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Xiangbiao Liao

Columbia University

Yanhui Long

Kunming University of Science and Technology

Yan Chen

Columbia University

Amirali Zangiabadi

Columbia University <https://orcid.org/0000-0003-3586-0687>

Hua Wang

Kunming University of Science and Technology

Qinggang Liu

Tsinghua University

Kongzhai Li (✉ kongzhai.li@foxmail.com)

Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology,
Kunming 650093, China <https://orcid.org/0000-0001-9269-5599>

Xi Chen (✉ xichen863@hotmail.com)

Columbia University

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**Polyfunctional perovskite oxides optimized for efficient CO₂ splitting
against oxidative impurity via chemical looping**

Xiangbiao Liao^{1†}, Yanhui Long^{2†}, Yan Chen^{1,3}, Amirali Zangiabadi⁴, Hua Wang²,
Qinggang Liu⁵, Kongzhai Li^{2,6*}, Xi Chen^{1,7*}

*¹Earth Engineering Center; Center for Advanced Materials for Energy and Environment,
Department of Earth and Environmental Engineering, Columbia University, New York, NY
10027, USA*

*²State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization
Engineering; Faculty of Chemical Engineering, Kunming University of Science and
Technology, Kunming 650093, China*

*³International Center for Applied Mechanics, State Key Laboratory for Strength and
Vibration of Mechanical Structures, School of Aerospace, Xi'an Jiaotong University, Xi'an
710049, China*

*⁴Department of Applied Physics and Applied Mathematics, Columbia University, New
York, NY 10027, USA*

⁵Department of Chemistry, Tsinghua University, Beijing, P. R. China

*⁶ Faculty of Metallurgical and Energy Engineering, Kunming University of Science and
Technology, Kunming 650093, China*

⁷School of Chemical Engineering, Northwest University, Xi'an 710069, P.R. China

*Correspondence to: Email: Kongzhai Li (kongzhai.li@foxmail.com), Xi Chen
(xichen@columbia.edu)

[†]These authors contributed equally to this work.

Abstract

Via redox chemistry, chemical looping reduction of CO₂ to CO provides a promising strategy for mitigating carbon emissions. However, it's still challenging to directly reduce CO₂/O₂ mixture gas due to lack of effective oxygen carriers towards reductive C–O bond scission in the presence of strongly oxidative gas. Here, we report an autocatalytic strategy of polyfunctional perovskite oxides to achieve enhanced C–O bond activation and superior performance of methane driven syngas generation. The self-generated Ni nanoparticles, through Ni cations migrating from the bulk lattice to the surface of LaFeO₃ perovskite under fast methane reduction, are identified as catalytically active sites for enhancing C-H activation in the methane oxidation step. The reduced Ni-LaFeO₃ oxygen carrier features multifunctional active sites with Ni species for accelerating C–O activation and oxygen vacancies for O₂ adsorption in the step of CO₂ splitting with the presence of abundant O₂. At 800°C, the 5 at.% Ni-LaFeO₃ perovskite stably exhibited high performances during 100 redox cycles: 98% CO selectivity in the methane oxidation step, and 98.5% CO₂ conversion in the step of CO₂ splitting even with the presence of 25 at.% O₂. This efficient and durable perovskite underpins an economic utilization of impure CO₂ from various carbon sources with no requirement for energy-costing purifications.

1. Introduction

CO₂ utilization not only mitigates global warming but also serves as a critical alternative energy source for traditional fossil fuels. Besides biological photosynthesis process, advanced progresses of thermal reforming, hydrogenation¹, photocatalytic² and electrochemical CO₂ reduction³ have devoted for producing multiple energy-rich carbon compounds (CO, HCOOH, MeOH, *etc.*)⁴⁻⁶. Most of previous studies used high-purity CO₂ gas in order to obtain relatively high reduction rate, but these studies may be difficult to scale up since the proposed catalytic conversion pathways cannot tolerate even a small trace of impurity, such as air or O₂. On the other hand, from a perspective of carbon loop engineering, carbon capture needs to be integrated with carbon utilization. There are increasing researches and industrial attentions in directly utilizing CO₂ source captured from either power plants or the atmosphere, which contains abundant gaseous impurities (*e.g.* O₂)⁷⁻⁹. Regardless of which carbon capture technology uses, the energy and cost skyrocket exponentially when the purity of captured CO₂ increases. Therefore, designing an efficient pathway of converting impure CO₂ represents a significant bottleneck for practical and large-scale carbon utilization. However, direct utilization of such CO₂ sources is challenging. Apart from obvious competitive inhibition of CO₂, the strong oxidative impurity of O₂ usually deactivates catalysts and leads to the formation of reactive oxygen species¹⁰⁻¹². To avoid energy-consuming purification of CO₂ feedstocks, it's of great importance to investigate alternative CO₂ reduction systems with oxygen-tolerant catalysts and high CO₂ conversion.

