Tailoring the crystal structure of CaTiO_3 by multielement doping for photo-assisted activation of NO

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Abstract

Although photocatalysis exhibits great prospects in selective catalytic reduction of NO_x (photo-SCR), the principles toward informed design of photo-SCR catalysts are lacking. Herein, based on inert CaTiO_3 , we tailor a crystal structure for high-efficiency de NO_x by partially substituting Ca with Ce, and Ti with Fe and Mn. The pristine CaTiO_3 is hard to remove NO in 100–300°C, while Ce-Fe-Mn doped CaTiO_3 could achieve nearly 100% NO conversion at 135°C under light irradiation (GHSV = 72000 h^{-1}). The dopants enable CaTiO_3 to activate NO and harvest visible light. By selectively activating gaseous molecules, Ti, Fe, and Mn present significant synergistic effects on accelerating the catalytic cycle of standard SCR. Moreover, it is firmly shown that the photocarriers intensify NO oxidation rather than NH_3 -to- NH_2 transformation. This work provides new insights into the structure-activity relationship of perovskite-based catalysts, and deepens the understanding of the light-driven mechanism.

Full Text

Cost-effective construction of NH_3 -SCR catalytic systems to realize NO_x removal in the low-temperature range has become urgent given the increasingly stringent environmental requirements. Since Tanaka group^{1,2} sparked the interest in photo-assisted selective catalytic reduction of NO (photo-SCR), a wealth of seminal studies³⁻⁶ have proved that photoirradiation is pretty efficacious in ameliorating NO conversion and N_2 selectivity in the low-temperature range. Although great achievements have been made in this field, to date, we still lack enough recognition of principles for constructing photo-SCR catalysts.

There are three fundamental issues that plague us. The first is that the reaction mechanism of NH_3 -SCR is disputed. NH_2NO and NH_4NO_2 are the two principal intermediates of standard SCR, which form following the Eley-Rideal (E-R) and Langmuir-Hinshelwood (L-H) mechanisms, respectively. The main point of contention is whether the catalytic cycle entails the involvement of NH_4NO_2 .⁷⁻¹¹ Some researchers^{10,12} proposed that whether NH_4NO_2 prevails depends on the catalyst nature and reaction temperature. Inexplicably, even for catalysts of the same ingredients, different reaction pathways have been reported.^{10,13} The inherent complexity of NH_3 -SCR reaction mechanism makes the informed construction of catalyst difficult.

The second issue is that the functions of photocarriers on the catalytic redox are unclear.^{5, 14} The mainstream view^{15,16} believed that light irradiation facilitates the transformation of chemisorbed NH_3 to NH_2 radical, thus accelerating the formation of the unstable intermediate NH_2NO proceeding via Eley-Ride kinetics. Recently, by illuminated *in situ* DRIFTS, Gang et al.¹⁷ found that photoirradiation could drive the oxidation of NO into nitrite and nitrate over Fe-doped TiO_2 . However, two questions remain to be answered : (i) is this promotional effect applicable to other types of photocatalysts, such as perovskites?

(ii) could the photocarriers transform the chemisorbed NH_3 to NH_2 species? Therefore, this fundamental issue about the light-driven effect has not been systematically conclusive.

The last is the elusive correlation between surface activity and optical property, both of which are intrinsically determined by the electronic structure of the catalyst. For perovskite oxides of the ABO_3 formula, the electron occupancy in e_g orbitals of the B-site element has been demonstrated as a useful descriptor to approximate the strength of adsorbate binding to the surface.¹⁸ Modifying the crystal structure also impacts the optical property, along with the quantum efficiency.^{19,20} The major challenge of photocatalyst design lies in how to tailor the crystal structure to harmonize the molecule adsorption and light response.

The perovskite structure is flexibly tunable since both A and B sites are easily doped by other elements.^{21,22} Previously, our group^{16,23} reported that perovskite-based catalysts have excellent photoactivity for NO removal, and doping perovskite with transition metal ions could evidently improve its performance. In this work, we choose the inert CaTiO_3 as a basal material and construct an efficient structure for photo-SCR de NO_x by doping it with Ce, Fe, and Mn elements. From Mn doping to Ce-Fe-Mn doping, each step modifies the crystal structure of CaTiO_3 , making it increasingly elaborate and efficient. By combining experiments with DFT calculations, a systematic investigation into the relationships between intrinsic activity and crystal structure is implemented, as well as the light-driven mechanism.

