

RESEARCH ARTICLE OPEN ACCESS

Tailoring an Fe–O_v–Ce–Triggered Phase-Reversible Oxygen Carrier for Intensified Chemical Looping CO₂ Splitting

Zhao Sun^{1,2} [b] | Kun Lei¹ [b] | Louise R. Smith² [b] | Nicholas F. Dummer² [b] | Richard J. Lewis² [b] | Haifeng Qi² [b] | Kieran J. Aggett² [b] | Stuart H. Taylor² [b] | Zhiqiang Sun¹ [b] | Graham J. Hutchings² [b]

¹Hunan Engineering Research Center of Clean and Low-Carbon Energy Technology, School of Energy Science and Engineering, Central South University, Changsha, China | ²Max Planck–Cardiff Center on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, UK

Correspondence: Zhiqiang Sun (zqsun@csu.edu.cn) | Graham J. Hutchings (Hutch@cardiff.ac.uk)

Received: 26 October 2024 | Revised: 15 February 2025 | Accepted: 16 February 2025

Funding: This work was supported by the National Key R&D Program of China (2022YFE0105900), the National Natural Science Foundation of China (52436006, 52476144, 52311530339, 42441835), and the Innovation-Driven Project of Central South University (2023ZZTS0721).

Keywords: chemical looping | CO2 splitting | electron-donating | phase-reversible oxygen carrier

ABSTRACT

Advanced oxygen carrier plays a pivotal role in various chemical looping processes, such as CO_2 splitting. However, oxygen carriers have been restricted by deactivation and inferior oxygen transferability at low temperatures. Herein, we design an $Fe-O_v-Ce$ -triggered phase-reversible CeO_{2-x} ·Fe·CaO \leftrightarrow CeO_2 ·Ca₂Fe₂O₅ oxygen carrier with strong electron-donating ability, which activates CO_2 at low temperatures and promotes oxygen transformation. Results reveal that the maximum CO_2 conversion and CO yield obtained with 50 mol% CeO_{2-x} ·Fe·CaO are, respectively, 426% and 53.6 times higher than those of Fe·CaO at 700°C. This unique multiphase material also retains exceptional redox durability, with no obvious deactivation after 100 splitting cycles. The addition of Ce promotes the formation of the Fe-O_v-Ce structure, which acts as an activator, triggers CO_2 splitting, and lowers the energy barrier of C=O dissociation. The metallic Fe plays a role in consuming $O^{2-}_{lattice}$ transformed from Fe-O_v-Ce, whereas CaO acts as a structure promoter that enables phase-reversible Fe⁰ \leftrightarrow Fe³⁺ looping.

1 | Introduction

The overdependence of humanity on fossil fuels has contributed to a continual increase in the atmospheric CO_2 concentration, to currently over 420 ppm [1, 2]. The excessive CO_2 levels will exacerbate global warming, disrupt biodiversity, and trigger other fatal environmental issues [3–5]. Such a severe scenario has driven extensive research efforts around CO_2 abatement [6]. Consequently, numerous CO_2 mitigation technologies have been developed in recent years [7–10]. Carbon capture and utilization technologies have attracted wide attention for the potential to deliver zero and even negative carbon emissions, which enables the conversion of CO_2 into value-added products. Compared with other conversion pathways, for example, photocatalysis [11] and electrocatalysis [12], the thermochemical route shows superior technological maturity, offering relatively high CO_2 conversion rates [13, 14].

Thermochemical CO_2 splitting can be initiated by concentrated solar power or the waste heat from nuclear power generation [15, 16]; the product, CO, can be used for synthesizing highvalue chemicals and fuels, such as light olefins [17], carbonyl

Zhao Sun and Kun Lei contributed equally to this work.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

^{© 2025} The Author(s). Carbon Energy published by Wenzhou University and John Wiley & Sons Australia, Ltd.

compounds [18], and acetic acid [19]. Despite the potential to generate CO, this technology is limited by the ultrahigh temperature (theoretically > 2000°C) required. The solar thermochemical cycle (STC) technology can visibly lower the operating temperature due to the separation of CO₂ splitting into two subreactions, oxygen evolution $(MeO_x \rightarrow MeO_{x-\delta} + O_2)$ and CO_2 splitting $(CO_2 + MeO_{x-\delta} \rightarrow MeO_x + CO)$, by using an oxygen carrier [20, 21]. However, the temperature difference between the oxygen evolution (>1300°C) and CO_2 -splitting (>850°C) reactions causes irreversible heat loss and contributes to the thermal fatigue of reactor infrastructure. Further, deactivation of the oxygen carrier also occurs, which greatly restricts the development of STC. Therefore, efforts have been made to address the above-mentioned issues [22-24]. To effectively lower the temperature in the oxygen evolution stage, hydrogen was used to promote the oxygen transformation rate, known as the reverse water-gas shift chemical looping (RWGS-CL; see Supporting Information S1: Figure S1) [25]. The use of lowgrade reducing gases, for instance, vented gas (composed of H₂, CO, CO₂, CH₄, CH₃OH, and inert gas), is also a promising route [26]. Despite prior efforts, reducing gas-assisted STC still has the drawback of low lattice oxygen transfer kinetics and ready deactivation of the oxygen carrier. To sum up, for accelerating the development of RWGS-CL, the screening of oxygen carriers with high oxygen ion transferability as well as electrondonating ability and redox durability is essential.

Fe-based oxygen carriers are among the most intensively investigated materials in chemical looping reactions due to their exceptional oxygen storage capacity (Fe \rightarrow FeO: 22.2 wt%; $FeO \rightarrow Fe_3O_4$: 6.9 wt%; $Fe_3O_4 \rightarrow Fe_2O_3$: 3.3 wt%), favorable thermodynamic properties, affordable synthesis cost, and satisfactory eco-friendly characteristics [27]. However, Fe-based oxygen carriers typically undergo severe sintering after successive hightemperature redox cycles. To overcome this issue, various types of composite Fe-containing oxygen carriers such as perovskites [28] and spinels [29, 30] have been developed. The phase segregation and reorganization are conducive to homogenizing the oxygen carriers on an atomic level, thereby hindering their sintering and agglomeration after long-term redox cycles. Lim et al. [31] constructed binary Ni-Fe sites in a double La₂NiFeO₆ perovskite for RWGS-CL and achieved an average CO₂ conversion rate of $214 \,\mu mol \cdot min^{-1} \cdot g_{cat}^{-1}$ at 700°C. Similarly, Orsini et al. [32] synthesized a double perovskite $Sr_2FeMo_{0.6}Ni_{0.4}O_{6-\delta}$ for RWGS-CL, with a maximum CO yield of 2377.0 $\mu mol \cdot g^{-1}$ at 850°C, but further improvements to the redox stability are required. Ma et al. [33] prepared a Mn_{0.2}Co_{0.8}Fe₂O₄ spinelstructured oxygen carrier for RWGS-CL and achieved a CO production rate of ~142.3 μ mol·min⁻¹·g⁻¹ at 650°C. Although the cyclic stability as well as CO₂ conversion rates and CO yields of oxygen carriers have been significantly improved, lowtemperature CO₂ splitting requires further optimization. Hence, the development of Fe-based oxygen carriers possessing high lattice oxygen mobility and strong electron-donating capability is crucial. A brownmillerite-type ferrite, Ca2Fe2O5, has received particular attention owing to its ABO2.5-type structure for facilitating fast oxygen ion transport [34-40]. In 2016, Ismail et al. [34] and Chan et al. [35] used Ca₂Fe₂O₅ to produce hydrogen from steam via chemical looping. Subsequently, Hosseini et al. [36] doped Ni and Cu into Ca₂Fe₂O₅ to improve the redox performance of chemical looping H₂ production, and Wang et al. [37] physically mixed $Zr_{0.5}Ce_{0.5}O_2$ and $Ca_2Fe_2O_5$ to enhance the CO yield from chemical looping CO₂ decomposition. We also used $Ca_2Fe_2O_5$ -derived oxygen carriers in the fields of chemical looping–based H_2O/CO_2 splitting [38], biomass gasification [39, 40], methanol reforming [41], and methane decomposition [42]. It was confirmed that Fe·CaO derived from $Ca_2Fe_2O_5$ shows a strong electron-donating ability at high temperatures, making it a potential candidate for highly efficient CO₂ and H_2O dissociation. Moreover, the presence of Ca enables the complete release of electrons of Fe, accomplishing the oxidation of Fe⁰ into Fe³⁺.