Chemical looping CO₂ splitting (CLCS) using oxygen carriers as redox mediums shows potential for overcoming the above-mentioned challenges^{13,14}. The CLCS process

consists of a cyclic redox scheme using oxygen carriers (OCs) occurring in two isolated steps: partial oxidation (POx) of methane into syngas by depleting lattice oxygen and CO₂ splitting into CO by replenishing lost oxygen¹⁵. Oxidants like O₂, H₂O and air have been widely used for regenerating OCs^{16,17}, and thus the CLCS process lowers the requirement for extra purification and exhibits the potential of directly utilizing impure CO₂. Different from well-known dry reforming of CO₂^{18,19}, the CLCS process takes advantage of producing syngas with controllable H₂/CO ratio and pure CO^{15,20}. In addition, the separately obtained syngas and CO products can be directly used for green acetic acid production¹⁵. As a two-step reaction, the conversion of methane is crucial for the following CO₂ splitting. CeO₂-based²¹⁻²³, Fe-based²⁴⁻²⁸, Ca-based²⁹, aluminate-typed³⁰ and V₂O₃-based³¹ mixed oxides have been reported to show activity for this process. However, potentials are still remained in improving the activity of oxygen carriers^{14,32}. It has been always of interest to develop specific tailor-made oxygen carriers for minimizing the reaction temperature with high methane conversion and syngas selectivity as well as improving CO yield in CO₂ splitting especially against oxidative impurities.

Due to the high dissociation energies of C-H bond in CH₄ and C=O band in CO₂, it's essential to design a polyfunctional oxygen carrier with unique surface structures for methane activation and defective lattice structures for oxygen transfer in the redox gas-solid reactions. Perovskite-typed oxides with a general formula of ABO₃ are highly recommended because of the abundant lattice defects, high ionic conductivity and tailorable surface/structure properties³³⁻³⁶. Earth-abundant 3d transition metal elements (*e.g.*, M=Mn, Fe, Co, and Ni) are ideal for occupying B sites by proper choice of A ions (*e.g.*, La). LaFeO₃-based perovskite oxides have outperformed other LaMO₃ samples in the

selectivity of syngas³⁵, however, high reaction temperatures ($\geq 850^{\circ}\text{C}$) were required for obtaining relatively high methane conversion³⁷⁻⁴⁰. Given the success of the intelligent (self-regeneration) catalysts, involving reversibly dissolution and segregation of precious metals into and out of the perovskite lattice at B site under oxidation or reduction condition⁴¹⁻⁴³, it is reasonable to optimize the perovskite oxygen carriers via doping suitable amount of active metal ions at B site of LaFeO_3 . Ni is one of the most active catalysts for CO_2 reforming with methane due to that the interaction between Ni metal and certain supports contributed to adsorption and dissociation of both CH_4 and CO_2 ^{44,45}. Interestingly, Ni or Ni oxides exhibited low binding ability for oxygen adsorption⁴⁶, which is helpful for promoting CO_2 splitting against O_2 impurities.

In the present work, we report a durable LaFeO_3 perovskite with Fe sites partially substituted by small amounts of Ni cations ($\text{LaNi}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$) for CLCS, not only enhancing syngas productivity at a relatively low temperature ($\sim 800^{\circ}\text{C}$) but also increasing CO_2 conversion even in the presence of O_2 . Ni nanoparticles segregating out of the perovskite lattice play critical catalytic roles for facilitating CO_2 splitting and activating methane into syngas. Consequently, the 5 at% Ni-doped perovskite ($\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$) exhibited synergic enhancements: 98.5% CO_2 conversion was maintained with 25% molar content of O_2 , and the 5.5 mol/kg syngas productivity with a H_2/CO ratio of 2.0 was simultaneously achieved.

2. Results

Catalytic performances for syngas production and CO_2 splitting. A series of $\text{LaNi}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.1$) were prepared for syngas production

from methane and CO₂ splitting. The crystal structures of all samples match well with the orthorhombic unit cell of LaFeO₃ without any impurity phases (**Figure S1**). Taking the 5 at% Ni-doped perovskite of LaNi_{0.05}Fe_{0.95}O_{3-δ} as an example, we performed the calculation based on Rietveld Refinement and confirmed the substitution of Fe sites with Ni cations (**Figure S2**). The elemental mapping (**Figure S3**) suggested that Ni were uniformly dispersed in the sample of LaNi_{0.05}Fe_{0.95}O_{3-δ}. The CH₄-TPR results (**Figure S4**) revealed that the incorporation of small amounts of Ni ions in the LaFeO₃ structure can significantly improve the formation of CO and H₂ at relatively low temperatures, which is consistent with the enhanced low-temperature reducibility of the Ni-doped samples in the H₂-TPR testing (**Figure S5**). To highlight the effect of Ni doping, we also performed the isothermal redox reactions of methane partial oxidation and CO₂ splitting at 800°C under a weight hourly space velocity (WHSV) of **60,000** cm³ g⁻¹ hour⁻¹.

Especially, **Figure 1a** compares the reaction behaviors of LaNi_{0.05}Fe_{0.95}O_{3-δ} and LaFeO₃ in the methane partial oxidation. Once methane fed into the perovskite bed, H₂ and CO productions fast raised and approached constant rates, while the CO₂ productions continuously decreased after a weak peak rate. During the reaction period, the stable productivities for H₂ and CO over LaNi_{0.05}Fe_{0.95}O_{3-δ} were maintained respectively to be 4.26 and 2.11 mmol kg⁻¹ s⁻¹ with the H₂/CO ratio of 2.01. In contrast, much smaller and unstable rates were observed over pure LaFeO₃. For accumulation, the H₂ productivity of 3.6 mol kg⁻¹ and the CO productivity of 1.8 mol kg⁻¹ over LaNi_{0.05}Fe_{0.95}O_{3-δ} were more than twice of those over LaFeO₃. Note that the POx reaction was suspended at the time when the CO production rate started decreasing so that the formation of coke deposition was avoided. Furthermore, Ni doping not only enhanced the methane

conversion from 37.8% to 78.3%, but also led to a higher CO selectivity of 95.5% over $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$. It is evident that 5 at% Ni substitution to Fe sites could assist the kinetics of reductivity and is desirable for methane selective oxidation.