Results

Synthesis and catalyst characterization. All the perovskite samples are extracted from Ti-bearing blast furnace slag (Ti-slag) using a molten salt method followed by acid leaching. The chemical compositions of Ti-slag are placed in supplementary Table 1. By roasting Ti-slag with NaOH at 1400°C , a molten system consisting of Na_2O - CaO - MgO - TiO_2 - Al_2O_3 - SiO_2 was acquired. With the decrease in temperature, CaTiO_3 crystallized from the molten salt, and the rest formed a zeolite phase (supplementary Fig. 1). Three metal oxides, including CeO_2 , Fe_2O_3 , and MnO_2 , are also added into the mixture to modify CaTiO_3 . EDS mapping analysis on the roasted slag in Fig. 1a illustrates that most of Ca, Ti, Ce, and Mn are preferentially concentrated into the perovskite, while Na, Mg, Al, and Si are enriched in the zeolite. The distribution of Fe shows little difference between perovskite and zeolite, perhaps due to its considerable solubility in both two phases. The zeolite is easily removed by acid leaching, and thus high-purity perovskite samples are obtained.

The perovskite obtained by introducing 10 wt% CeO_2 is designated as 10Ce, and so on. The chemical compositions of the resultant samples are listed in supplementary Table 2. All the additional metal oxides are well incorporated into the samples, such as 19.7 wt% CeO_2 of 10Ce, 12.0 wt% Fe_2O_3 of 10Fe, and 10.4 wt% MnO of 10Mn. XRD analysis in Fig. 1b demonstrates that each sample is comprised of a perovskite phase. The (112) peaks from both 10Ce and 10Fe shift to the left relative to pure CaTiO_3 ,

showing that either Ce or Fe doping enlarges the unit cell. Conversely, Mn doping (10Mn) causes a right shift of (112) peak, lessening the lattice.

The morphology of the 5Ce5Fe10Mn specimen is investigated by HAADF-STEM and displayed in supplementary Fig. 2. In general, the particles from 5Ce5Fe10Mn are irregular and vary from dozens to several hundred nanometers. Elemental mapping on a typical particle (Fig. 1c) revealed that Ca, Ti, Fe, Ce, and Mn uniformly disperse in the particle at the nanometer scale. Hence, the dopants of Ce, Fe, and Mn are incorporated into the CaTiO_3 , forming a homogeneous solid solution rather than a mixture of metal oxides.

EXAFS spectra of 5Ce5Fe10Mn and 10Ce samples are recorded to reveal the positions of dopants in perovskite (Fig. 2). The Fourier-transformed k-space EXAFS spectra are displayed in supplementary Fig. 3, and the fitting parameters are placed in supplementary Table 3–5. The fitted coordination number of the Fe atom in 5Ce5Fe10Mn is 6.0. The coordination number of the Mn atom is constrained as 6.0 in the fitting for Mn K-edge EXAFS spectra, and the R factor is returned as 1.5%. These results confirmed that both Fe and Mn substitute Ti in CaTiO_3 and occupy the B sites. Constraining the coordination number of Ce atom as 12.0 returns 0.5% of R factor, substantiating that Ce substitutes Ca and occupies the A site. A diagram is presented in Fig. 2d to illustrate the crystal structure of Ce-Fe-Mn doped CaTiO_3 .

The specific surface areas of the samples are in a range of 14.9–16.5 m^2/g (supplementary Table 6), and the pore volumes are in 0.022–0.033 cm^3/g . The two parameters are almost one magnitude less than the nanocomposites fabricated by homogeneous precipitation²⁴, probably due to the fact that the samples are prepared by a high-temperature process.

NH_3 -SCR activity of single-element doped CaTiO_3 . The pure CaTiO_3 is hard to remove NO_x in 100–300°C (Fig. 3a). After introducing Ce, Fe, or Mn, the modified CaTiO_3 becomes active, showing that both A and B sites are responsible for the catalytic activity of perovskite. In terms of identical doping amount in mass ratio, 5Mn is superior to 5Ce and 5Fe. In particular, 10Mn could achieve 97.7% NO_x conversion at 250°C, exhibiting outstanding advantage of Mn doping to gift CaTiO_3 activity for NH_3 -SCR de NO_x .