Nonstoichiometric cerium oxide (CeO_{2-x}) shows exceptional oxygen storage-release capability, as the oxygen vacancies can be formed or eliminated with the reversible conversion of Ce⁴⁺ and Ce^{3+} via $O^{2-} \leftrightarrow O_v + 2e^- + 1/2O_2(g)$ [43]. The reduced cerium oxide (CeO_{2-x}) possesses abundant oxygen vacancies, which are expected to promote the mobility of lattice oxygen and boost the oxygen transferability of the oxygen carrier, thereby accelerating the CO₂ dissociation rate and lowering the splitting temperature required. Herein, we aim to reveal the effect of cerium doping on the redox-looping performance of the ABO_{2.5}-type oxygen carrier. To the best of our knowledge, Ce-doped ABO_{2.5}-type Ca₂Fe₂O₅ oxygen carriers for RWGS-CL have not yet been explored. Results show that the Ce-doped Ca₂Fe₂O₅ oxygen carrier displays a high oxygen migration rate; meanwhile, the H₂-reduced material shows very strong electron-donating ability, enabling combustion under atmospheric and room-temperature conditions (Supplementary movie). We show that the formed Fe-O_v-Ce structure is the activator that induces low-temperature CO₂ splitting, whereas Fe and CaO serve as the active components for the lattice oxygen accepter and the ABO_{2.5} structure formation promoter, respectively. Specifically, the maximum CO₂ conversion of the 50 mol% Ce-doped oxygen carrier increased by 426%, whereas the CO yield $(546 \,\mu mol \cdot min^{-1} \cdot g^{-1})$ increased by 53.6 times compared with Fe CaO without Ce doping at 700°C. Moreover, the designed oxygen carrier possesses exceptional durability after 100 redox cycles, with the corresponding CO yield decreasing by only 4.1%.

2 | Materials and Methods

2.1 | Chemicals

Iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 98.5%~100.0%), calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, 98.5%), cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99.0%), and citric acid monohydrate (C₆H₈O₇·H₂O, 99.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Copper nitrate trihydrate (Cu(NO₃)₂·3H₂O) was obtained from Aladdin Chemical Reagent Company. All received chemicals were analytical grade and used directly without further purification.

2.2 | Oxygen Carrier Synthesis

Oxygen carriers of $yCeO_2 \cdot Ca_2Fe_2O_5$ were prepared using the modified Pechini method [44], where *y* (0, 25, 50, 75, or 100 mol%)

denotes the mole ratios of CeO₂:Ca₂Fe₂O₅. The metal precursor additions corresponding to the calcined *y*CeO₂·Ca₂Fe₂O₅ oxygen carriers are listed in Supporting Information S1: Table S1. Typically, 0.03 mol of both Fe(NO₃)₃·9H₂O and Ca(NO₃)₂·4H₂O, 0.03*y* mol of Ce(NO₃)₃·6H₂O, and a specific amount of C₆H₈O₇·H₂O were dissolved in 200 mL of deionized water. The mole ratio of citric acid to the total metal ions (Fe³⁺ + Ca²⁺ + Ce⁴⁺) was maintained at 1.3. The resulting solution was continuously stirred at 80°C for 0.5 h and then transferred to a drying oven at 180°C for 6 h to produce a gel. The dried gel was ground and subsequently calcined in a muffle furnace at 850°C for 4 h at a heating rate of 2°C·min⁻¹. The precursors of Fe, CaO, CeO_{2-x} 50 mol% CeO_{2-x}·Fe, and 50 mol% CeO_{2-x}·CaO were also prepared as control samples based on the aforementioned procedures.

2.3 | Characterization

X-ray diffraction (XRD) measurements were conducted on an X-ray diffractometer (Rigaku Miniflex 600, Japan) by Cu-K α radiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA. The scan range was 5°~90°, with a scan rate of 5°·min⁻¹ and a step of 0.02°. The crystallite sizes of the calcined oxygen carriers were calculated using the Scherrer equation.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements were performed using an Agilent 5110 DV device to obtain the actual contents of Ce, Fe, and Ca of oxygen carriers with different Ce doping.

 N_2 physisorption analysis was measured using a Novatouch 2LX device at -196°C and the obtained data were processed using Anton Paar Kaomi software. The surface area and pore volume as well as the average pore diameter of the calcined oxygen carriers were calculated using the Brunauer-Emmett-Teller (BET) method and the Barret-Joyner-Halenda (BJH) method, respectively.

Transmission electron microscopy (TEM) images of 50 mol% CeO₂·Ca₂Fe₂O₅ were obtained using a JEOL JEM-2100 microscope operating at 200 kV, supported by Integrated Lab Solutions GmbH (ILS). Aberration-Corrected High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (AC HAADF-STEM) measurement was performed using a JEM-ARM200F instrument. Energy-dispersive spectroscopy (EDS) mappings (Fe, Ca, Ce, and O) and Electron energy loss spectroscopy (EELS) were acquired to observe the element distributions, atomic structure, and surface defect of the hydrogen-reduced 50 mol% CeO_{2-x}·Fe·CaO oxygen carrier. The TEM and HAADF-STEM images as well as the elemental mapping results of the once- and twice-reduced 50 mol% CeO₂·Ca₂Fe₂O₅ were obtained using a JEOL JEM-2100F instrument.

In situ X-ray absorption spectroscopy (XAS) measurements were conducted in transmission mode at the Shanghai Synchrotron Radiation Facility. A home-made cell (Supporting Information S1: Figure S2A) was used to heat the oxygen carrier to the target temperature. The 50 mol% $CeO_2 \cdot Ca_2Fe_2O_5$ oxygen carrier was in situ reduced under the conditions of 30 vol% H₂ in N₂ (60 mL·min⁻¹) and 800°C for 0.5 h (Supporting Information S1: Figure S3). The entire measurement procedure can be divided

into three steps: (i) Sample loading. The tested sample and the graphene were mixed and homogeneously ground. Then, the mixture was pressed into a disc with a diameter of 10 mm and loaded into the cell (Supporting Information S1: Figure S2B). (ii) Room-temperature measurements. Fe foil, as a standard sample, was first measured for energy calibration. After that, the Fe K-edge and Ce L₃-edge signals of 50 mol% CeO₂·Ca₂Fe₂O₅ at room temperature were captured. (iii) The in situ X-ray absorption fine structure (XAFS) experiments. Specifically, 50 mol% CeO₂·Ca₂Fe₂O₅ was first heated to 800°C at a rate of 10°C·min⁻¹ at N₂ (40 mL·min⁻¹), and then reduced at 800°C for 0.5 h under $30 \text{ vol}\% \text{ H}_2$ in N₂ ($60 \text{ mL} \cdot \text{min}^{-1}$). Subsequently, the temperature was cooled to 20°C under N₂ (40 mL·min⁻¹). Finally, the resulting Fe K-edge and Ce L₃-edge signals of the in situ reduced 50 mol% CeO₂·Ca₂Fe₂O₅ were obtained. A detailed data analysis process is provided in the supplementary information.

Thermogravimetric analysis (TGA) was performed using an STA 2500 Regulus, NETZSCH analyzer. Before the experiments, both the hydrogen-reduced $Ca_2Fe_2O_5$ and 50 mol% $CeO_2 \cdot Ca_2$ - Fe_2O_5 were passed through a 200-mesh sieve to minimize the effect of internal diffusion. In a typical experiment, ~10 mg of the sieved sample was placed in the thermogravimetric crucible and heated to the desired temperature (700°C, 750°C, 800°C, 850°C, or 900°C) at a heating rate of 20°C·min⁻¹ under argon (80 mL·min⁻¹). After reaching the target temperature, the atmosphere was switched to 20 vol% CO_2 in Ar (100 mL·min⁻¹) to carry out the CO_2 -splitting experiment. Effects of different gas feed rates (100, 120, and 140 mL·min⁻¹) on the oxygen carrier oxidation were studied to minimize the effect of external diffusion (Supporting Information S1: Figure S4). The experiments for each sample were conducted at least twice.

Scanning electron microscopy (SEM) measurements were carried out using Tescan Clara microscope equipment with an EDS instrument (Xplore 30) at 20 keV to detect the morphologies and element distributions (Fe, Ca, O, or Ce) of the oxygen carriers.

