Catalyst coking was performed at 430°C for 8 h in reactant gas stream containing 3000 ppm C₂H₄ to promote coking. CO₂ evolution during temperature programmed oxidation was followed using the mass spectrometer signal at $m/z = 44$.

Raman spectra were recorded on pre-treated powder samples using a Raman spectrometer (CW Raman RXN1-PhAT-785-D-laser Invictus, Kaiser Optical Systems Sarl) equipped with a CCD camera (1024 x 256 EEC MPP Type, Kaiser Optical Systems) with collimated incident radiation and a probe size of ca. 3 mm. Spectra were collected at ambient conditions by averaging 20 scans with 10 s exposure time at 1 cm^{-1} spectral resolution and at an average power of 100 mW.

Ni K-edge (8.333 keV) X-ray absorption spectroscopy (XAS) data were collected at the beamline X10DA (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 N_2 to measure incoming beam intensity and a Passivated Implanted Planar Silicon (PIPS) detector mounted at 90° to the incoming X-ray beam and the sample mounted at 45° . The 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 at 2 Hz.^{[39][39]} 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 quenching in Ar. Reference spectra of metallic Ni (Ni^0) and NiO (Ni^{2+}) were collected on calcined and reduced (600°C , 10 vol% H_2/Ar , 1 h) 4.8 wt% Ni/LaFeO₃ type materials, respectively. Ni was deposited on LaFeO_{3 $\pm$ δ} via wet impregnation with an aqueous solution of $\text{Ni}(\text{NO}_3)_2$ (Sigma-Aldrich, 99.999 % trace metals basis) followed by drying (70°C , 12 h, reduced pressure) and calcination (500°C , air, 2 h). These references were chosen because all spectra collected in fluorescence mode were influenced by self-absorption. Due to the strong absorbing nature of the sample, determination of a self-absorption correction factor was not possible. Using reference samples with similar composition and thus similar degrees of self-absorption was regarded as a suitable alternative. The Demeter software package (version 0.9.24)^{[40][40]} was used for data reduction and linear combination fitting within the energy range 8.313 - 8.363 keV.

The Ni surface area was measured with a Quantachrome Autosorb I instrument through H₂-chemisorption on 2 g of reduced sample. The measurement was performed at 40°C on outgassed samples (600°C, 2 h) using H₂ (Carbagas, 4.8). The monolayer adsorption at 0 mbar was determined using a 7-point measurement method ($107 \text{ mbar} \leq P \leq 747 \text{ mbar}$) and back extrapolation of the linear adsorption isotherm.

Results

LaFe_{0.8}Ni_{0.2}O_{3±δ} (LFNO, 12.4 m²g⁻¹) has been previously shown to exhibit complete structural reversibility under the reoxidation conditions (20 vol% O₂, 650°C, 2 h) also applied in this work.^[28] It was also demonstrated that Ni is preferentially reduced from LFNO and segregated to the LFNO surface, forming metallic Ni particles under reducing conditions. An increase in Ni segregation was found over five consecutive oxidation-reduction treatments after which complete redox stability was observed. Nickel coordination and oxidation states vary reversibly between octahedral Niⁿ⁺ (n≥2) inside the perovskite upon oxidation (corresponding to B-site occupancy and termed incorporated Ni) and Ni⁰ upon reduction. Metallic Ni particles form under reducing conditions. Figure 1 shows the progress of CH₄ yield during an isothermal coking experiment on reduced LFNO at 430°C over the course of 9 h. CH₄ evolution was monitored throughout the experiment not only to determine catalyst activity but it was the relative change in CH₄ yield, which reflects changes in number, size and morphology of the catalytically active Ni particles that was of outmost interest to observe over the course of the experiment. First, the reaction was operated at 430°C for 30 min without C₂H₄ addition (activity regime I in Figure 1). CO₂ conversion in this regime was 21% and the catalyst exhibited a total methane yield of 7%, which corresponds to a turnover frequency (TOF) of 0.7 mol_{CH₄}mol_{Ni}⁻¹s⁻¹ assuming that only surface Ni atoms are involved in CH₄ production. These TOF values should be treated with caution and only serve as indicators as several assumptions, which are listed in the experimental section, were made for their calculation. CO was the other reaction product at higher yields of 19% since the Ni-free perovskite surface is active towards the reverse water gas shift reaction.^[28] CH₄ yield progressed rapidly through a maximum when 3,000 ppm of C₂H₄ was introduced before