In situ DRIFTS spectra of adsorbing $\text{NO} + \text{O}_2$ over CaTiO_3 and 10Mn were given in Fig. 3b. Three strong bands peaking at 1565 cm^{-1} , 1423 cm^{-1} , and 1343 cm^{-1} from 10Mn are assigned to bidentate nitrate, nitro compounds, and bridged nitrites, respectively. However, all the three bands from CaTiO_3 are quite weak, indicating that pure CaTiO_3 is difficult to activate gaseous NO molecule.

DFT calculations were performed to further investigate the effect of Mn doping on CaTiO_3 activity. The (001)-plane termination exposing TiO_2 atoms is chosen as a basal surface of CaTiO_3 , which is relatively stable under the anoxic condition.^{25,26} As shown in Fig. 3c, pure CaTiO_3 is capable of adsorbing NH_3 on the five-coordinated (Ti_{5c}) site with an adsorption energy of -0.86 eV, but hard to capture NO as the adsorption energy is -0.19 eV (Fig. 3d). With the introduction of Mn into CaTiO_3 (supplementary Fig. 4),

the adsorption energy of NH_3 slightly increases to -1.09 eV (Fig. 3e). Intriguingly, NO could bond strongly to the Mn_{5c} site of $\text{Ca}(\text{Ti}, \text{Mn})\text{O}_3$ ($E_{\text{ads}} = -1.37$ eV) as a bidentate anion carrying 0.20 electrons according to Bader charge analysis (Fig. 3f).

The adsorption configuration of NO on MnO_5 pyramids well satisfies the requirement of spatially symmetric overlap between NO π^* orbitals and MnO_5 e_g orbitals.²⁷ The redundant electrons in NO anion prefer occupying the antibonding orbital 2π of NO, weakening the N-O bond so that the chemisorbed NO is vulnerable to the lattice or chemisorbed oxygens to generate NO_2 (fast SCR)^{28–32}, or the chemisorbed NH_3 on adjacent Ti_{5c} to yield intermediate NH_2NO (L-H pathway). As depicted in supplementary Fig. 5, the formation of NH_2NO on the surface of Mn-doped CaTiO_3 is energetically favorable. Therefore, the SCR activity of $\text{Ca}(\text{Ti}, \text{Mn})\text{O}_3$ derives from the activation of NO by the Mn_{5c} site.

NH_3 -SCR activity of multielement doped CaTiO_3 . Compared with 10Mn, the activity of 5Fe10Mn is significantly improved in 100–300°C (Fig. 4a). The NO_x conversion over 5Fe10Mn reached 99% at 175°C, far more than the sum of these over sole 5Fe and 10Mn (Fig. 3a). Fe-Mn doping of CaTiO_3 presents synergistic effects on removing NO_x . Nevertheless, if we continued doping 5Fe10Mn with 5 wt% CeO_2 , the performance showed little difference between 5Ce5Fe10Mn and 5Fe10Mn in 100–300°C (Fig. 4a).

XPS analysis in Fig. 4b showed that with the incorporation of Fe into 10Mn, the peak assigned to O 1s shifts from 529.0 eV to the higher energy of 529.3 eV, indicating that the surface oxygens from 10Mn carried more electrons than those from 5Fe10Mn. It is easy to understand that the substitution of B-site Ti^{4+} by aliovalent Fe^{3+} leads to the decrease in the valence electrons transferring to the oxygen anions (Charge distribution of lattice oxygen is placed in supplementary Fig. 6).

The redox behaviors of 10Mn and 5Fe10Mn were also evaluated by H_2 -TPR experiments (supplementary Fig. 7). The strongest peak from 10Mn is centered at 604.4°C, and that from 5Fe10Mn at 566.3°C. Fe addition shifts the reduction peak to the lower temperature, enhancing the diffusion of O^{2-} anion within the lattice.³³ This might be partially ascribed to the oxygen vacancies introduced by the p-type doping of perovskite, which facilitates the movements of electrons and oxygen ions.³⁴ The oxygen vacancies also provide energetically favorable connection channels for gaseous O_2 molecules, triggering the dissociation of O_2 into O atoms, further expediting the oxidation of NO.³⁵ However, considering that the 5Fe sample as a p-type doped perovskite possesses similar features, the synergetic effects between Fe and Mn dopants could not be ascribed to the oxygen vacancies.