In the following step of CO_2 splitting, the gaseous compounds elution profiles for LaFeO_3 and $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ are shown in **Figure 1b**. The breakthrough time is defined as the period between the starting time and the time when the rate of eluted CO_2 is 2% of that at the inlet. Both of the maximum CO production rates over LaFeO_3 and $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ were $2.5 \text{ mmol kg}^{-1} \text{ s}^{-1}$ coinciding with the flow rate of CO_2 . It underpinned that almost complete CO_2 conversion (100%) was achieved over these two perovskites during the period. However, the breakthrough time for $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ (750 s) was twice of that for LaFeO_3 (320 s), and thus a much higher yield produced over $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ (2.01 mol kg^{-1}) was achieved than that over LaFeO_3 (0.87 mol kg^{-1}). It was evident that the Ni doping plays an important role in this perovskite in terms of efficiently splitting CO_2 for CO production.

To illustrate the effect of doping ratio, the performances of different $\text{LaNi}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ samples for POx and CO_2 splitting are summarized in **Figure 1c**, and the details on methane conversion or CO_2 splitting can be found in **Figures S6** and **S7**. With increasing doping amount of Ni, both of syngas and CO productivities were continuously enhanced in the two reaction steps, and the increasing trend in methane conversion efficiency further confirmed the benefit of Fe substitution by Ni in the perovskite. However, the formation of coke was observed in the perovskite samples doped with 7 at% and 10 at% Ni, while no carbon deposition in those with less than 7 at% of Ni during the same reaction time. Moreover, the H_2/CO ratio in the cases of high dopants (7 at% and 10 at%) seriously

deviated from the value of 2, meaning that excessive Ni dopants resulted in lower CO selectivity and higher amount of coke produced in the methane POx. Therefore, the doping amount of 5 at% Ni in LaFeO₃ perovskite was optimized to achieve high productivity of syngas and CO with excellent stability in both steps.

To demonstrate the redox durability of LaNi_{0.05}Fe_{0.95}O_{3-δ}, successive redox cycles of methane POx and CO₂ splitting were conducted for 100 times at 800 °C, as shown in **Figure 1d**. For the POx step, the syngas (H₂/CO≅2.0) yield maintained at 5.7 mol/kg with the stable methane conversion at around 80.0% and CO selectivity at 95.5%. In the step of CO₂ splitting, the CO productivity of 2.0 mol/kg was kept without apparent decay after 100 cycles. We further confirmed the structural stability by XRD analysis (**Figure S8**), demonstrating the identical XRD pattern of perovskite crystal structure for the as-prepared and re-oxidized samples. The excellent structural reversibility thus contributed to the long-term redox reactions and the stability of such performances.

Here, we list the performances of syngas and CO productivity for LaNi_{0.05}Fe_{0.95}O_{3-δ} and previously reported oxygen carriers (**Figure 1e**). It shows that either a high syngas yield of 5.7 mol kg⁻¹ at the high temperature (1000 °C) was obtained or a low yield of 2.5 mol kg⁻¹ at the relatively low temperature of 800 °C over other perovskites or metal oxides. It was challenged to simultaneously achieve a low operating temperature and high productivity. In contrast, LaNi_{0.05}Fe_{0.95}O_{3-δ} exhibited the highest syngas yields of 6.1 and 6.7 mol kg⁻¹ at the temperature of 850 °C and 900 °C, respectively, and even a high yield of 5.6 mol kg⁻¹ was achieved at 800 °C without the formation of carbon deposition. In addition, the best performances of CO yield (2.07 mol kg⁻¹ at 800 °C and 2.3 mol kg⁻¹ at 900 °C) were also obtained over the as-synthesized 5 at% Ni-doped LaFeO₃ for splitting

CO₂. Therefore, as-synthesized LaNi_{0.05}Fe_{0.95}O_{3-δ} showed exceptional performances in both chemical looping syngas production and CO₂ splitting, especially at relatively low temperature.

Figure 1. Performances of syngas yield and CO₂ splitting over pure and Ni-doped LaFeO₃.