decreasing to ca. 40 % of the initial value (regime II). After 15 min, CH₄ formation started increasing steadily at a low rate (III) until C₂H₄ was removed from the feed after 8.5 h, after which CH₄ yield rapidly dropped (IV). This observation suggests that the initial increase in CH₄ production originated from the decomposition of C₂H₄ and is a strong indication of the high reactivity of C₂H₄.^[41] We consider that the observed increase in CH₄ production over time in regime III originates from decomposition of C₂H₄ as the drop in CH₄ yield in regime IV demonstrates. During catalyst deactivation also CO yield dropped to 7%. Over the subsequent temperature programmed oxidation (TPO, 20 vol% O₂/Ar) up to 650°C, the temperature at which Ni was found to disperse and revert into LaFeO_{3±δ}, significant amounts of CO₂ were produced due to the oxidation of the formed carbon residues (vide infra). After oxidation at 650°C, the subsequent catalyst reduction at 600°C completed the regeneration of the active Ni metal species. CH₄ yield after this redox cycle (V) was higher compared to that measured in the reaction time before coking (I) and the TOF reached 0.8 mol_{CH₄}mol_{Ni}⁻¹s⁻¹. CO yield also increased back to its original value and even slightly above (20% in regime V). The activation in terms of CH₄ yield is in line with previous observations on the same material showing that the amount of Ni particles present on the surface increased after redox cycling^[28] but also likely as a result of the prolonged reaction time in the reducing feed used in this work. This latter possibility was checked by the measurement of the specific Ni surface area by H₂-chemisorption during isothermal reduction of LFNO at 430°C and at various reduction times. Because of the typically low specific BET surface area of LFNO a large mass of the material had to be used. While we could not obtain a meaningful value from chemisorption after the first reduction of calcined LFNO for 1 h indicating the segregation of a very low fraction of surface Ni atoms after a single reduction event, the specific Ni surface area was 0.26±0.01 m²g⁻¹ and 0.36±0.01 m²g⁻¹ after reduction for 10 h and 50 h, respectively. The detection limit of the instrument and technique was around 0.1 m² of total Ni surface area, which leads to the conclusion that after the initial 1 h reduction the specific Ni surface area was less than 0.05 m²g⁻¹.

To demonstrate the advantage of the structural reversibility in the case of a coked catalyst, the deactivation and regeneration processes were followed by characterizing the catalyst with respect to its textural and microstructural properties after each of the consecutive treatments depicted in Scheme 1: in its calcined state (calcined), oxidized after five redox cycles (5x redox), after subsequent reduction (reduced), after reaction and coking (coked), after reoxidation (reoxidized) and after the final reductive treatment to complete catalyst regeneration (regenerated).

Figure 2 shows a series of electron microscopy images of LFNO after these treatments. The surface of the calcined sample appeared clean and individual perovskite crystallites of 30 – 100 nm in size were clearly visible (Figure 2-a). After the reductive treatment (after five redox cycles) the perovskite surface was covered by particles (Figure 2-b) containing mainly metallic Ni, which is preferentially reduced and segregates to the perovskite surface to form catalytically active particles, whereas both La and Fe remain in their original oxidation states.^[28, 30] Particle sizes range from less than 5 nm to around 25 nm, where the lower limit was given by the resolution of the scanning electron microscope used during analysis. Subjecting the activated material to the CO₂ methanation reaction feed containing 3000 ppm C₂H₄ resulted in formation of filamentous carbon clearly visible in the scanning electron (SEM) image in Figure 2-c. Individual filaments grew multiple microns in length and some were terminated by Ni particles. This is in good agreement with the mechanism proposed for the formation of filamentous carbon on Ni catalysts, where dissociated carbon initially adsorbed on the Ni surface diffuses through the bulk of the particle to the Ni/support interface. There it builds up the carbon filament detaching and lifting up the Ni particle.^[14, 15, 42] The separation of Ni particles from the perovskite host lattice could have serious implications on the reversible segregation of Ni back into the perovskite lattice as the close contact between particle and support is lost. If contact to the support surface can be re-established during reoxidation, differences in local composition between the original and new particle location may prevent reincorporation. Transmission electron (TEM) imaging on these carbon filaments revealed the presence of graphitic carbon, which can be identified by the