H₂-temperature-programmed reduction (TPR). measurements were conducted using a Micrometrics AutoChem II 2920 chemisorption analyzer. In a typical measurement, 30 mg of oxygen carriers (Ca₂Fe₂O₅ and 50 mol% CeO₂·Ca₂Fe₂O₅) were first preheated from room temperature to 300°C at a heating rate of 10°C·min⁻¹, maintained for 0.5 h under an Ar atmosphere (40 mL·min⁻¹), and then cooled to 50°C. When the baseline stabilized, the temperature was increased to 900°C at a heating rate of 10°C·min⁻¹ under a mixed gas of 10 vol% H₂ in Ar (40 mL·min⁻¹), and the hydrogen consumption of the two oxygen carriers was calculated based on the standard sample CuO (Supporting Information S1: Figure S45).

In situ reduced CO₂-temperature-programmed desorption (TPD) measurements were performed using a Micrometrics AutoChem II 2920 instrument connected to a TILON LC-D200M mass spectrometer (MS). All the samples were in situ reduced at 920°C with 20 vol% H₂ in He atmosphere (50 mL·min⁻¹) for 2 h. After that, the sample was saturated with 10 vol% CO₂ in He (25 mL·min⁻¹) at 50°C for 1 h, followed by isothermal purging for another 1 h in He (25 mL·min⁻¹). Meanwhile, MS was used to detect the outlet gas products to ensure a stable signal. After the baseline stabilized, the sample

was heated to 900°C at a heating rate of 10°C·min⁻¹ in He (25 mL·min⁻¹). The products, CO₂ (m/z = 44) and CO (m/z = 28), were recorded by MS during this heating process.

The activation procedures of in situ reduced CO_2 -temperatureprogrammed oxidation (TPO) were the same as those of CO_2 -TPD. After activation, the samples for the CO_2 -TPO tests were heated from 50°C to 900°C at a heating rate of 10°C·min⁻¹ in 10 vol% CO_2 in He (25 mL·min⁻¹). The product signals (CO and CO_2) were recorded by MS, as mentioned above.

In situ electron paramagnetic resonance (EPR) measurements were performed using Bruker A300 equipment to detect the oxygen vacancy formation of the reduced $Ca_2Fe_2O_5$ and 50 mol % $CeO_2 \cdot Ca_2Fe_2O_5$. First, the sample was reduced at 920°C for 2 h or 800°C for 0.5 h in a mixture of N₂ (40 mL·min⁻¹) and H₂ (20 mL·min⁻¹) in a tube furnace. When the furnace temperature cooled to room temperature, the reduced sample was then transferred to a quartz capillary under nitrogen protection. After that, the quartz capillary was placed in an EPR quartz tube, thereby obtaining the room-temperature EPR signal.

In situ Raman measurement was carried out using a Horiba HR800 Raman spectrometer with a laser wavelength of 532 nm. Specifically, an appropriate amount of 50 mol% $CeO_2 \cdot Ca_2Fe_2O_5$ was first placed in the in situ cell (Linkam, UK) and then preheated from room temperature to 800°C at a ramping rate of 20°C·min⁻¹ under N₂ (20 mL·min⁻¹). After reaching 800°C, the sample was isothermally reduced for 0.5 h under 20 mL·min⁻¹ N₂ and 10 mL·min⁻¹ H₂. Once the reduction was complete, the temperature was decreased to room temperature under N₂ (20 mL·min⁻¹) to avoid the impacts of high-temperature heat radiation. Finally, roomtemperature Raman data of the reduced sample were recorded.

The room-temperature ⁵⁷Fe Mössbauer spectrum was collected using a SEE Co W304 Mössbauer spectrometer with a ⁵⁷Co/Rh source in transmission geometry [45]. The 50 mol% CeO₂·Ca₂-Fe₂O₅ sample was first reduced for 0.5 h under the conditions of H₂:N₂ = 20:40 (40 mL·min⁻¹) and 800°C. The resulting 50 mol% CeO_{2-x}·Fe·CaO was then pretreated in a glovebox before Mössbauer measurement. Finally, the collected data were fitted using MössWinn 4.0 software.

X-ray photoelectron spectroscopy (XPS) results were recorded by a Thermo ESCALAB 250 spectrometer equipped with an Al K α X-ray ($h\nu$ = 1486.6 eV) radiation excitation source at a step size of 0.05 eV. The binding energy data were first calibrated by correcting the C 1s peak to 284.8 eV and then deconvolved using the Gaussian–Lorentzian method.

2.4 | Performance Evaluation

A vertical tube furnace (BTF-1200C-S-SVT), purchased from Anhui Beiyike Equipment Technology Co. Ltd, was used to conduct the performance evaluation at atmospheric pressure. In a typical test, 0.300 ± 0.0005 g of oxygen carrier supported by quartz wool was loaded in the constant-temperature region of the quartz tube with an inner diameter of 8 mm. The mass ratio of the oxygen carrier to quartz wool was maintained at 5. Before the CO₂-splitting reaction, the oxygen carrier was reduced at 920°C for 2 h in a mixed gas composed of N₂ (40 mL·min⁻¹) and H₂ (20 mL·min⁻¹). After that, the furnace temperature was decreased to the target one. Once the temperature stabilized, for testing CO₂-splitting performance, the mixed gas was switched to 20 vol% CO₂ in N₂, with the total flow rate ranging from 25 to 100 mL·min⁻¹. During the experiments, the flow rates of N₂, H₂, and CO₂ were controlled by Sevenstar CS200 mass flow controllers, as calibrated by a soap film flowmeter. The composition of outlet gas was monitored by an INFICON Micro GC Fusion equipped with a 5A molecular sieve column and a Plot Q column. The cyclic tests can be divided into four stages: (i) H₂ reduction under 40 mL·min⁻¹ N₂ and 20 mL·min⁻¹ H₂ (40 min); (ii) N₂ purge (5 min); (iii) CO₂ splitting under 40 mL·min⁻¹ N₂ and 10 mL·min⁻¹ CO₂ (10 min); and (iv) N₂ purge (5 min). All the stages were operated at an identical temperature of 800°C.

2.5 | Data Analysis

The outlet gas production rate (P_{total} , μ mol·min⁻¹) during the CO₂-splitting stage was defined as

$$P_{\text{total}} = P(N_2)/C(N_2)_{\text{outlet}},$$
(1)

where $P(N_2)$ represents the inlet N_2 feeding rate; $C(N_2)_{outlet}$ denotes the N_2 concentration of the outlet gas. Based on the above equation, CO_2 conversion $[X(CO_2)]$ and CO yield [Y(CO)] were calculated as

$$X(\text{CO}_2) = \frac{G(\text{CO}_2)_{\text{inlet}} - P_{\text{total}} \times C(\text{CO}_2)_{\text{outlet}}}{G(\text{CO}_2)_{\text{inlet}}} \times 100\%,$$
(2)

$$Y(CO) = \frac{P_{\text{total}} \times C(CO)_{\text{outlet}}}{m_{\text{oc}}},$$
(3)

Normalized Y(CO) =
$$\frac{P_{\text{total}} \times C(\text{CO})_{\text{outlet}}}{m_{\text{oc}} \cdot M(\text{Fe})}$$
, (4)

where $G(CO_2)_{inlet}$ is the inlet CO_2 flow rate, $C(CO_2)_{outlet}$ and C (CO)_{outlet} are the CO₂ and CO concentrations of the outlet gas, respectively, m_{oc} is the mass of the oxygen carrier, and M(Fe) is the actual Fe content measured by ICP-OES.

2.6 | Computational Details

Density functional theory (DFT) calculations were conducted using a Vienna Ab initio Software Package (VASP) integrated with the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation and the projected augmented wave (PAW) method [46–49]. The cutoff energy of the plane-wave basis set was maintained at 400 eV. The exposed Fe(110), CaO(200), and CeO_{2-x}(200) planes were used to construct the model according to the AC HAADF-STEM results. A vacuum layer of 15 Å was used to prevent interactions between periodic images. The Brillouin zone of the surface unit cell was sampled by Monkhorst–Pack (MP) grids, with different k-point meshes for structure optimizations [50]. The surface was determined by a $2 \times 2 \times 1$ Monkhorst–Pack grid. The convergence criterion for the electronic self-consistent iteration and force were set to 10^{-5} eV and 0.01 eV/Å, respectively. The climbing image nudged elastic band (CI-NEB) [51–53] method was used to confirm the transition states with only one imaginary frequency along the reaction coordinates. The adsorption energy (E_{ads}) of the surface species is expressed as

$$E_{\rm ads} = E_{\rm total} - E_{\rm surface} - E_{\rm species},\tag{5}$$

where E_{total} represents the total energy of the adsorbed species with oxygen carrier surface, E_{surface} is the empty surface energy, and E_{species} denotes the energy of the gas phase species. The activation barrier (E_{a}) and reaction energy (E_{r}) are defined as

$$E_{\rm a} = E_{\rm TS} - E_{\rm IS},\tag{6}$$

$$E_{\rm r} = E_{\rm FS} - E_{\rm IS},\tag{7}$$

where E_{IS} , E_{TS} , and E_{FS} are the initial state, the transition state, and the final state energies, respectively.