To explore the underlying mechanism, we built a CaTiO_3 model with Fe and Mn atoms situated in the B sites (supplementary Fig. 6c). In this model, the FeO_6 and MnO_6 octahedra are conjoined with each other by a bridged oxygen. DTF calculations reveal that for Mn-doped CaTiO_3 , the gaseous O_2 molecule prefers binding to the Mn_{5c} and Ti_{5c} sites with an adsorption energy of -1.26 eV (Fig. 4c). The chemisorbed O_2 could further combine with gaseous NO to produce monodentate nitrate binding to the Mn_{5c} site ($\Delta E =$

-1.65 eV) as shown in Fig. 4d (supplementary Video 1). By contrast, for Fe-Mn doped CaTiO_3 , the gaseous O_2 molecule selectively binds to the Fe_{5c} site rather than the Mn_{5c} or Ti_{5c} site (Fig. 4e, $E_{\text{ads}} = -1.12$ eV). The subsequently generated nitrate is still attached to the Fe_{5c} site (Fig. 4f, $E_{\text{ads}} = -2.56$ eV, supplementary Video 2). The addition of Fe into Mn-doped CaTiO_3 converts the oxidation center of NO to nitrate from the Mn_{5c} site to the Fe_{5c} site. This conversion exerts profound influence on the reaction pathway of the SCR process since nitrate is the precursor of NH_4NO_2 .

Based on DFT calculations, we propose two reaction routes to describe the standard SCR over Mn and Fe-Mn doped CaTiO_3 . As shown in Fig. 5, the catalytic cycle over $\text{Ca}(\text{Ti}, \text{Mn})\text{O}_3$ (the outer ring) comprises thirteen steps involving the NH_2NO and NH_4NO_2 intermediates.^{9,11,13} In this cycle, both two intermediates bind to the Mn_{5c} site thus their formations have to proceed by sequence. Fe-Mn doping makes O_2 selectively bind to the Fe_{5c} site, lightening the burden of the Mn_{5c} site, and also increasing the NO coverage on Mn_{5c} sites. More importantly, NH_4NO_2 could form in tandem with the generation of NH_2NO , markedly shortening the reaction pathway. The catalytic cycle over $\text{Ca}(\text{Ti}, \text{Mn}, \text{Fe})\text{O}_3$ could be completed within eight steps (the inner ring in Fig. 5).

Photo-SCR activity of doped CaTiO_3 . Under light irradiation, the performance of perovskite for NO removal is significantly improved, especially in 100–200 °C (Fig. 6a). The 99%-conversion temperature over illuminated 5Ce5Fe10Mn is about 135°C, far lower than 175°C over ground-state 5Ce5Fe10Mn (Fig. 4a). As the light turns on at 125°C (Fig. 6b), NO_x conversion over 5Ce5Fe10Mn rises from about 56–71% at 125°C without the decrease in N_2 selectivity, demonstrating that photocatalysis could serve as a green and effective technique to promote NO removal.

Pristine CaTiO_3 is hard to harvest the visible light due to its wide bandgap of 3.2 eV. By introducing dopants, the light wavelength absorbed by perovskite extends from the ultraviolet band to the visible band (Fig. 6c). The calculations on the projected density of states (Fig. 6d) disclose that Mn doping introduces an impurity band composed of Mn 3d and O 2p orbitals between the valence and conduction band. For Fe-Mn doped CaTiO_3 , there are four impurity bands, including the donor levels composed of Fe 3d, Mn 3d, and O 2p orbitals below Fermi level, and the acceptor levels composed of Mn 3d and O 2p orbitals above Fermi level. The impurity levels narrow the bandgap and enable the perovskite to harvest the visible light.

Although 5Ce5Fe10Mn shows little difference in NO removal with 5Fe10Mn in the dark (Fig. 4a), the former is notably superior to the latter under light irradiation (Fig. 6a). Li et al.⁵ previously reported that PrFeO_3 doped with Ce displays a redshift of UV-vis absorption. Similar phenomena are observed in Fig. 6c. Relative to 5Fe10Mn, 5Ce5Fe10Mn exhibits enhanced light adsorption in the wavelength range from 500 nm to 800 nm. The optimization of optical property by Ce doping improves the perovskite photoactivity.