regularly spaced layers on the image due to graphene layers (inset of Figure 2-d). The spacing of these layers (0.330 nm) is close to the theoretical value of 0.335 nm for graphene layer spacing in graphite. TPO followed by isothermal reoxidation at 650°C for 2 h removed all carbon filaments (Figure 2-e). Ni particles also disappeared thus restoring the appearance of the material surface to that of the initial calcined catalyst (Figure 2-a). This suggests complete re-incorporation of Ni into the perovskite lattice.^[28] Ni particles reappeared after subsequent reduction, which concluded catalyst regeneration (Figure 2-f).

Figure 3-a shows X-ray diffractograms of LFNO after each subsequent treatment. Calcined LFNO only exhibited reflections of a single perovskite phase corresponding to the orthorhombic crystal symmetry (Pm-3m). The presence of secondary phases (Ni^0 , NiO , La_2O_3 , $\text{La}_2\text{Ni}_2\text{O}_5$, $\text{La}_2\text{O}_2\text{CO}_3$ etc.) especially after reductive treatments could not be determined by X-ray diffraction (XRD). However, the presence of these phases should still be considered due to the possible existence of such particles with small crystallite size (<3 nm) or amorphous character. Structural changes caused by the pre-treatments can only be recognized in XRD by the shift of the characteristic reflections of the perovskite phase. The angular range of 32-33°, magnified in the inset of Figure 3-a, contains the main perovskite reflection (121). Two positions were observed systematically that are evidence for this reflection depending on whether the sample was subjected to an oxidative (e.g. calcination and reoxidation, $2\theta = 32.298^\circ$) or reductive (for reduction and coking, $2\theta = 32.226^\circ$) treatment prior to the XRD measurement. The distances between 121 reflection planes (d_{121}) determined by Bragg's law were $d_{121} = 2.770 \text{ \AA}$ for the oxidized material and $d_{121} = 2.776 \text{ \AA}$ in case of the reduced material. The difference can be assigned to the unit cell expansion during reduction caused by the increased ionic radii of partially reduced vs. completely oxidized Ni atoms within the perovskite lattice ($R_{\text{Fe}^{3+}}=0.55 \text{ nm}$; $R_{\text{Ni}^{3+}}=0.56 \text{ nm}$ vs. $R_{\text{Ni}^{2+}}=0.69 \text{ nm}$)^[43] as well as the likely formation of defects as a consequence of reduction and Ni segregation.^[44] The reversibility in the diffraction pattern suggested complete structural reversibility of LFNO over coking and regeneration and indicated that the perovskite-type host did not suffer from irreversible degeneration throughout the cycle.

Hydrogen temperature programmed reduction (TPR) as well as Ni K-edge X-ray absorption near edge structure (XANES) analysis were used to confirm the incorporation of Ni during TPO and isothermal oxidation. When Ni was incorporated in the LFNO perovskite lattice as Ni^{n+} ($n > 2$), during TPR the material exhibited a low temperature reduction event starting at 150°C, peaking at 242°C and accompanied by a low temperature shoulder (Figure 3-b). This shape and its origin have already been discussed elsewhere.^[28] However, it is important to realize here that a difference in reduction temperature exists between incorporated Ni^{n+} and NiO. NiO reduces at temperatures between 250°C and 400°C, whereas incorporated Ni^{n+} reduces at lower temperatures of 150°C - 250°C. The high reduction temperatures are not only valid for bulk NiO but also for NiO deposited on $\text{LaFeO}_{3\pm\delta}$ by impregnation.^[28] Since NiO was not present in calcined LFNO, its presence in the reoxidised sample after coking would suggest that Ni had not re-incorporated into the perovskite and remained at the surface as NiO, thus contradicting structural regeneration of the catalyst during coke removal and re-oxidation. Hence, the evident absence of the reduction feature of NiO between 300°C and 400°C suggests the successful re-incorporation of Ni during TPO and the subsequent isothermal oxidation at 650°C for 2 h. Furthermore, the total H_2 consumption of the two oxidized samples ($0.13 \pm 0.01 \text{ mol}_{\text{H}_2}/\text{mol}_{\text{LFNO}}$) as determined from the area below the reduction profile did not change indicating that the total amount of Ni did not change neither over coking and regeneration. The histogram in Figure 3-c visualizes the similarities in particle size distributions observed on LFNO after reduction (Figure 2-b) and after regeneration (Figure 2-f). The largest Ni particle size observed after either pre-treatment was around 25 nm. The Ni particle density cannot be accurately determined in powder samples due to their inherent surface roughness but no relevant changes were observed between the two samples.