3 | Results and Discussion

3.1 | Oxygen Carrier Characterization

After H₂ reduction, the phases of the as-calcined oxygen carriers evolved from CeO₂ and Ca₂Fe₂O₅ to CeO_{2-x}, CaO, and Fe, according to the ex situ and quasi-in situ XRD patterns (Supporting Information S1: Figures S5 and S6). This confirms the deep reduction of Fe³⁺ and partial reduction of Ce⁴⁺, as confirmed by the peak shift of 0.28° (Supporting Information S1: Figure S6). The physicochemical properties of the calcined oxygen carriers with different Ce dopant loadings are summarized in Supporting Information S1: Table S2, and representative TEM images of 50 mol% CeO₂·Ca₂Fe₂O₅ are shown in Supporting Information S1: Figure S7.

The 30-min H₂-reduced 50 mol% CeO_{2-x}·Fe·CaO sample was selected and analyzed using an AC HAADF-STEM, and it showed a sheet-like morphology. EDS mapping illustrates the partial overlap of Ca and Ce with Fe at 30 min of H₂ reduction, whereas those of Ca-Fe and Ce-Fe coincide well under deep oxidation and reduction (Figure 1A, B and Supporting Information S1: Figures S8 and S9). This phenomenon could be attributed to the oxygen carrier segregation and recombination (Supporting Information S1: Figure S10). The lattice fringes with interplanar spacings of 0.207, 0.244, and 0.276 nm in Figure 1C-E were consistent with Fe(110), CaO(200), and $CeO_{2-x}(200)$ planes, respectively. The selected area electron diffraction (SAED) indicated that the CeO_{2-x} has a cubic crystal [space group: Fm-3m(225)] and is oriented along the [011] direction. EELS scans of Fe and Ce were also conducted, to further analyze the electron distribution of the selected lines (see Figure 1F and Supporting Information S1: Figure S11). Fe L_3 and L_2 edges of four EELS lines showed identical positions, corresponding to 708.7 and 721.5 eV, resembling an Fe²⁺ reference (Figure 1G) [54]. The above results illustrate the nearly complete reduction of Fe in the bulk phase of 50 mol% CeO_{2-x} ·Fe·CaO with the presence of Fe²⁺ at the surface. On inspecting the profiles in Figure 1H, two distinctive edges were identified for Ce M_5 and M_4 , indicating the existence of Ce³⁺ and Ce⁴⁺ (Figure 1I). Quantitative results revealed that the Ce³⁺ distribution of the four lines was 57%, 68%, 74%, and 78%, respectively (Supporting Information S1: Tables S3 and S4 and Figure S12).

To further determine the chemical state and local coordination environment, in situ XAS measurements were conducted. The Fe K-edge X-ray absorption near-edge structures (XANES) of the calcined and 30-min reduced 50 mol% CeO2·Ca2Fe2O5 are presented in Figure 1J. The adsorption threshold energy E_0 of the calcined 50 mol% CeO2 ·Ca2Fe2O5 showed slightly higher than that of Fe₂O₃, which could be attributed to the electron transfer from $Fe \rightarrow Ca$, resulting in the intensified Fe–O bond. Specifically, the energy of the rising edges followed the sequence of Fe foil < reduced 50 mol% $CeO_2 \cdot Ca_2Fe_2O_5 < Fe_2O_3 < 50 mol\%$ CeO₂·Ca₂Fe₂O₅, testifying to the partial reduction of 50 mol% CeO₂·Ca₂Fe₂O₅. The Ce L₃-edge XANES spectra show a doublet due to the interaction between the 4 f orbitals of Ce and 2p orbitals of oxygen ligands [55]. Among the divided four sub-peaks (Supporting Information S1: Figure S13 and Table S5), component C can be assigned as Ce³⁺, and the C peak ratio of reduced CeO₂·Ca₂Fe₂O₅ is higher than that of the calcined sample, confirming the partial reduction of Ce^{4+} .

The Fourier-transformed (FT) extended X-ray absorption fine structure (EXAFS) spectra of Fe K-edge and Ce L₃-edge at k and R space are displayed in Figure 1K,L and Supporting Information S1: Figure S14, respectively. For the Fe K-edge, both the lengths of the Fe-O bond for calcined and reduced 50 mol% $CeO_2 \cdot Ca_2Fe_2O_5$ samples decreased compared with Fe_2O_3 , demonstrating the enhancement of the Fe-O bond energy due to the electron transfer (Table S6). Compared with the Fe-O-Fe structure of Fe₂O₃, the second-shell bond lengths of calcined CeO₂·Ca₂Fe₂O₅ increased by 0.10 Å, possibly owing to the formation of Fe-O-Ca. The second-shell length of reduced 50 mol% CeO₂·Ca₂Fe₂O₅ increases compared with that of the calcined sample, which could be attributed to the formation of the primary Fe-O-Ce structure. This structure could be the dominant factor that leads to the strong electron-donating capability. A new metallic Fe-Fe path (2.50 Å) with a coordination number (CN) of 5.4 appeared in the reduced 50 mol% CeO₂·Ca₂Fe₂O₅ spectrum, indicating the formation of Fe⁰ species. Wavelet transform results of the Fe K-edge and the Ce L₃edge for reduced 50 mol% CeO₂·Ca₂Fe₂O₅ also featured typical Fe-O-Ce coordination (Figure 1M-P and Supporting Information S1: Figure S15). The above-discussed results indicate the formation of the Fe-O-Ce interface, which could be dominant to the CO₂ activation and dissociation.

3.2 | CO₂-Splitting Performance

The CO₂ conversion and CO yield of the samples with different Ce dopant loadings tested at 700°C are shown in Figure 2A,B. At this temperature, irrespective of the Ce doping amount, both CO₂ conversion and CO yield over the modified oxygen carriers were increased significantly compared with Fe-CaO. In terms of the CO yield, 50 mol% CeO_{2-x}·Fe-CaO performs the best in CO₂ splitting among these materials, which achieves 546 µmol·min⁻¹·g⁻¹ at the



FIGURE 1 | Morphology and structure characterization. (A-F) AC HAADF-STEM images of reduced 50 mol% CeO_{2-x} ·Fe·CaO, whose reduction condition was $H_2:N_2 = 20:40 (40 \text{ mL}\cdot\text{min}^{-1})$ at 800°C for 30 min. (A1–A4) and the inset of (E) show the EDS element mappings and SAED pattern, respectively. EELS spectra of (G) Fe $L_{2,3}$ and (H) Ce $M_{4,5}$ edges along the four lines in (F). (I) Quantitative analysis results of the Ce $M_{4,5}$ edges. (J) Normalized XANES spectra at the Fe K-edge. (K, L) EXAFS analysis of the Fe K-edge at (K) *k* and (I) *R* space. Wavelet transform analysis of EXAFS for (M) Fe foil, (N) Fe₂O₃, (O) 50 mol% CeO₂·Ca₂Fe₂O₅, and (P) reduced 50 mol% CeO₂·Ca₂Fe₂O₅.