To unravel photocarriers roles in NO removal, *in situ* IR spectra of 5Ce5Fe10Mn with gaseous molecules adsorbed were recorded in the dark and light at 125°C. The dark spectra of NH₃-adsorbed 5Ce5Fe10Mn (black line in Fig. 6e) have four strong peaks. Two peaks around 931 cm⁻¹ and 966 cm⁻¹ are assigned to weakly absorbed NH₃,³⁶ the one centered at 1250 cm⁻¹ corresponds to NH₃ coordinated on Lewis acid site,³⁷ and that around 1366 cm⁻¹ belongs to NH₄⁺ bonded to Bronsted acid site.³⁸ The illuminated spectra (red line in Fig. 6e) vary little in comparison to the dark counterpart. Most peaks remain unchanged except for those at 1250 cm⁻¹ and 1366 cm⁻¹. The intensity of the former increases while the latter becomes a bit weak, suggesting that under light irradiation, the adsorption of NH₃ on the Lewis acid site is enhanced while the adsorption on the Bronsted acid site is mildly inhibited.

The characteristic absorption peaks of NH₂ species are generally distributed in the range of 1505–1580 cm⁻¹.³⁹ Nevertheless, none of such peaks appears in the dark or illuminated spectra, clearly substantiating that the N-H bond from the chemisorbed NH₃ on 5Ce5Fe10Mn is hard to break at 125°C, even assisted by light irradiation.

There are four strong peaks in the dark spectra of 5Ce5Fe10Mn with NO + O₂ adsorbed (black line in Fig. 6f). These located at 1600 cm⁻¹ and 1630 cm⁻¹ are assigned to the bridged nitrate,¹⁷ and those at 1850 cm⁻¹ and 1960 cm⁻¹ are ascribed to the weakly adsorbed NO species. The illuminated spectra (red line in Fig. 6f) show apparent differences from the dark counterpart. On the one hand, the intensities of the above four peaks become stronger. On the other, a series of strong peaks appear in the range from 1495 cm⁻¹ to 977 cm⁻¹. The peak at 1100 cm⁻¹ is assigned to nitrito monodentate species,⁴⁰ those around 1200 cm⁻¹, 1332 cm⁻¹, and 1465 cm⁻¹ are attributed to nitrites,^{33,41} and that at 1495 cm⁻¹ corresponds to monodentate nitrate.³⁶ These results manifest that light irradiation dramatically promotes NO oxidation rather than NH₃-to-NH₂ transformation.

Discussion

The conventional fabrication of Ti-based perovskite always uses expensive tetrabutyl titanate as a precursor.⁴² Nowadays, titanium extraction from minerals still needs to go through complicated procedures with high costs. In this work, CaTiO₃ is synthesized by a molten-salt method with sodium aluminosilicate as the flux. This method provides a possibility to directly extract high-purity Ti-based perovskite from the Ti-bearing minerals because most titanium in the earth exists in the form of oxides. According to our experiments, a series of Ti-based perovskite could be fabricated by this method at low cost, such as PbTiO₃, BaTiO₃, LaTiO₃, and so on.

No matter by Fe-Mn doping or light irradiation, the deNO_x activity of modified CaTiO₃ mainly originates from the activation of NO. Hence, constructing photo-SCR catalysts from Ti-based perovskite should focus the principle issue on how to activate NO. Jonathan et al.²⁷ proposed that the binding strength of NO on perovskite surface depends on the B-site e_g filling, specifically, increasing with the decrease in e_g

filling in the range from 1 to 0.5. According to our results, NO adsorption rises as the e_g filling increases from 0 of CaTiO_3 to 0.06 of $\text{Ca}(\text{Ti}, \text{Mn})\text{O}_3$, indicating a volcano shape of NO adsorption as a function of e_g filling in the range from 0 to 1. The results also suggest that doping Ti-based perovskite with metal ions of e_g filling greater than 0, such as Co^{3+} , and Ni^{3+} , could augment NO adsorption. Furthermore, doping CaTiO_3 simplifies the regulation of electronic structure on the optical property so that more attention could be put into how to activate NO. This strategy also extends the material range for photo-SCR deNO_x to semiconductors of the wide bandgap.

It is widely accepted that NH_2NO is a requisite in the cycle of standard SCR, but the involvement of NH_4NO_2 is in dispute. Powerful evidence by the time-resolved spectroscopy from Marberger et al.¹⁰ showed that NH_3 coordinated to Bronsted site (B_{NH_3}) of $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ does not participate in the catalytic cycle. NH_3 binding to Lewis sites (L_{NH_3}) could react with gaseous NO to form NH_2NO , generating a Bronsted acid site. However, if L_{NH_3} could combine with this as-obtained Bronsted site, a new B_{NH_3} would be produced. This B_{NH_3} could be consumed by forming NH_4NO_2 so that the total amount of B_{NH_3} remains constant, also explaining the results of Fig. 1 in ref 10. Therefore, the reaction mechanisms involving both NH_2NO and NH_4NO_2 are also supported by Marberger's results.