(a) Comparison of instantaneous production rate of syngas and CO₂ between LaFeO₃ and LaNi_{0.05}Fe_{0.95}O_{3-δ} during the POx step. (b) Comparison of instantaneous production rate of CO and CO₂ between LaFeO₃ and LaNi_{0.05}Fe_{0.95}O_{3-δ} during the step of CO₂ splitting. (c) Productivity of syngas and CO in the steps of methane PO_x and CO₂ splitting over LaFeO₃ perovskites doped with different Ni contents: 0 at%, 1 at%, 3 at%, 5 at%, 7 at% and 10 at%. (d) The cyclic performances (syngas yield, CO yield, CH₄ conversion and CO selectivity) of LaNi_{0.05}Fe_{0.95}O_{3-δ} for 100 cycles. (e) Performances summary of syngas and CO yields with respect to the reaction temperature among LaNi_{0.05}Fe_{0.95}O_{3-δ} and other reported the state-of-the-art oxygen carriers. ①

②⁴⁷, ③⁴⁸, ④⁴⁹, ⑤⁵⁰, ⑥⁵¹, ⑦⁵², ⑧⁵³, ⑨⁵⁴, ⑩⁵⁵, ⑪⁵⁶, ⑫⁵⁷, ⑬⁴⁸, ⑭⁵⁸, ⑮⁵⁹.

Segregation of Ni species over $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ surface. In order to explain the effect of Ni dopant on the enhanced performances, we traced its electronic and local atomic structures of the $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ sample through X-ray absorption near-edge structure (XANES) spectroscopy. The XANES spectra of Ni-K edge for samples successively reduced by methane for different time and re-oxidized by CO_2 are shown in **Figure 2a**, together with the XANES spectra of a NiO and a Ni foil as reference materials. For the fresh $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$, the XANES spectrum with strong signal at 8350.6 eV matched well with that for NiO, which indicated the oxidation state of Ni^{2+} . The calculated six-fold coordination of Ni with oxygen further confirmed the occupancy of Fe-site by Ni in the ABO_3 perovskite, echoing with the XRD results. The absorption edge position for the sample reduced by methane for 3 min was between those for the fresh sample and Ni foil. This indicated that the average Ni oxidation state was between Ni^0 and Ni^{2+} in this reduced sample, which was verified by the co-existence of Ni^0 and Ni^{2+} through the x-ray photoelectron spectroscopy (XPS) (**Figure S9**). The radial structure function around Ni were calculated by Fourier transform of extended X-ray absorption fine structure (EXAFS) oscillations (**Figure 2b**). Compared to the fresh sample, the reduced sample exhibited a lower intensity for the first nearest peak (1.5 Å), which corresponds to Ni-O bond. However, a significant enhancement was observed for the peak height between 1.8 Å and 2.5 Å corresponding to Ni-Ni bonds. Both the XANES and XPS measurements suggested the segregation of metallic Ni on the surface of perovskite crystal in the early stage of the reaction with methane.

The exsolution of metallic Ni particles on the reduced perovskite were also demonstrated by the images of TEM and EDS mapping (**Figures 2(c1) and (c2)**). The

high-resolution TEM image (**Figure 2(c3)**) showed Ni metal nanoparticles with the size of about 6 nm on the surface, and electron diffraction spots corresponding to (111), (200) and (220) planes of metallic Ni was found in **Figure 2(c4)**. Moreover, there was negligible change in XANES spectra between the samples reduced by 3 min and 10 min. This implied that once feeding reductive methane gas, fast segregation of metallic Ni nanoparticles on the perovskite surface occurred. The metallic Ni on surface may provide catalytic sites for activating methane molecules.

When the reduced sample was successively re-oxidized by oxidative CO₂ gas, we found that the measured XANES spectrum was between that of fresh and reduced samples (**Figure 2a**), but the signal of Ni⁰ disappeared in the XPS results. Moreover, the peak corresponding to Ni-Ni bonds significantly decreased, and the recovery of the peak intensity for Ni-O bonds was also observed (**Figure 2b**). Since XPS is a surface characterization technology, these phenomena illustrated that the surface layers of the metallic Ni nanoparticles should be re-oxidized, while metallic Ni still existed in the bulk. On the other hand, we cannot conclude that Ni fully moved back to the B-site of perovskite crystal under the soft oxidative environment of CO₂, unlike other intelligent perovskites re-oxidized by oxygen at atmosphere. Evidently, nanoparticles with concentrated Ni elements were remained according to TEM images, EDS mapping and electron diffraction for the re-oxidized samples (**Figures 2d**). Nanoparticles with a core/shell structure (10-15 nm) was remained on the surface, and the interplanar distance of 0.117 nm was measured for the core. In the electron diffraction images, the spots on red circles corresponded to (220), (311) and (222) planes of NiO, and simultaneously, (024), (133) and (113) planes of metallic Ni were illustrated by spots on green circles (**Figure 2(d4)** and **Figure S10**). These evidences demonstrated that surface Ni nanoparticles was re-oxidized into NiO by

the oxidative gas of CO₂. With the reference of EFAXS spectra of Ni and NiO foils, the obvious peak between 2.0 and 2.5 Å might be assigned to the combination of Ni-Ni scattering in NiO and Ni-Fe/Ni in the perovskite crystal. Herein, it's proved that Ni nanoparticles fast segregate out of the LaNi_{0.05}Fe_{0.95}O_{3-δ} crystal during methane partial oxidation, while core-shell Ni@NiO nanoparticles contribute for catalytically splitting CO₂ (Figure 2e).