5th minute. Figure 2C shows the enhancement in CO_2 conversion and the improvement in the CO yield of the 50 mol% CeO_{2-x} ·Fe·CaO relative to Fe·CaO. As the splitting reaction proceeded, the enhancement of CO_2 conversion showed an initial increase in activity, followed by a decrease, with that of CO yield gradually reducing. Notably, the maximum enhancement of CO_2 conversion was as high as 426% at the 10th minute of CO_2 splitting. The effect of temperatures on the CO_2 splitting performances



FIGURE 2 | CO₂-splitting performance. (A) CO₂ conversion and (B) CO yield over various Ce-doped Fe-CaO for splitting, and (C) enhanced CO₂ conversion and CO yield of 50 mol% CeO_{2-x} ·Fe·CaO relative to Fe·CaO at $T = 700^{\circ}$ C, N₂: CO₂ = 40: 10 mL·min⁻¹, and WHSV = 10000 mL·g⁻¹ · h⁻¹. (D) Comparison of the apparent activation energy between Fe·CaO and 50 mol% CeO_{2-x} ·Fe·CaO. (E) Comparisons of the CO₂-splitting rate between the present work and the published literature. The results of the present work are calculated using the cumulative CO yields for the first 2 min of splitting at 700°C, 750°C, 800°C, 850°C, and 900°C. (F) 100 isothermal redox cycles of 50 mol% CeO_2 ·Ca₂Fe₂O₅ at 800°C. (G) Schematic illustration of the exsolution/dissolution behavior of 50 mol% CeO_2 ·Ca₂Fe₂O₅.

of Fe·CaO and 50 mol% CeO₂·Ca₂Fe₂O₅ was also explored (Supporting Information S1: Figures S16–S18). As the temperature increased from 600°C to 900°C, the CO₂ conversion and CO yield at the 5th minute time on line showed a similar trend; activities first increased slightly, then dramatically, and finally reached a plateau as the temperature approached 900°C. The critical temperatures of Fe·CaO and 50 mol% CeO_{2-x}·Fe·CaO to ensure

efficient CO₂ splitting were 750°C and 700°C, respectively, highlighting the promotional effect of Ce doping in facilitating lowtemperature CO₂ splitting. However, at 900°C, both 50 mol% CeO_{2-x}·Fe·CaO and Fe·CaO showed satisfactory performance at the initial stage of CO₂ splitting, owing to the outstanding electron-donating ability of Fe·CaO as well as the similar oxygen ion transferability of both materials at high temperatures [39]. On comparing the CO yield per mass of Fe, the normalized CO yield of 50 mol% $CeO_{2-x} \cdot Fe \cdot CaO$ was 44% higher than that of Fe \cdot CaO at 900°C (Supporting Information S1: Figure S19). When the weight hourly space velocity (WHSV) decreased from 10,000 to 5000 mL·g⁻¹·h⁻¹, the maximum CO₂ conversion at the 5th minute time on line of splitting increased from 46% to 70% at 700°C for 50 mol% $CeO_{2-x} \cdot Fe \cdot CaO$, whereas that of Fe · CaO achieved only 11%, highlighting the superior performance of 50 mol% $CeO_{2-x} \cdot$ Fe · CaO (Supporting Information S1: Figure S20). As the WHSV varied between 10,000 and 20,000 mL·g⁻¹·h⁻¹, both CO₂ conversion and CO yield decreased. Moreover, significant discrepancies between CO₂ conversion and CO yield for Fe · CaO at a WHSV of 10,000 mL·g⁻¹·h⁻¹ were observed, which can be attributed to CO₂ adsorption at 700°C (Supporting Information S1: Figure S21A) [56].

We conducted XRD, temperature-programmed transient (TPT) experiments, and TGA to clarify the transformation characteristics of CO₂ adsorption to splitting as a function of time and temperature. XRD results of Fe·CaO and 50 mol% CeO2-x·Fe·CaO oxidized by CO₂ at various durations of time at 700°C confirmed the presence of CO₂ adsorption by CaO due to the formation of CaCO₃ (Supporting Information S1: Figure S21B,C). However, 50 mol% CeO_{2-x}·Fe·CaO only formed trace amounts of CaCO₃, whereas abundant CaCO3 was observed for Fe-CaO. The appearance of trace amounts of CaFe₂O₄ on both samples may be due to imperfect mixing between CaO and Fe₂O₃ and slow solid-state diffusion [34]. Moreover, an MRU Vario Plus New gas analyzer equipped with a nondispersive infrared sensor and electrochemical cells was used to conduct the TPT experiments (Supporting Information S1: Figures S22 and S23; see detailed procedures in Supporting Information). Quantitative results revealed that the CO₂ splitting and adsorption proportions at 700°C for Fe-CaO were 16% and 84%, respectively, and for 50 mol% CeO_{2-x} · Fe·CaO, these were 94% and 6%, respectively (Supporting Information S1: Figure S24). The significant increase in the proportion of CO₂ splitting was in agreement with the ceria gateway effect, which promotes the dissociation of CO₂ into CO and the transformation of oxygen ions into Fe CaO [57]. Transient CO₂ conversion results demonstrated that the CO₂-splitting performance of 50 mol% CeO_{2-x} · Fe·CaO was comparable to that of Fe-CaO at relatively high temperatures (Supporting Information S1: Figure S25). To eliminate the impact of CO_2 adsorption at low temperatures, kinetic measurements for CO₂ splitting were conducted at 800°C, 850°C, and 900°C (Figure 2D and Supporting Information S1: Figures S26 and 27). Moreover, the zero-order reaction model was used to acquire reaction rate constants (Supporting Information S1: Figures S28-S32 and Tables S7-S9). The apparent activation energies of Fe CaO and 50 mol% CeO_{2-x} · Fe·CaO were calculated to be 29.9 ± 1.2 and $26.6 \pm 1.1 \text{ kJ} \cdot \text{mol}^{-1}$, respectively, demonstrating the role of Ce doping in lowering the energy barrier of CO₂ splitting (Supporting Information S1: Table S10).

Compared with the previously reported CO_2 -splitting rates, our proposed 50 mol% $CeO_{2-x} \cdot Fe \cdot CaO$ oxygen carrier is highly competitive and outperforms most of the literature examples reported (Figure 2E and Supporting Information S1: Table S11). 50 mol% $CeO_{2-x} \cdot Fe \cdot CaO$ showed remarkable cyclic performance even after the 100th redox cycle (Figure 2F and Supporting Information S1: Figures S33–S36). SEM images and elemental distributions of calcined, first reduced, and second reduced 50 mol% CeO₂·Ca₂Fe₂O₅ revealed the presence of Fe nanoparticle exsolution and dissolution under corresponding reduction and oxidation conditions (Supporting Information S1: Figures S37–S43). This effect was also highlighted recently [45], which suppresses sintering and agglomeration of the oxygen carrier. To facilitate an understanding of the exsolution behavior, a schematic illustration of this process is provided (Figure 2G). The Ca₂Fe₂O₅ samples without Ce doping show no obvious exsolution under identical reduction conditions, implying the promotion of Ce on the exsolution of Fe nanoparticles from the oxide substrate (Supporting Information S1: Figures S44–S46). This may be to the benefit of consuming $O^{2-}_{lattice}$ transformed from the Fe–O_v–Ce interface, thus enhancing fast oxygen acceptance.

3.3 | Mechanistic Investigation

Analysis of H₂-TPR patterns indicated that the reduction peak following Ce doping decreased from 717.0°C to 678.2°C, demonstrating the enhanced lattice oxygen transferability (Figure 3A). The quantitative analysis of H_2 consumptions confirms the lattice oxygen consumption from CeO₂ to CeO_{1.96} (Supporting Information S1: Figure S47). To analyze the CO_2 desorption and splitting behaviors, we conducted in situ reduced CO₂-TPD measurements (Figure 3B and Supporting Information S1: Figure S48). We attributed the higher CO peak intensity observed to the existence of the Ce–O_v structure being more favored for CO₂ splitting at low temperatures (Supporting Information S1: Figure S49). The desorption properties of Fe--CaO and 50 mol% CeO_{2-x}·Fe·CaO show obvious differences, suggesting a transition from CO₂ desorption to splitting after Ce doping. Here, the CO₂ activation temperature of 50 mol% CeO_{2-x}·Fe·CaO reduces by 464.3°C compared with that of Fe-CaO, as determined by in situ reduced CO₂-TPO (Figure 3C and Supporting Information S1: Figure S50), confirming the capability of Ce doping to contribute toward low-temperature CO₂ splitting. In situ EPR spectra of 50 mol% CeO_{2-x}·Fe·CaO reduced at both 800°C and 920°C reveal peaks at g = 2.003, confirming the generation of the oxygen vacancies, whereas this was not observed for Fe_·CaO (Figure 3D). Combined with the XAS results, we ascribe the enhanced properties of the Cedoped sample to the presence of oxygen vacancies and the formation of Fe-O_v-Ce sites within the Ca-Fe-Ce system, which act as an initiator for enhanced CO₂ splitting.