A lot of enlightening studies^{12,13,43,44} reported that catalysts composed of different metal oxides are always superior to single metal oxide in terms of SCR performance. Most of the authors believed that the redox cycle between multivalent metal ions promotes NO-to- NO_2 oxidation, triggering the fast SCR reaction. Our results demonstrate that Fe-Mn doping of CaTiO_3 acts on the standard SCR by shortening the reaction pathway, providing new insights into the synergistic effect between multivalent metal ions.

Emphasizing the synergistic effect between Fe and Mn does not mean that Ti is dispensable in this system. Instead, Ti of $\text{Ca}(\text{Ti}, \text{Mn}, \text{Fe})\text{O}_3$ has two momentous effects in the SCR process. First, the Ti_{5c} site selectively adsorbs NH_3 , initiating the catalytic cycle by reacting with chemisorbed NO on the Mn_{5c} site. The cooperation between Ti and Mn boosts the formation of NH_2NO , and is more efficient than that between two Mn sites since the high adsorption strength of NO on the Mn_{5c} site, to some extent, inhibits NH_3 adsorption along with NH_2NO formation. Second, Ti 3d orbitals are the main components of the valence band, dictating the optical property of perovskite. Owing to the unique function of Ti, CaTiO_3 is a suitable framework to construct efficient catalytic units for photo-SCR deNO_x .

NH_3 -SCR deNO_x involves three feeding gases, namely NO, NH_3 , and O_2 . A single type of active site may lead to excessive coverage of the catalyst surface by specific gas molecules, thus lowering the reaction efficiency. Compared with modulating gas adsorption strength, constructing disparate sites to selectively activate gas molecules could be a more feasible alternative to heighten the SCR reaction rate.

Methods

Materials. The perovskite-based catalyst was directly extracted from Ti-bearing blast furnace slag (Ti-slag), which is a kind of metallurgical solid waste. More details about Ti-slag could be acquired in the supporting material. The Ti-slag was provided by Pangang Group Co., Ltd., China, and its chemical analysis is shown in Table 1. The slag was crushed, ground and sieved through a 200-mesh sieve before use. Unless otherwise specified, all of the rest reagents used in this study were of analytical grade and provided by Sinopharm Chemical Reagent Co., Ltd., China.

Catalyst preparation. To obtain the target perovskite from Ti-slag, a process involving mineral phase reconstruction followed by acid leaching was adopted. To be specific, a powder mixture composed of 100.0 g of Ti-slag, 23.0 g of NaOH, 10.0 g of MnO₂, 5.0 g of Fe₂O₃, and 5.0 g of CeO₂ was placed in the MgO crucible and roasted at 1400°C for one hour. As the sintered sample was cooled to room temperature, it was crushed and ground into fine particles for acid leaching and characterization.

15.0 g of the sintered sample power was placed in a glass beaker of 500 mL, and then 225 mL of 8% hydrochloric acid was added into the beaker. The mixture was stirred with a Teflon agitator at 25°C for 60 min. In this way, almost all the aluminosilicates were dissolved and transferred into the solution. After the slurry was filtered, the solid residue was dried at 105 °C for four hours for further analysis. The as-obtained sample was denoted as 5Ce5Fe10Mn, in which the number represents the mass ratio of the following oxide to Ti-slag. Likewise, the label '10Mn' meant that the mass ratio of MnO₂ to Ti-slag in the powder mixture was 10%, and neither CeO₂ nor Fe₂O₃ was incorporated into the mixture.

Catalyst characterization. X-ray diffraction (XRD) patterns were collected by the Rigaku X-ray diffractometer (Ultima ®) with Cu K α radiation. Mineralogy analysis of the specimen was performed by field emission scanning electron microscopy (SEM, JSM-6490LV) equipped with an Oxford energy dispersive X-ray spectroscope (EDS). Morphology analysis was carried out by scanning transmission electron microscopy in high-angle annular dark field (HAADF-STEM, FEI TalosF200x). The high-resolution mapping of elements was implemented by Super-X EDS.