Ni K-edge XANES on LFNO samples at the various stages of the catalytic cycle are displayed in Figure 4-a. The spectra obtained on LFNO samples that experienced oxidation (calcination and reoxidation during regeneration) showed several differences compared to the spectra obtained for NiO and Ni^0 references: the plateau at 8360 eV (denoted as A in

Figure 4-a) compared to the local minimum in normalized absorbance observed for NiO. The NiO absorption edge was found at lower energies compared to LFNO indicating a higher oxidation state in Ni^{n+} than in NiO, i.e. $n > 2$ (B). Metallic Ni did not show a whiteline feature (C) but instead it showed the prominent absorption edge at 8333 eV that can be taken as a descriptor of reduced Ni (D). The absence of a whiteline is typical for metallic samples. The spectra of oxidized LFNO after five redox cycles (red) and of the reoxidized LFNO (after coking, orange) were nearly identical to the one obtained for calcined LFNO and characteristic of Ni^{n+} ($n \geq 2$) adopting the coordination environment of Fe inside the LFNO lattice.^[28] Upon reduction, the spectra displayed a decreased whiteline at the absorption edge but reduction was not complete. The spectra were composed of a linear combination of the spectra of calcined LFNO, Ni foil and NiO. The fraction of the different Ni components were determined by linear combination fitting (LCF), the results of which are displayed in Figure 4-b. Fitted spectra as well as statistical data of these fits are included in Figure S1 and Table S1, respectively. LFNO contained 100% of incorporated Ni^{n+} ($n \geq 2$) after the redox pretreatment consisting of the five consecutive oxidation-reduction cycles as well as after reaction, coking and reoxidation (reoxidized). The reduced sample (corresponding to the sample at the start of the activity regime I in Figure 1) contained 42.4% Ni^0 and 4.6% NiO, while the remaining Ni was incorporated Ni^{n+} (53%). The large fraction of reduced Ni is taken as evidence that the particles observed by SEM (Figure 2) are of metallic nature. The regenerated sample (at the start of regime V) resembled a combination of the three species including 45.6% Ni^0 and 7% NiO. The presence of NiO is a likely consequence of conducting these measurements ex situ on pelletized samples. The increased Ni^0 content in LFNO on the regenerated sample compared to the reduced sample indicated that indeed more Ni may have been available to catalyze CO_2 methanation. LCF fits as well as the similarity of the spectra obtained on LFNO after the initial redox pretreatment and after reoxidation after coking to the spectrum obtained on calcined LFNO demonstrated that besides the host perovskite-type oxide (see XRD Figure 3-a) also the state of Ni was completely reversible. Loss of segregated Ni particles during reoxidation of coked catalyst might also result in

reversible XANES spectra in the absence of Ni reincorporation. However, since the total amount of Ni did not change between the calcined and regenerated states (TPR, Figure 3-b) we can conclude that all Ni is reincorporated into LFNO even after Ni particles had been detached from the support by filamentous carbon.

Coke deposition during addition of C_2H_4 to the reaction feed for 8 h was significant. Figure 5-a shows the evolution of CO_2 during the subsequent TPO, according to an established procedure.^{[45][45]} CO_2 release (the only product) indicated that the oxidation of carbon deposits started at $350^\circ C$ and curve integration returned a total carbon content of $108 \pm 1 \text{ mg/g}_{cat}$. In contrast, in the absence of the added hydrocarbon, less than $1 \text{ mg}_{carbon}/\text{g}_{cat}$ was obtained by TPO. The exothermicity of the oxidation of carbon deposits can be seen in the temperature reading during the temperature ramp. CO_2 evolution continued (at much lower levels) up to temperatures of around $550^\circ C$, which justifies and illustrates the necessity of using high temperatures for catalyst regeneration ($650^\circ C$). However, TPO conducted on coked LFNO up to $980^\circ C$ (not shown) did not reveal further CO_2 formation, indicating that coke removal was complete after oxidation at $650^\circ C$. Figure 5-b shows the Raman spectra of the catalyst after reduction, coking and full regeneration in the range $900 - 1800 \text{ cm}^{-1}$. Compared to the featureless spectrum of the reduced catalyst, two broad signals appeared after coking. These signals can be assigned to the D (1300 cm^{-1}) and G (1600 cm^{-1}) bands of filamentous carbon, which was at least partially graphitic.^[46-48] Fitting of the bands with Gaussian type functions revealed the additional contributions of D2 and G2 bands typically assigned to defect contributions.^[49] The absence of all bands after regeneration further illustrates the removal of coke during the oxidative treatment after coking.