Figure 2. Electronic states of Ni atom and structural characterizations of LaNi_{0.05}Fe_{0.95}O_{3-δ} during the cyclic redox scheme. (a) Ni K-edge XANES spectra and Fourier transformation of the EXAFS spectra for fresh LaNi_{0.05}Fe_{0.95}O_{3-δ}, the samples treated by methane reduction for 3 min and 10 min and full CO₂ re-oxidization at 800 °C. The TEM images, EDS mapping, HRTEM images and the corresponding Fast Fourier Transform images for LaNi_{0.05}Fe_{0.95}O_{3-δ} samples treated by (c) 7-min methane reduction and (d) subsequent 12-min CO₂ re-oxidization at 800 °C. (e) Schematic of structural evolution in LaNi_{0.05}Fe_{0.95}O_{3-δ} during the cyclic redox scheme.

Effect of O₂ impurity in CO₂ splitting. To evaluate the perovskites' robustness against oxidative impurities, isothermal oxidation reactions were performed with co-feeding mixture gases of O₂ and CO₂ as oxidative reactants over the spent LaFeO₃ and LaNi_{0.05}Fe_{0.95}O_{3-δ} samples, both of which were fully reduced in the step of methane POx. We presented the production rate of gaseous compounds eluted from those reactions in **Figure 3a**, and the molar ratio of O₂/CO₂ in the mixture gas was $\theta_{O_2} = 0.25$. Even in the presence of O₂, negligible influence in splitting CO₂ was found over LaNi_{0.05}Fe_{0.95}O_{3-δ}, which was illustrated by matched values between the maximum rate of produced CO and the feeding rate of CO₂ (1.35 mmol kg⁻¹ s⁻¹). However, the production rate of CO was much slower than the feeding rate of CO₂ over LaFeO₃, and the maximum rate was only 0.8 mmol kg⁻¹ s⁻¹, meaning that the CO₂ splitting was suppressed by the co-feeding gas of oxygen. Moreover, the duration for producing CO over LaNi_{0.05}Fe_{0.95}O_{3-δ} (1250 s) was much longer than that over LaFeO₃ (750 s), and the calculated yield of CO (1.32 mol kg⁻¹) was tripled. These results underpinned excellent oxygen tolerance for the Ni-doped perovskite towards splitting CO₂.

With varying the concentration of O₂ in mixture gas, we evaluated the influence of O₂ in CO production via the efficiency parameter defined as $\eta = \frac{CO \text{ production}}{\text{maximum CO production} * (1 - \theta_{O_2})}$ (**Figure 3b and Figure S11**). Here, the maximum CO productivities for LaFeO₃ and LaNi_{0.05}Fe_{0.95}O_{3-δ} are the values for splitting pure CO₂ (0.87 and 2.01 mol/kg), respectively. For LaNi_{0.05}Fe_{0.95}O_{3-δ}, a high CO production efficiency of 98.5% was maintained even when 25 at% O₂ was fed into the reactor, suggesting negligible influence of O₂ on CO₂ splitting. However, the existence of O₂

harmfully affected the CO₂ splitting over pure LaFeO₃, since only 88% and 75% efficiencies were obtained in the case of $\theta_{O_2} = 10\%$ and 25%, respectively. Evidently, the competition between CO₂ and O₂ splitting was mitigated due to the Ni doping, and LaNi_{0.05}Fe_{0.95}O_{3- δ} exhibited excellent robustness against strongly oxidative impurities and has the potential for economically utilizing impure CO₂ sources.

Figure 3. Effect of co-existing O₂ on CO₂ splitting over pure and Ni-doped LaFeO₃. (a) Comparison of instantaneous production rate of CO, O₂ and CO₂ between LaFeO₃ and LaNi_{0.05}Fe_{0.95}O_{3- δ} during the step of CO₂ splitting in the presence of 25 at% O₂. (b) The CO production efficiency as a function of the molar ratio of O₂ in the feedstock of CO₂.

Reaction mechanism during the methane POx step. To elucidate the robustness of Ni-doped perovskite against oxidative impurities, *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was conducted to track mechanisms of surface reaction: 1) reducing fresh perovskites in the step of CH₄ POx; 2) subsequently re-oxidizing the spent perovskite in the step of co-splitting O₂/CO₂ mixture. We present the *in-situ* DRIFT spectra over LaNi_{0.05}Fe_{0.95}O_{3- δ} during the methane POx step in **Figure 4a**. At 400-750 °C, the adsorption band at 1303 cm⁻¹ were respectively identified to the

deformation vibration of C–H in adsorbed methane molecules. Notably, an intense peak at 1360 cm⁻¹ appeared at 675 °C, assigned to the bending vibration of the C-H bond of methyl group (-CH₃). With increasing temperature, adsorbed CH₄ molecules were splitting into methyl groups, followed by methoxy groups and other formate-like species. At the reaction temperature above 675 °C, the vibrational signature at 2858 cm⁻¹ was ascribed to the asymmetric and symmetric C-H stretching vibrations of methoxy group (-CH₃O). Subsequently, the formation of -COOH (1568 cm⁻¹), CO (2153 cm⁻¹) and CO₂ (2353 cm⁻¹) was observed with the temperatures at above 700 °C. With longer time for LaNi_{0.05}Fe_{0.95}O_{3-δ} reacting with methane at 750 °C, signals of produced CO were stably while little intensity for CO₂. For comparison, only carbonate (1430 cm⁻¹) and CO₂ (2353 cm⁻¹) bands were detected during the reaction of pure LaFeO₃ with methane at above 700 °C, while no CO or other species were detected (**Figure 4b**).