The Raman spectrum of CeO₂ is generally dominated by the Raman-active F_{2g} band at 465 cm⁻¹ and the vacancy-induced (D) band at 600 cm⁻¹, which represents a symmetrical stretching of oxygen around the Ce cation and a defect space containing oxygen vacancies, respectively [58]. We explored the coordination structure and the electronic states of 50 mol% CeO_{2-x}·Fe·CaO by in situ Raman spectroscopy and observed F_{2g} and D bands centered at 445 and 575 cm⁻¹ (Figure 3E). The former peak showed a strong red shift and asymmetrical broadening for the bulk counterpart, caused by shrinkage of the unit cell, owing to the permeation of Fe into the oxygen vacancy of CeO_{2-x}. This result was consistent with the variations in the CN in Supporting Information S1: Table S6, confirming the formation of the Fe–O_v–Ce structure. The variation of the latter peak was caused by a dramatic increase in oxygen



FIGURE 3 | CO₂-splitting mechanism analysis. (A) H₂-TPR results of Ca₂Fe₂O₅ and 50 mol% CeO₂·Ca₂Fe₂O₅. (B) CO₂-TPD-MS and (C) CO₂-TPO-MS results of Fe·CaO and 50 mol% CeO_{2-x}·Fe·CaO. (D) In situ EPR spectra of Fe·CaO and 50 mol% CeO_{2-x}·Fe·CaO. (E) In situ Raman spectrum and (F) [45] Fe Mössbauer spectrum of 50 mol% CeO_{2-x}·Fe·CaO. The inset of (E) presents the schematic of Fe interacting with the CeO_{2-x}. XPS spectra of (G) Ce 3d and (H) O 1s for 50 mol% CeO₂·Ca₂Fe₂O₅ reduced at different durations of time at H₂:N₂ = 20:40 (40 mL·min⁻¹) and 800°C. (I) Ratios of Ce³⁺/(Ce³⁺ + Ce⁴⁺) and O_β/(O_α + O_β + O_γ) versus reduction time.

deficiency and charge accumulation, supporting the in situ EPR results. The chemical states of corresponding Fe were also tested by [45] Fe Mössbauer spectroscopy (Figure 3F and Supporting Information S1: Table S12). Results revealed the existence of metallic α -Fe, γ -Fe, and Fe²⁺, whose contents were 85.5%, 12.6%, and 1.9%, respectively, confirming the existence of Fe–O and Fe–O–Ce bonds.

To elucidate the evolution of oxygen vacancy concentration as a function of reduction time, XPS measurements were performed (Figure 3G,I and Supporting Information S1: Tables S13 and 14). The Ce 3d XPS spectra were divided into 10 sub-peaks, which were labeled, as v^0 , v, v', v'', v''', u⁰, u, u', u'', and u'''. The notations v^0 , v', u⁰, and u' represent the Ce³⁺ species, whereas the rest

represent the Ce⁴⁺ species [59, 60]. Three characteristic peaks were identified from the O 1s XPS spectra, corresponding to the lattice O (O_{α}), defect O (O_{β}), and weakly bound O species (O_{γ}) such as surface hydroxyl groups [59, 60]. With increasing reduction time, both Ce³⁺/(Ce³⁺ + Ce⁴⁺) and O_{β}/(O_{α} + O_{β} + O_{γ}) increased as a whole, indicating the positive association of the oxygen vacancy concentration with the reduction time (see Supporting Information S1: Figure S51 for Ca 2p and Fe 2p spectra).

3.4 | DFT Calculations

To further clarify the low-temperature CO_2 -splitting mechanism, DFT calculations were conducted, and the crystallographic plane



FIGURE 4 | Theoretical calculations and proposed reaction mechanism. (A) Different CO₂ adsorption sites of isolated CeO_{2-x} (i) and 50 mol% CeO_{2-x} ·Fe·CaO (ii~vi). (B) CO₂ adsorption energies of the isolated CeO_{2-x} site (i) and five sites for 50 mol% CeO_{2-x} ·Fe·CaO (ii~vi). (C) Relative energy evolutions for the Fe/CeO_{2-x} interface of 50 mol% CeO_{2-x} ·Fe·CaO, the Fe/CaO interface of Fe·CaO, the CaO/CeO_{2-x} interface of 50 mol% CeO_{2-x} ·Fe·CaO, and the CeO_{2-x} site of isolated CeO_{2-x} ·Fe·CaO, the Fe/CaO interface of Fe·CaO, the CaO/CeO_{2-x} interface of 50 mol% CeO_{2-x} ·Fe·CaO, and the CeO_{2-x} ·Fe·CaO, the Fe/CaO interface of 50 mol% CeO_{2-x} ·GaO during CO₂ adsorption, activation, and dissociation. (D) CO₂ Bader charge for the Fe/CeO_{2-x} interface of 50 mol% CeO_{2-x} ·Fe·CaO, the Fe/CaO interface of 50 mol% CeO_{2-x} ·Fe·CaO during CO₂ adsorption, activation, and dissociation. (E) Schematic illustration of the low-temperature CO₂-splitting mechanism of 50 mol% CeO_{2-x} ·Fe·CaO.

of CeO_{2-x}(200)/Fe(110)/CaO(200) was selected according to the HR-TEM results together with Fe(110)/CaO(200) and CeO_{2-x}(200)/CaO(200) for comparison. The CO₂ adsorption energies of the isolated CeO_{2-x} site (i) and five sites for 50 mol% CeO_{2-x}·Fe·CaO, including the CaO site (ii), the Fe/CaO interface (iii), Fe site 1 (iv), Fe site 2 (v), and Fe/CeO_{2-x} interface (vi), were -0.30, -1.93, -1.60, -1.37, -1.39, and -1.87 eV, respectively (Figure 4A,B). The CO₂ activation on CaO(200) was found to have the lowest adsorption energy, which mainly occurs due to the preference of CO₂ adsorption to form carbonate. The adsorption of CO_2 beyond the Fe/CeO_{2-x} interface was selected for transition-state calculations due to its relatively high CO2 adsorption energy. The reaction barriers of CO₂ dissociation from CO* to CO beyond CeO2-x(200)/Fe(110)/CaO(200), Fe(110)/ CaO(200), CeO_{2-x}(200)/CaO(200), and isolated CeO_{2-x}(200) were calculated (Figure 4C and Supporting Information S1: Figure S52). Among these three cases, the Fe/CeO_{2-x} interface of $CeO_{2-x}(200)/Fe(110)/CaO(200)$ showed the lowest dissociation energy barrier of 0.31 eV, which was 0.40, 1.08, and 1.20 eV lower than those of Fe(110)/CaO(200), CeO_{2-x}(200)/CaO(200), and isolated CeO_{2-x}(200), confirming the superiority of the three-phase CeO_{2-x}(200)/Fe(110)/CaO(200) for CO₂ splitting. The Bader charges at Fe–Ce, Fe–Ca, and Ce–Ca interfaces also demonstrate the superiority of Fe/CeO_{2-x} in supplying electrons (Figure 4D).

Based on the above discussions, the low-temperature CO₂-splitting pathway with 50 mol% CeO_{2-x} ·Fe·CaO is summarized in Figure 4E, in which the synergistically intensified mechanism between CaO, Fe, and CeO_{2-x} was preliminarily deduced: first, the CO₂ was activated to form CO₂* beyond the Fe/CeO_{2-x} interface or CaO surface; second, the absorbed CO₂* was dissociated into CO* and O*; and third, the generated O* was bound by the Fe–O_v–Ce site; meanwhile, CO* was desorbed to generate CO. Finally, the captured lattice oxygen ($O^{2-}_{lattice}$) transformed and was consumed by Fe⁰ under the promotion of CaO. In

summation, the concerted interplay between the $\rm Fe-O_v-Ce$ interface and CaO promotes both $\rm CO_2$ conversion and CO yield.

4 | Conclusions

In this study, we have demonstrated the effectiveness of the Cedoped Fe₂CaO in low-temperature CO₂ splitting and elucidated the activation, dissociation, and O²⁻lattice consumption mechanism beyond the Fe-O_v-Ce and CaO microenvironment. Both the CO₂ conversion and CO yield over 50 mol% CeO_{2-x}·Fe·CaO were significantly enhanced at 700°C relative to Fe CaO, which achieved 46% and 546 μ mol·min⁻¹·g⁻¹, respectively. Moreover, the Ce-doped oxygen carrier showed exceptional redox durability after 100 CO₂ splitting cycles, accompanied by an exsolution + dissolution transformation, which is thought to inhibit sintering. Results from in situ reduced CO2-TPD-MS also indicated the superiority of Ce doping in CO₂ splitting at low temperatures. Results from in situ characterizations such as XAFS, Raman, and EPR confirmed the formation of abundant oxygen vacancies and the existence of an Fe-O_v-Ce structure. DFT results demonstrated the superiorities of the Fe(110)/ $CeO_{2-y}(200)$ interface for the activation and dissociation of CO_{2^*} into CO* and O*. To conclude, the engineered Fe-Ov-Ce microenvironment is the activator that triggers low-temperature CO₂ activation and dissociation, Fe is the active site for electron donation and O²⁻lattice consumption, whereas CaO acts as the structural promoter to enable $Fe^0 \rightarrow Fe^{3+}$ transformation. These findings provide valid strategies for the design and development of new-generation oxygen carriers with strong reducing abilities and satisfactory redox stability.