After assessing the suitability of LFNO for structural reversibility under redox cycles at high temperature and the potential exploitation of this property to counteract deactivation by carbon without loss of Ni surface area, we proceeded to the evaluation of the repeatability of this process over several reaction-coking-regeneration cycles. Regeneration of the coked catalyst occurred multiple times without any indication of catalyst deactivation over the number of regeneration cycles. This is shown in Figure 6 where CH_4 yield before (regime I in

Figure 1) and after C₂H₄ introduction (regime IV) is plotted for ten regeneration cycles (oxidation-reduction) identical to the one in Figure 1 (total experiment duration 180 h). The catalyst deactivated severely over each cycle (up to 90% loss of CH₄ yield) due to coking in the presence of C₂H₄. A comparably small deactivation (max. 10%) of the catalyst was also visible in the absence of C₂H₄, which can be attributed to the growth of Ni particles over the time on stream. However, it is interesting to observe that CH₄ yield continued to increase over the number of alternate reaction-regeneration cycles when C₂H₄ was added to the feed. The activation was negligible when the catalyst was subjected to the same experiment but with C₂H₄-free methanation feeds. This could either indicate increased Ni reduction in the presence of C₂H₄ or reveal size and morphological changes occurring to the Ni particles causing an increase in CO₂ conversion to CH₄.^{[7][7]} Increased Ni reduction in this context seems rather unlikely if one compares the reduction potential of the additional 3000 ppm C₂H₄ compared to the 32 vol% H₂ present in both cases. No increase in concentration of reduced Nickel was observed after LCF of Ni K-edge XANES (Figure 4-b). However, neither morphological changes nor significant changes in Ni particle size were detected by any characterization technique used in this work, which leaves room for speculation. The absence of catalyst deactivation over the number of redox cycles indicates that also no loss of Ni occurred in the catalyst bed despite the observation that some Ni particles had been clearly detached from their support by carbon filaments during coking.

The total carbon content detected during each reoxidation step of the regeneration cycle is also displayed in Figure 6 in both cases and shows that the carbon content was rather stable over the number of cycles. Without C₂H₄ addition, the amount of carbon was negligible, whereas a small increase by ~7% (116±1 mg/g_{cat} compared to 108±1 mg/g_{cat}) was measured in the first four cycles in the experiment with C₂H₄ after which the carbon content decreased steadily to 106±1 mg/g_{cat} after ten cycles. However, there is no apparent correlation between variation of the carbon content and catalyst activation. Since carbon content should in theory correlate to the amount of surface Ni and therefore also CH₄ yield, the absence of any correlation indicates that multiple factors contribute to catalyst activation due to C₂H₄. This is

currently the subject of further study. Nevertheless, together with the results of all other characterization methods the absence of long term catalyst deactivation over the number of coking-regeneration cycles can be interpreted as proof that the reversible segregation of Ni from the perovskite-type LFNO and reincorporation back into the host was possible also on severely coked materials. This property protected the catalyst from Ni particle growth during high temperature coke oxidation.

Conclusion

Successful catalyst regeneration from carbon deposition without loss of specific Ni surface area was demonstrated on a $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_{3\pm\delta}$ derived Ni catalyst used for the methanation of CO_2 . Catalyst deactivation was induced by the addition of C_2H_4 to the reaction feed resulting in the formation of filamentous carbon, which was partially graphitic in nature. Subsequent coke removal by oxidation in air required temperatures above 600°C . After catalyst reoxidation all carbon was removed as observed by electron microscopy and Raman spectroscopy. Coke deposition did not affect the self-regenerating property of $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_{3\pm\delta}$. The reversible segregation of Ni from the bulk of the perovskite-type metal oxide to the surface during reductive treatments and incorporation during reoxidation protected the catalyst from Ni sintering during the high-temperature oxidation-reduction cycle needed for catalyst regeneration. Such a perovskite material was regenerated a number of times and no indications were found that within the time scale of the measurements presented in this work the reversible segregation of Ni and the number of possible catalyst regeneration cycles are limited.