During the conversion of methane into syngas, methane was conventionally believed to be activated on surface defects of oxygen carriers to form carbon intermediates, and CO was produced by the reaction of those carbon compounds with lattice oxygens, which usually required relatively high temperatures⁶⁰⁻⁶³. Combined with the structural information results in **Figure 2** and the *in-situ* DRIFTS results in **Figures 4(a)** and **(b)**, metallic Ni nanoparticles segregated on LaNi_{0.05}Fe_{0.95}O_{3-δ} played a catalytic function in the partial oxidation of methane, which may change the reaction pathway. The schematic mechanisms of catalytically decomposing methane into syngas are proposed in **Figure 4c**. Methane molecules could be adsorbed at the sites of segregated Ni nanoparticles instead of sites of surface oxygen vacancies. Methane were activated to create hydrogen atoms and the intermediates of methyl, which was followed by the combination of methyl with

released lattice oxygen into the formation of methoxy as $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ was continuously reduced. Furthermore, methoxy groups were dehydrogenated into formate-like species, which were selectively oxidized to CO by lattice oxygen continuously supplied from the bulk perovskite. And simultaneously, the hydrogen atoms were recombined in pairs to H_2 molecules. For pure LaFeO_3 , methane molecules should be adsorbed at surface oxygen vacancies (**Figure 4d**) to form carbonates, which may be the intermediate of the side-product CO_2 . The absence of detectable intermediates (e.g., methyl and methoxy) indicates that CO may be generated via carbon species as intermediates, like other CeO_2 -based⁶¹ or perovskite oxygen carriers^{62,63}. The above phenomena indicated that the catalytic role of Ni particles resulted in the decomposition of C-H in methane into methyl and methoxy, and those intermediates with higher activity than carbon species were bonded on the surface to react with lattice oxygen. This mechanism underpinned a lower reaction temperature and a higher yield of syngas compared to pure LaFeO_3 .

To highlight the improved reactivity, we compared the gaseous profiles of methane temperature-programmed reduction (CH_4 -TPR) between $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ and LaFeO_3 (**Figure 4e**). The onset temperature of methane oxidation over $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ was 650 °C, which is roughly 100 °C lower than that over pure LaFeO_3 . This echoes with our observation that higher intensity of DRIFT spectra for methane vibrational peaks on $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$. With increasing the reaction temperature, cationic Ni in the bulk perovskite fast converted to the metallic state and segregated on the surface, and the production of H_2 from decomposing methane rise sharply. Furthermore, the methane cracking for $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ corresponding to the maximum CO production occurred at 774 °C. In contrast, we observed a significantly slow production rate of H_2 and a higher

temperature of 889 °C for methane cracking over LaFeO₃. It demonstrated that Ni-doping in LaFeO₃ perovskite leads to fast mobility of lattice oxygen and fast segregation of metallic Ni, which contributes to the significantly enhanced reactivity for methane POx at a relatively lower activation temperature.

On the other hand, the comparison on reactivity of the LaNi_{0.05}Fe_{0.95}O_{3-δ} sample with impregnated Ni (5at%)-LaFeO₃ sample was also performed to highlight the role of exsolved Ni species. More CO₂ and less CO were detected over the Ni (5at%)-LaFeO₃ compared with the LaNi_{0.05}Fe_{0.95}O_{3-δ} sample (**Figures S12**), which resulted in relatively low methane conversion and CO selectivity (**Figures S13**). This indicated that the states of the exsolved Ni species from the LaNi_{0.05}Fe_{0.95}O_{3-δ} lattice should be different with the that for the impregnated one, and the former was beneficial for the conversion of methane to syngas. Another interesting phenomenon is that both the two sample showed an induction period for the oxidation of methane at the early stage (**Figures S14**), which resulted in relatively low methane conversion, likely due to the slow formation of active Ni species during the reaction. However, the induction period disappeared after one redox cycle for the LaNi_{0.05}Fe_{0.95}O_{3-δ} sample, while it still existed for the Ni (5at%)-LaFeO₃. This suggests that, unlike the impregnated Ni species, the active Ni species originating from the exsolution from the perovskite lattice need no reactivation after re-oxidized by CO₂.

Additionally, performances of syngas yield and methane conversion at different temperature were summarized in **Figure 4f**. It is worth to stress that, at a low temperature of 750 °C, a methane conversion of 59.8%, a CO selectivity of 92.5% and a syngas yield at 3.6 mol kg⁻¹ can be obtained over the LaNi_{0.05}Fe_{0.95}O_{3-δ} sample, and the syngas yield

is 6.5 times as that for the pure LaFeO_3 sample. This is unexpected, because oxygen carriers without the presence of precious metals usually show very low activity for the conversion of methane to syngas at temperatures lower than $800\text{ }^\circ\text{C}$ ⁶⁴. In addition, 95% of methane conversion was achieved over the Ni-doped perovskite while only 60% of methane conversion over LaFeO_3 at $900\text{ }^\circ\text{C}$. To the best of our knowledge, this conversion efficiency outperforms among other reported studies of methane POx.