Acknowledgments

This work was supported by the National Key R&D Program of China (2022YFE0105900), the National Natural Science Foundation of China (52436006, 52476144, 52311530339, 42441835), and the Innovation-Driven Project of Central South University (2023ZZTS0721).

Conflicts of Interest

The authors declare no conflicts of interest.

References

1. Q. Chen, S. Meng, R. Liu, et al., "Plasma-Catalytic CO₂ Hydrogenation to Methanol Over CuO-MgO/Beta Catalyst With High Selectivity," *Applied Catalysis B: Environmental* 342 (2024): 123422.

2. S. Du, P. Yang, M. Li, L. Tao, S. Wang, and Z. Q. Liu, "Catalysts and Electrolyzers for the Electrochemical CO_2 Reduction Reaction: From Laboratory to Industrial Applications," *Chemical Communications* 60, no. 10 (2024): 1207–1221.

3. R. P. Ye, J. Ding, W. Gong, et al., "CO₂ Hydrogenation to High-Value Products Via Heterogeneous Catalysis," *Nature Communications* 10 (2019): 5698.

4. J. Zhu, P. Wang, X. Zhang, et al., "Dynamic Structural Evolution of Iron Catalysts Involving Competitive Oxidation and Carburization during CO_2 Hydrogenation," *Science Advances* 8, no. 5 (2022): eabm3629.

5. J. Liang, J. Liu, L. Guo, et al., "CO₂ Hydrogenation Over Fe-Co Bimetallic Catalysts With Tunable Selectivity Through a Graphene Fencing Approach," *Nature Communications* 15, no. 1 (2024): 512. 6. C. Hepburn, E. Adlen, J. Beddington, et al., "The Technological and Economic Prospects for CO₂ Utilization and Removal," *Nature* 575, no. 7781 (2019): 87–97.

7. T. Pinheiro Araújo, C. Mondelli, M. Agrachev, et al., "Flame-Made Ternary Pd-In₂O₃-ZrO₂ Catalyst With Enhanced Oxygen Vacancy Generation for CO₂ Hydrogenation to Methanol," *Nature Communications* 13, no. 1 (2022): 5610.

8. Z. Sun, C. K. Russell, K. J. Whitty, et al., "Chemical Looping-Based Energy Transformation Via Lattice Oxygen Modulated Selective Oxidation," *Progress in Energy and Combustion Science* 96 (2023): 101045.

9. X. Wu, Y. Guo, Y. Gu, et al., "In Operando-Formed Interface Between Silver and Perovskite Oxide for Efficient Electroreduction of Carbon Dioxide to Carbon Monoxide," *Carbon Energy* 5, no. 4 (2023): e278.

10. M. Guan, N. Lu, X. Zhang, et al., "Engineering of Oxygen Vacancy and Bismuth Cluster Assisted Ultrathin $Bi_{12}O_{17}Cl_2$ Nanosheets With Efficient and Selective Photoreduction of CO₂ to CO," *Carbon Energy* 6, no. 4 (2024): e420.

11. J. Zhang, Y. Wang, H. Wang, D. Zhong, and T. Lu, "Enhancing Photocatalytic Performance of Metal-Organic Frameworks for CO_2 Reduction by a Bimetallic Strategy," *Chinese Chemical Letters* 33, no. 4 (2022): 2065–2068.

12. S. Vijay, W. Ju, S. Brückner, S. C. Tsang, P. Strasser, and K. Chan, "Unified Mechanistic Understanding of CO_2 Reduction to CO on Transition Metal and Single Atom Catalysts," *Nature Catalysis* 4, no. 12 (2021): 1024–1031.

13. K. J. Noh, B. J. Park, Y. Wang, et al., "Tailoring Local Structures of Atomically Dispersed Copper Sites for Highly Selective CO₂ Electroreduction," *Carbon Energy* 6, no. 4 (2024): e419.

14. D. Song, Y. Lin, S. Fang, et al., "Unraveling the Atomic Interdiffusion Mechanism of NiFe₂O₄ Oxygen Carriers During Chemical Looping CO_2 Conversion," *Carbon Energy* 6, no. 8 (2024): e493.

15. W. C. Chueh, C. Falter, M. Abbott, et al., "High-Flux Solar-Driven Thermochemical Dissociation of CO₂ and H₂O Using Nonstoichiometric Ceria," *Science* 330, no. 6012 (2010): 1797–1801.

16. C. Agrafiotis, M. Roeb, and C. Sattler, "A Review on Solar Thermal Syngas Production Via Redox Pair-Based Water/Carbon Dioxide Splitting Thermochemical Cycles," *Renewable and Sustainable Energy Reviews* 42, no. C (2015): 254–285.

17. W. Fang, C. Wang, Z. Liu, et al., "Physical Mixing of a Catalyst and a Hydrophobic Polymer Promotes CO Hydrogenation Through Dehydration," *Science* 377, no. 6604 (2022): 406–410.

18. L. Lu, F. Qiu, H. Alhumade, H. Zhang, and A. Lei, "Tuning the Oxidative Mono- or Double-Carbonylation of Alkanes With CO by Choosing a Co or Cu Catalyst," *ACS Catalysis* 12, no. 15 (2022): 9664–9669.

19. C. Dong, M. Marinova, K. B. Tayeb, et al., "Direct Photocatalytic Synthesis of Acetic Acid From Methane and CO at Ambient Temperature Using Water as Oxidant," *Journal of the American Chemical Society* 145, no. 2 (2023): 1185–1193.

20. D. Marxer, P. Furler, M. Takacs, and A. Steinfeld, "Solar Thermochemical Splitting of CO_2 Into Separate Streams of CO and O_2 With High Selectivity, Stability, Conversion, and Efficiency," *Energy & Environmental Science* 10, no. 5 (2017): 1142–1149.

21. K. Gao, X. Liu, Q. Wang, et al., "Remarkable Solar Thermochemical CO_2 Splitting Performances Based on Ce- and Al-Doped SrMnO₃ Perovskites," *Sustainable Energy & Fuels* 7, no. 4 (2023): 1027–1040.

22. M. Tou, R. Michalsky, and A. Steinfeld, "Solar-Driven Thermochemical Splitting of CO_2 and in Situ Separation of CO and O_2 Across a Ceria Redox Membrane Reactor," *Joule* 1, no. 1 (2017): 146–154.

23. J. I. Makiura, T. Higo, Y. Kurosawa, et al., "Fast Oxygen Ion Migration in Cu-In-Oxide Bulk and Its Utilization for Effective CO_2

Conversion at Lower Temperature," *Chemical Science* 12, no. 6 (2021): 2108–2113.

24. A. Haeussler, S. Abanades, J. Jouannaux, and A. Julbe, "Demonstration of a Ceria Membrane Solar Reactor Promoted by Dual Perovskite Coatings for Continuous and Isothermal Redox Splitting of CO_2 and H_2O ," *Journal of Membrane Science* 634 (2021): 119387.

25. M. Wenzel, L. Rihko-Struckmann, and K. Sundmacher, "Thermodynamic Analysis and Optimization of RWGS Processes for Solar Syngas Production From CO_2 ," *AIChE Journal* 63, no. 1 (2017): 15–22.

26. Y. Kang, Y. Han, C. Wei, et al., "A Novel Carbon Cycle Process Assisted by Ni/La_2O_3 Catalyst for Enhanced Thermochemical CO_2 Splitting," *Journal of Energy Chemistry* 61 (2021): 297–303.

27. Y. Kim, H. S. Lim, H. S. Kim, M. Lee, J. W. Lee, and D. Kang, "Carbon Dioxide Splitting and Hydrogen Production Using a Chemical Looping Concept: A Review," *Journal of CO2 Utilization* 63 (2022): 102139.

28. D. Maiti, B. J. Hare, Y. A. Daza, A. E. Ramos, J. N. Kuhn, and V. R. Bhethanabotla, "Earth Abundant Perovskite Oxides for Low Temperature CO_2 Conversion," *Energy & Environmental Science* 11, no. 3 (2018): 648–659.

29. Y. Qiu, L. Ma, D. Zeng, et al., "Efficient CO_2 to CO Conversion at Moderate Temperatures Enabled by the Cobalt and Copper Co-Doped Ferrite Oxygen Carrier," *Journal of Energy Chemistry* 46 (2020): 123–132.