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Supporting information. Ni K-edge XANES linear combination fit results including plots of the weighted contribution of each reference to the fit and tabular representation of Ni speciation as well as goodness of fit.

Keywords. coking, Nickel catalyst, perovskite-type oxides, self-regeneration

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Figure captions

Figure 1

Time dependence of CH₄ yield on reduced LFNO during CO₂ methanation at 430°C (32 vol% H₂/ 8 vol% CO₂ rest Ar). After 30 min, 3000 ppm C₂H₄ were added to the feed for 480 min. Regeneration included reoxidation at 650°C for 2 h followed by reduction at 600°C for 1 h. Roman numbers indicate activity regimes discussed in the text.

Figure 2

Scanning electron microscopy images of LFNO after a) calcination; b) reduction in 20 vol% H₂/Ar / 600°C / 1 h; c) coking at 430°C in 32 vol% H₂, 8 vol% CO₂, 3000 ppm C₂H₄ for 8 h; e) LFNO after coking and oxidation and f) LFNO after coking, oxidation and subsequent reduction. Scale bars in a), b), e) and f) represent 400 nm. d) Bright field transmission electron image of the sample shown in c). Scale bar in c) and d) show 2 µm and 20 nm, respectively. Scale bar in the inset of d) represents 2 nm. The dashed circles identify Ni particles.

Figure 3

a) Powder X-ray diffraction patterns of LFNO after calcination, reduction, coking at 430°C (3000 ppm C₂H₄) for 8 h, reoxidation (20 vol% O₂/Ar, 650°C, 2 h) and after complete regeneration (reoxidation followed by reduction). The inset shows magnification of the 2θ range 31.5° - 33.0° to illustrate the reversible shift in reflection position. b) Temperature programmed reduction (10 vol% H₂, 5°C/min) of calcined LFNO as well as after coking and subsequent reoxidation. TPR profile of NiO reference is displayed for comparison. c) Ni particle size distribution on reduced and regenerated catalysts observed on SEM images similar to those depicted in Figure 2-b and Figure 2-f.

Figure 4

a) X-ray absorption near edge structure region around the Ni K-edge (8333 eV) of LFNO in its calcined state (black), oxidized after five redox cycles (600°C, 20 vol% H₂/Ar, 1 h; 650°C, 20 vol% O₂/Ar, 2 h), reduced (dark blue, 20 vol% H₂/Ar / 600°C / 1 h), reoxidized after 8 h coking at 430°C (orange) and after subsequent reduction at 600°C to complete catalyst regeneration (light blue). Reference spectra of NiO (dashed) and metallic Ni (dotted) are included for comparison. b) Linear combination analysis results of the spectra displayed in

(a). Grey, perovskitic Ni^{n+} ($n \geq 2$); red, NiO and blue, Ni^0 . Error bars represent standard fitting errors. Spectra of calcined LFNO, NiO and Ni^0 served as references for quantification.

Figure 5

a) CO_2 evolution during temperature programmed oxidation of the coked catalyst (20 vol% O_2/Ar , $10^\circ\text{C}/\text{min}$, $50\text{--}650^\circ\text{C}$). b) Raman spectra of pre-reduced, coked and regenerated LFNO.

Figure 6

CH_4 yield over ten reaction-coking-regeneration cycles with (black) and without the addition of 3000 ppm C_2H_4 (red). Solid bars indicate CH_4 yield after the first 30 min of reaction (regime I in Figure 1) whereas the hatched bars represent CH_4 yield after 8.5 h (IV in Figure 1). The amount of carbon released during the subsequent catalyst reoxidation is represented by the open symbols (black, with C_2H_4 ; red, without C_2H_4). The dotted lines serve to guide the eye.

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Schemes

Scheme 1 – representation of consecutive treatments of $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_{3\pm\delta}$ and corresponding sample denotations used throughout this work. The expected oxidation and coordination state of Ni is also represented schematically and alternates between Ni^{n+} inside the perovskite structure and Ni^0 at the surface depending on the nature of the pre-treatment.