Figure 4. Surface reaction mechanism during the methane POx. *In situ* DRIFTS spectra of (a) $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ and (b) LaFeO_3 reacted with methane at different temperatures and durations. Schematics of surface reaction mechanism over (c) $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ and (d) LaFeO_3 with methane. (e) The gaseous profiles of methane temperature-programmed reduction (CH₄-TPR) between $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ and LaFeO_3 . (f) Comparison of syngas yield and methane conversion between $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ and LaFeO_3 at different temperatures.

384

385 **Mechanism of reaction competition between O₂ and CO₂ splitting.** The *in-situ* DRIFT
386 spectra for co-splitting the O₂/CO₂ mixture ($\theta_{O_2} = 0.25$) over the reduced
387 LaNi_{0.05}Fe_{0.95}O_{3- δ} and LaFeO₃ perovskites at 800 °C are shown in **Figures 5a** and **5b**,
388 respectively. Consistent intermediates of carbonate were detected over the both oxygen
389 carriers, but the accumulation of carbonate species was observed on the surface of reduced
390 LaFeO₃ with increasing the reaction time, which was likely due to the inhibiting effect of
391 O₂ on the conversion of carbonate species into CO. By contrast, a stable and lower intensity
392 of carbonate peaks was observed on the reduced LaNi_{0.05}Fe_{0.95}O_{3- δ} , and the signal of
393 produced CO was detected during the whole reaction. Based on the structural information
394 (**Figure 2**), Ni species were remained on the surface of Ni-doped perovskite. Shown in the
395 schematic (**Figure 5c**), CO₂ molecules were adsorbed on the sites of either surface
396 vacancies or Ni species, and then activated into the intermediate of carbonates. Meanwhile,
397 the adsorbed O₂ molecules were fast split into oxygen atom, which filled the surface
398 vacancies. Thanks to the catalytic role of Ni sites, CO₂ was fast activated into CO, and the
399 produced oxygen atoms exchanged into oxygen vacancies on the surface or into the bulk
400 crystal due to excellent mobility of lattice oxygen. The reaction mechanism echoes with
401 that for splitting pure CO₂, and thus the presence of O₂ has negligible influence on splitting
402 CO₂. Compared to the dual sites (Ni species and surface defects) over the reduced
403 LaNi_{0.05}Fe_{0.95}O_{3- δ} , both CO₂ and O₂ had to be adsorbed on the only site of surface
404 vacancies over the reduced LaFeO₃, which resulted in the accumulation of carbonate
405 because most of vacancies in LaFeO₃ may be preferentially replenished by the active
406 oxygen from O₂ gas (**Figure S15**). These phenomena demonstrated that while the splitting

of CO₂ was suppressed over the pure LaFeO₃, the catalytic role of segregated Ni nanoparticles on LaNi_{0.05}Fe_{0.95}O_{3-δ} enhances the activation of CO₂ and narrow the reactivity difference between O₂ and CO₂.

The reaction mechanism over Ni-doped LaFeO₃ for splitting CO₂ was further explored via *ab initio* simulations. We calculated the binding free energy and reaction barrier for CO₂ splitting reaction on the (110) surface of reduced LaFeO₃ structures with the active sites of oxygen vacancies and metallic Ni adatoms (**Figure S16**). The CO₂ binding energy at the Ni sites exhibited a significant enhancement by 0.46 eV compared to that at the sites of surface oxygen vacancy, and the most stable adsorption sites of CO₂ on both sites on the reduced LaFeO₃ (110) surface were illustrated in **Figure S17 and S18**. These changes confirmed that CO₂ molecules are preferentially adsorbed at Ni⁰ sites over the reduced LaNi_{0.05}Fe_{0.95}O_{3-δ} sample with segregated Ni species, while CO₂ molecules have to compete with O₂ molecules at the surface defects over the reduced LaFeO₃ during the co-splitting. Furthermore, CO₂ splitting was accelerated in the presence of metallic Ni adatom due to the free energy barrier for C-O bond breaking is reduced by 47.8% compared with that with the only binding site of surface defects in reduced pure LaFeO₃ (**Figure 5d**). These results echoes with the DRIFT spectra showing less intensity for carbon intermediates, and confirms the CO₂-TPO results (**Figure S19**), which shows lower decomposition temperature of CO₂ over the reduced LaNi_{0.05}Fe_{0.95}O_{3-δ} sample. Overall, the catalytical function of Ni atoms could enhance the rate of CO₂ splitting, which mitigates the competition with O₂ splitting and improves the performance of CO₂ splitting in the presence of O₂.

The effect of Ni-doping on CO₂/O₂ co-splitting was also investigated through isotopic

exchange experiments. As shown in **Figures 5e** and **5f**, after feeding the mixture gas ($^{18}\text{O}_2/\text{C}^{16}\text{O}_2 = 25\%$), the co-production of C^{16}O and C^{18}O was observed with depleting reactant gases over both reduced LaFeO_3 and $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$. This phenomenon indicated that ^{18}O atoms splitting from $^{18}\text{O}_2$ not only diffused into the bulk perovskites, but also combines with C atoms into C^{18}O . Quantitatively, the amount of ^{18}O exchanged into the C^{18}O molecules over the reduced $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ was approximately twice than that over the reduced LaFeO_3 . It illustrated that compared to that over LaFeO_3 , the sites of exposed Ni species with excellent reactivity not only accelerate full C-O bond scission in C^{16}O_2 but also favor exchanging adsorbed oxygen. This catalytic role of dispersed Ni nanoparticles contributed to efficiently CO_2 splitting over $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ in the environment of high-concentration O_2 .