Fe and Mn K-edge EXAFS measurements were carried out at the BL01B1 beamline at Spring-8 of the Japan Synchrotron Radiation Research Institute (JASRI). Ce L_{III}-edge EXAFS measurement was collected at the Beamline of TPS44A1 in National Synchrotron Radiation Research Center (NSRRC). All the measurements were performed at room temperature, and XAFS data were recorded in the fluorescent mode. The X-ray energy was calibrated using Fe and Mn foils, and the data analyses were performed utilizing Athena and Artemis in the Demeter software package.

X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific K-Alpha spectrometry using Al K α irradiation. Raman spectra were obtained by the Renishaw Raman spectrophotometer. UV-vis diffuse reflectance spectra (DRS) of the specimens were recorded by a PerkinElmer Spectrometer (Lambda 950). The specific surface area of the specimen was measured by Brunauer-Emmett-Teller (BET) method. Both temperature-programmed reduction of H₂ (H₂-TPR) and desorption of NH₃ (NH₃-TPD) were implemented on a Huasi instrument (DAS-7000).

In situ DRIFT experiments were performed on a Nicolet 6700 spectrometer in the wavenumber range of 2000 to 1000 cm^{-1} with 4 cm^{-1} resolution. *In situ* IR spectra were collected on a PerkinElmer spectrometer in the wavenumber range of 2000 to 800 cm^{-1} with 4 cm^{-1} resolution. The detailed procedures for *in situ* IR spectrum are as follows. First, the specimen was treated at 300 °C under N_2 flow for 0.5 h to remove the species adsorbed on the specimen surface. Second, the specimen was regulated to the target temperature to obtain a background spectrum which should be subtracted from the specimen spectrum. Then, the specimen was exposed to a flow of 1000 ppm NH_3 or 1000 ppm NO + 3 vol% O_2 for one hour, and the IR spectrum in the dark was recorded. Finally, the Xe lamp was turned on, and the IR spectrum under light irradiation was collected 15 min later.

Catalytic activity test. The SCR activity was tested in a fixed-bed reactor equipped with a Xenon lamp. The simulated gas consisted of 1000 ppm NO , 1000 ppm NH_3 , 3 vol% O_2 , and a balance of N_2 , corresponding to a gas hourly space velocity (GHSV) of 72000 h^{-1} . Both NO and NO_2 were determined by a BUV150 flue gas analyzer, NH_3 determined by a BLD200 analyzer, and N_2O by a BGM250 analyzer. During the catalytic process, the reactor was cooled by circulating water to offset the temperature fluctuation caused by light irradiation. The NO conversion percentage and N_2 selectivity were calculated by the following formula:

$$\text{NO conversion (\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selectivity} = \left(1 - \frac{2 [\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}]_{\text{out}} - [\text{NH}_3]_{\text{out}}}\right) \times 100\% \quad (2)$$

Computational details. The structural relaxation and singlet energy point energy calculations were performed using the density functional theory (DFT) method as implemented in Vienna Ab initio Simulation Package (VASP)^{45,46}. The generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) functional was used to evaluate the exchange-correlation potential⁴⁷. The project-augmented wave approach was employed to represent the core-electron interaction. The atomic orbitals treated as valence states were as follows: 3s3p4s of Ca, 3d4s of Ti, 3p3d4s of Mn, 3p3d4s of Fe, and 2s2p of O. Hubbard corrections with $U_{\text{eff}} = 3.9$ eV and 5.3 eV were applied to describe the 3d-orbitals of Fe and Mn atoms, respectively.

The lattice constant of relaxed bulk CaTiO_3 was 5.36×5.46×7.62 Å in reasonable agreement with the experimental value of 5.38×5.44×7.64 Å (PDF 078-1013)⁴⁸. A periodic CaTiO_3 (001) slab separated by a vacuum layer of 15 Å was built from this lattice. In total, there are 80 atoms in each slab, containing 16 Ca, 14 Ti, 1 Mn, 1 Fe, and 48 O. The self-consistent field method with the tolerance of 1.0×10^{-6} eV/atom and the plane wave basis sets with an energy cutoff of 500 eV were adopted. The structural optimization was relaxed until the Hellman-Feynman force on each ion was less than 0.02 eV/Å.