30. Y. Qiu, L. Ma, M. Li, et al., "Copper and Cobalt Co-Doped Ferrites as Effective Agents for Chemical Looping CO₂ Splitting," *Chemical Engineering Journal* 387 (2020): 124150.

31. H. S. Lim, Y. Kim, D. Kang, M. Lee, A. Jo, and J. W. Lee, "Fundamental Aspects of Enhancing Low-Temperature CO_2 Splitting to CO on a Double La₂NiFeO₆ Perovskite," *ACS Catalysis* 11, no. 19 (2021): 12220–12231.

32. F. Orsini, D. Ferrero, S. F. Cannone, et al., "Exsolution-Enhanced Reverse Water-Gas Shift Chemical Looping Activity of $Sr_2FeMo_{0.6}Ni_{0.4}O_{6-\delta}$ Double Perovskite," *Chemical Engineering Journal* 475 (2023): 146083.

33. L. Ma, Y. Qiu, M. Li, et al., "Spinel-Structured Ternary Ferrites as Effective Agents for Chemical Looping CO_2 Splitting," *Industrial & Engineering Chemistry Research* 59, no. 15 (2020): 6924–6930.

34. M. Ismail, W. Liu, M. T. Dunstan, and S. A. Scott, "Development and Performance of Iron Based Oxygen Carriers Containing Calcium Ferrites for Chemical Looping Combustion and Production of Hydrogen," *International Journal of Hydrogen Energy* 41, no. 7 (2016): 4073–4084.

35. M. S. C. Chan, W. Liu, M. Ismail, Y. Yang, S. A. Scott, and J. S. Dennis, "Improving Hydrogen Yields, and Hydrogen: Steam Ratio in the Chemical Looping Production of Hydrogen Using Ca₂Fe₂O₅," *Chemical Engineering Journal* 296 (2016): 406–411.

36. D. Hosseini, F. Donat, P. M. Abdala, S. M. Kim, A. M. Kierzkowska, and C. R. Müller, "Reversible Exsolution of Dopant Improves the Performance of $Ca_2Fe_2O_5$ for Chemical Looping Hydrogen Production," *ACS Applied Materials & Interfaces* 11, no. 20 (2019): 18276–18284.

37. L. Wang, Y. Lin, Z. Huang, K. Zeng, and H. Huang, "Conversion of Carbon Dioxide to Carbon Monoxide: Two-Step Chemical Looping Dry Reforming Using Ca₂Fe₂O₅-Zr_{0.5}Ce_{0.5}O₂ Composite Oxygen Carriers," *Fuel* 322 (2022): 124182.

38. Z. Sun, S. Chen, J. Hu, et al., " $Ca_2Fe_2O_5$: A Promising Oxygen Carrier for CO/CH₄ Conversion and Almost-Pure H₂ Production With Inherent CO₂ Capture Over a Two-Step Chemical Looping Hydrogen Generation Process," *Applied Energy* 211 (2018): 431–442.

39. Z. Sun, X. Wu, C. K. Russell, et al., "Synergistic Enhancement of Chemical Looping-Based CO₂ Splitting With Biomass Cascade Utilization Using Cyclic Stabilized Ca₂Fe₂O₅ Aerogel," *Journal of Materials Chemistry A* 7, no. 3 (2019): 1216–1226.

40. Z. Sun, H. Liu, H. Bai, et al., "The Crucial Role of Deoxygenation in Syngas Refinement and Carbon Dioxide Utilization During Chemical Looping-Based Biomass Gasification," *Chemical Engineering Journal* 428 (2022): 132068.

41. Z. Sun, X. Zhang, H. Li, et al., "Chemical Looping Oxidative Steam Reforming of Methanol: A New Pathway for Auto-Thermal Conversion," *Applied Catalysis B: Environmental* 269 (2020): 118758.

42. Z. Sun, T. Cai, C. K. Russell, et al., "Highly Efficient Methane Decomposition to H_2 and CO_2 Reduction to CO Via Redox Looping of $Ca_2Fe_xAl_{2-x}O_5$ Supported $Ni_yFe_{3-y}O_4$ Nanoparticles," *Applied Catalysis B: Environmental* 271 (2020): 118938.

43. C. Yang, Y. Lu, L. Zhang, et al., "Defect Engineering on CeO₂-Based Catalysts for Heterogeneous Catalytic Applications," *Small Structures* 2, no. 12 (2021): 210058.

44. H. J. Harbin, D. K. Unruh, D. J. Casadonte, and S. J. Khatib, "Sonochemically Prepared Ni-Based Perovskites as Active and Stable Catalysts for Production of CO_x -Free Hydrogen and Structured Carbon," *ACS Catalysis* 13, no. 7 (2023): 4205–4220.

45. Z. Sun, C. Hao, S. Toan, et al., "Recent Advances in Exsolved Perovskite Oxide Construction: Exsolution Theory, Modulation, Challenges, and Prospects," *Journal of Materials Chemistry A* 11, no. 34 (2023): 17961–17976.

46. J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized Gradient Approximation Made Simple," *Physical Review Letters* 77, no. 18 (1996): 3865–3868.

47. B. Hammer, L. B. Hansen, and J. K. Nørskov, "Improved Adsorption Energetics Within Density-Functional Theory Using Revised Perdew-Burke-Ernzerhof Functionals," *Physical Review B* 59, no. 11 (1999): 7413–7421.

48. P. E. Blöchl, "Projector Augmented-Wave Method," *Physical Review B* 50, no. 24 (1994): 17953–17979.

49. G. Kresse and D. Joubert, "From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method," *Physical Review B* 59, no. 3 (1999): 1758–1775.

50. H. J. Monkhorst and J. D. Pack, "Special Points for Brillouin-Zone Integrations," *Physical Review B* 13, no. 12 (1976): 5188–5192.

51. G. Henkelman and H. Jónsson, "Improved Tangent Estimate in the Nudged Elastic Band Method for Finding Minimum Energy Paths and Saddle Points," *Journal of Chemical Physics* 113, no. 22 (2000): 9978–9985.

52. G. Henkelman, B. P. Uberuaga, and H. Jónsson, "A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths," *Journal of Chemical Physics* 113, no. 22 (2000): 9901–9904.

53. D. Sheppard and G. Henkelman, "Paths to Which the Nudged Elastic Band Converges," *Journal of Computational Chemistry* 32, no. 8 (2011): 1769–1771.

54. L. Cavé, T. Al, D. Loomer, S. Cogswell, and L. Weaver, "A STEM/ EELS Method for Mapping Iron Valence Ratios in Oxide Minerals," *Micron* 37, no. 4 (2006): 301–309.

55. V. K. Paidi, D. L. Brewe, J. W. Freeland, C. A. Roberts, and J. Van Lierop, "Role of Ce 4*f* Hybridization in the Origin of Magnetism in Nanoceria," *Physical Review B* 99, no. 18 (2019): 180403.

56. M. Ismail, W. Liu, M. S. C. Chan, M. T. Dunstan, and S. A. Scott, "Synthesis, Application, and Carbonation Behavior of $Ca_2Fe_2O_5$ for Chemical Looping H_2 Production," *Energy & Fuels* 30, no. 8 (2016): 6220–6232.

57. M. Machida, T. Kawada, H. Fujii, and S. Hinokuma, "The Role of CeO_2 as a Gateway for Oxygen Storage Over CeO_2 -Grafted Fe_2O_3 Composite Materials," *Journal of Physical Chemistry C* 119, no. 44 (2015): 24932–24941. 58. E. Sediva, A. J. Carrillo, C. E. Halloran, and J. L. M. Rupp, "Evaluating the Redox Behavior of Doped Ceria for Thermochemical CO₂ Splitting Using Time-Resolved Raman Spectroscopy," *ACS Applied Energy Materials* 4, no. 2 (2021): 1474–1483.

59. Z. Chen, Q. Jiang, H. An, et al., "Platinum Group Metal Catalyst (Ruo_x, PtO_x, and Iro_x)-Decorated Ceria-Zirconia Solid Solution as High Active Oxygen Carriers for Solar Thermochemical CO₂ Splitting," *ACS Catalysis* 12, no. 13 (2022): 7719–7736.

60. L. Zhang, R. Chen, Y. Tu, et al., "Revealing the Crystal Facet Effect of Ceria in Pd/CeO_2 Catalysts Toward the Selective Oxidation of Benzyl Alcohol," *ACS Catalysis* 13, no. 4 (2023): 2202–2213.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.