Figure 5. Surface reaction mechanism during the step of co-splitting CO_2 and O_2 . *In situ* DRIFTS spectra of reduced (a) LaFeO_3 and (b) $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ samples reacting with O_2 -containing CO_2

($\theta_{O_2} = 0.25$) at different reaction times. (c) Mechanism schematic of co-splitting CO_2 and oxygen the reduced $LaNi_{0.05}Fe_{0.95}O_{3-\delta}$ (110) surfaces. (d) Reaction pathways of splitting CO_2 into CO on the reduced $LaFeO_3$ (110) surface with and without exposed Ni species. Instantaneous productions of $C^{16}O$, $C^{18}O$ and $^{18}O_2$ gases over the reduced (e) $LaFeO_3$ and (f) $LaNi_{0.05}Fe_{0.95}O_{3-\delta}$ samples during the step of co-splitting the mixture gas ($^{18}O_2/C^{16}O_2 = 25\%$).

3. Conclusion

In summary, we have demonstrated Ni-doped $LaFeO_3$ perovskite centering with the high reactivity for chemical looping CO_2 reduction, even in the presence of O_2 . Once accessing reductive methane, metallic Ni nanoparticles segregate out of the perovskite surface and are remained in the subsequent reaction of CO_2 splitting. The catalytic role of metallic Ni not only contributes to enhanced methane activation for syngas production at low temperatures, but also highly improves the rate of C-O cleavage in CO_2 so that the competition of strong oxidant O_2 to CO_2 splitting can be mitigated. The excellent robustness for polyfunctional Ni-doped perovskite against strongly oxidative impurities underpins economic pathway for utilizing impure CO_2 sources.

Author contributions

X.B. Liao, Y.H. Long and K.Z. Li performed the catalyst preparation, catalytic tests, data analysis. Y. Chen conducted DFT calculations and wrote the computational section. A. Zangiabadi contributes to the TEM and EDS characterizations. Q.G. Liu and H. Wang helped to analysis the results of the DRIFT and isotope exchange experiments. K. Li, X. Chen and X.B. Liao designed the study and wrote the paper. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Figures

Figure 1

Performances of syngas yield and CO₂ splitting over pure and Ni-doped LaFeO₃. (a) Comparison of instantaneous production rate of syngas and CO₂ between LaFeO₃ and LaNi_{0.05}Fe_{0.95}O₃ during the POx step. (b) Comparison of instantaneous production rate of CO and CO₂ between LaFeO₃ and LaNi_{0.05}Fe_{0.95}O₃ during the step of CO₂ splitting. (c) Productivity of syngas and CO in the steps of methane POx and CO₂ splitting over LaFeO₃ perovskites doped with different Ni contents: 0 at%, 1 at%, 3 at%, 5 at%, 7 at% and 10 at%. (d) The cyclic performances (syngas yield, CO yield, CH₄ conversion and CO selectivity) of LaNi_{0.05}Fe_{0.95}O₃ for 100 cycles. (e) Performances summary of syngas and CO yields with respect to the reaction temperature among LaNi_{0.05}Fe_{0.95}O₃ and other reported the state-of-the-art oxygen carriers. [47]; [48]; [49]; [50]; [51]; [52]; [53]; [54]; [55]; [56]; [57]; [48]; [58]; [59].

Figure 3

Effect of co-existing O₂ on CO₂ splitting over pure and Ni-doped LaFeO₃. (a) Comparison of instantaneous production rate of CO, O₂ and CO₂ between LaFeO₃ and LaNi_{0.05}Fe_{0.95}O₃ during the step of CO₂ splitting in the presence of 25 at% O₂. (b) The CO production efficiency as a function of the molar ratio of O₂ in the feedstock of CO₂.

Figure 4

Surface reaction mechanism during the methane POx. In situ DRIFTS spectra of (a) $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ and (b) LaFeO_3 reacted with methane at different temperatures and durations. Schematics of surface reaction mechanism over (c) $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ and (d) LaFeO_3 with methane. (e) The gaseous profiles of methane temperature-programmed reduction (CH_4 -TPR) between $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ and LaFeO_3 . (f) Comparison of syngas yield and methane conversion between $\text{LaNi}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$ and LaFeO_3 at different temperatures.

Figure 5

Surface reaction mechanism during the step of co-splitting CO₂ and O₂. In situ DRIFTS spectra of reduced (a) LaFeO₃ and (b) LaNi_{0.05}Fe_{0.95}O_(3-δ) samples reacting with O₂-containing CO₂ ($\theta_{(O_2)}=0.25$) at different reaction times. (c) Mechanism schematic of co-splitting CO₂ and oxygen the reduced LaNi_{0.05}Fe_{0.95}O_(3-δ) (110) surfaces. (d) Reaction pathways of splitting CO₂ into CO on the reduced LaFeO₃ (110) surface with and without exposed Ni species. Instantaneous productions of C¹⁶O, C¹⁸O and ¹⁸O₂ gases over the reduced (e) LaFeO₃ and (f) LaNi_{0.05}Fe_{0.95}O_(3-δ) samples during the step of co-splitting the mixture gas (¹⁸O₂/C¹⁶O₂ = 25%).

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