Adsorption energies of gas molecules, E_{ads} , in this paper were calculated as the following equation:

$$E_{\text{ads}} = E_{\text{slab+gas}} - E_{\text{slab}} - E_{\text{gas}}$$

3

where $E_{\text{slab+gas}}$ is the total energy of the perovskite slab with a gas molecule bound to it, E_{slab} is the total energy of the clean CaTiO_3 slab, and E_{gas} is the total energy of the gas molecules.

Declarations

Acknowledgments

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Figures

Figure 1

Phases and morphology of the roasted oxides and perovskite sample. **a**, Typical section morphology and element mapping of the composite oxides (1400°C-roasted Ti-slag with NaOH, CeO₂, Fe₂O₃, and MnO₂) obtained by SEM and EDS analysis. **b**, XRD patterns of the perovskite samples. The right part is the high-

resolution XRD patterns within 32.7° to 33.7°. The dashed line denotes the position of the (112) peak from pure CaTiO_3 . **c**, HAADF-STEM image and EDS mapping of sample 5Ce5Fe10Mn.

Figure 2

Crystal structure of the perovskite sample. **a**, Fe K-edge EXAFS (points) and curvefit (line) for 5Ce5Fe10Mn, shown in R -space (FT magnitude and imaginary component); **b**, Mn K-edge EXAFS (points) and curvefit (line) for 5Ce5Fe10Mn; **c**, Ce L_{III}-edge EXAFS (points) and curvefit (line) for 10Ce. All the data are k^3 -weighted and not phase-corrected. **d**, Diagram of the crystal structure of CaTiO_3 doped with Ce, Fe, and Mn.

Figure 3

NH₃-SCR activity of single-element doped CaTiO₃. **a**, Temperature-dependent NO_x conversion over CaTiO₃ doped with a single element in the dark. (1000 ppm NO, 1000 ppm NH₃, 3 vol% O₂, GHSV = 72000 h⁻¹). **b**, *In situ* DRIFT of CaTiO₃ and 10Mn with NO + O₂ adsorbed at 25°C in the dark. The adsorption of NH₃ (**c**) and NO (**d**) on the TiO₂-(001) termination of CaTiO₃; the adsorption of NH₃ (**e**) and NO (**f**) on the TiO₂-(001) termination of Ca(Ti, Mn)O₃.

Figure 4

NH_3 -SCR activity of multielement doped CaTiO_3 . **a**, Temperature-dependent NO_x conversion over CaTiO_3 doped with multiple elements in the dark. (1000 ppm NO , 1000 ppm NH_3 , 3 vol% O_2 , GHSV = 72000 h^{-1}). **b**, XPS of O1s from 10Mn and 5Fe10Mn. The adsorption of O_2 (**c**) and $\text{O}_2 + \text{NO}$ (**d**) on the $(\text{Ti, Mn})\text{O}_2$ -(001) termination of $\text{Ca}(\text{Ti, Mn})\text{O}_3$; the adsorption of O_2 (**e**) and $\text{O}_2 + \text{NO}$ (**f**) on the $(\text{Ti, Mn, Fe})\text{O}_2$ -(001) termination of $\text{Ca}(\text{Ti, Mn, Fe})\text{O}_3$.

Figure 5

Proposed reaction pathways of Standard SCR over the perovskite. The reaction pathways of the regeneration of active sites from $\text{Ca}(\text{Ti}, \text{Mn})\text{O}_3$ (the outer ring) and $\text{Ca}(\text{Ti}, \text{Mn}, \text{Fe})\text{O}_3$ (the inner ring) partially based on the DFT calculations.

Figure 6

Photo-SCR activity of doped CaTiO_3 . **a**, Temperature-dependent NO_x conversion over 10Mn, 5Fe10Mn, and 5Ce5Fe10Mn under visible light irradiation; **b**, Light on-off cycle tests over 5Ce5Fe10Mn at 125°C. **c**, UV-vis absorption spectra of the perovskite. **d**, PDOS of $\text{Ca}(\text{Ti}, \text{Mn})\text{O}_3$ and $\text{Ca}(\text{Ti}, \text{Mn}, \text{Fe})\text{O}_3$. **e**, *in situ* IR spectra of 5Ce5Fe10Mn with NH_3 adsorbed in the dark and visible light at 125°C; **f**, *in situ* IR spectra of 5Ce5Fe10Mn with $\text{NO} + \text{O}_2$ adsorbed in the dark and visible at 125°C.

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