Low-Dose Element-Doped CeCrM/TiO₂ (M = La, Cu, Fe, LaCu, LaFe) Catalyst for Low-Temperature NH₃-SCR Process: Synergistic Effect of LaCu/LaFe

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1. INTRODUCTION

Nitrogen oxides (NOₓ) derived from the burning of fossil fuels such as coal, oil, etc., are harmful to human beings and the environment. As one of the main pollutant gases, NOₓ not only causes acid rain and photochemical pollution but is also a major component of PM 2.5.¹ Thus, it is imperative to control the emission of harmful NOₓ. In recent years, selective catalytic reduction of ammonia (NH₃-SCR) has been widely used in NOₓ removal. In this process, NH₃ acts as a reducing agent to reduce NOₓ to harmless N₂ and H₂O with the action of the catalyst, which is the core of NH₃-SCR technology. At present, the commercial catalyst for NH₃-SCR is mainly a V₂O₅-based catalyst, which shows excellent catalytic performance in the NH₃-SCR reaction in the temperature range of 300–400 °C. However, the catalyst has disadvantages, such as narrow operating temperature window, toxicity of VO₂⁺ species, inactivation of alkali metals, and decrease of N₂ selectivity at high temperatures.² Therefore, non-V₂O₅-based catalysts have been extensively studied.

Currently, anatase TiO₂, Al₂O₃, molecular sieves, and carbon-based materials are usually used as denitrification catalyst supports. The supports are important for the SCR reaction. A good support can disperse the active components well. Moreover, the interaction of supports and active components also has an important effect on the catalytic performance.³ Therefore, anatase TiO₂ has been widely studied due to its low cost, good sulfur resistance, nontoxicity,⁴ and rich Lewis acid sites.⁵

In addition, catalysts with polyvalent oxides as active components can improve the NH₃-SCR performance due to the synergistic effect between components, which has also been widely studied.⁶–⁸ Ce-based catalysts are expected to be potential substitutes for V₂O₅-based catalysts. CeO₂ is widely used as NH₃-SCR catalysts for excellent redox ability of Ce⁴⁺/Ce³⁺ reversible redox pair, abundant surface oxygen vacancy, and high oxygen storage capacity.⁹–¹³ The oxidation state of chromium oxide (CrO₃) is variable, especially for exposed chromium ions, and the most common valence states are Cr³⁺ and Cr⁴⁺.¹⁴ The presence of Cr makes the surface acidity and reducibility of the CeZr catalyst stronger, and more ad-NOₓ and ad-NH₃ on the catalyst surface are conducive to the NH₃-SCR
reaction. Furthermore, Ce can promote the conversion between Cr\(^{3+}\) and Cr\(^{6+}\) and increase the proportion of lattice oxygen, which improves the activity of the catalyst. Thus, the interaction between Ce and Cr can improve the redox property and accelerate the redox circle, which are beneficial to the improvement of NH\(_3\)-SCR activity.

However, the mass percentages of Cr and Ce in most of the catalysts prepared by researchers are greater than 5%, and some even exceed 30%. The low-dose CeCr/Ti catalyst has limited redox performance, which is insufficient to show excellent NH\(_3\)-SCR activity. To optimize the catalytic performance, the supported catalyst can be doped with some transition metals to improve the catalytic activity through the synergistic effect of multiple metals. Lanthanide is a rare earth element abundant in China. La-doped catalysts have been widely studied in SCR reactions due to their excellent oxygen storage capacity and unique redox properties. Studies have shown that La\(^{3+}\) could be partly integrated into ceria fluorite lattice to induce an expansion of the crystal cell dimensions, which concomitantly induces more lattice defects and improves the lattice oxygen mobility. Yi et al. studied the effects of rare earth element (La, Ce) modification on oxidation performance, and the results showed that La, Ce modification could promote the oxidation performance of adsorbents and reduce the pore diameter of the adsorbents. Therefore, the interaction between Ce and La is also conducive to the improvement of NH\(_3\)-SCR activity. The state of Cu species has a great impact on the SCR activity of the CeO\(_2\)-CuO catalyst, and Cu\(^{2+}\) can improve the low-temperature activity, while CuO would decrease the high-temperature activity. The interaction between Cu and Ce can reduce the crystallinity of CeO\(_2\), enhance the oxygen storage capacity and acidity of the catalyst, and increase the types of Ce\(^{3+}\) species. Thus, the interaction between Cu and Ce is helpful to improve the surface acidity and redox performance of the catalyst. In addition to copper, the presence of Fe can increase the surface area, enhance the redox properties, increase the number of surface acid sites, and increase the surface adsorbed oxygen. Zhang et al. reported that Fe\(^{3+}\) replaces Ce\(^{4+}\) to form Ce–Fe solid solution. This change of crystal phase structure facilitated the homogeneous dispersion of the active component on the catalyst surface, increased acid sites and specific surface area, and exposed more oxygen vacancies. Ge et al. found that the addition of Cr greatly increased the specific surface area, the number of weak and medium-strong acid sites, and the ratio of Fe\(^{3+}\)/Fe\(^{2+}\) on the surface of the Fe/AC catalyst, thus promoting the low-temperature SCR activity of the catalyst. Therefore, the interaction between Fe and Ce or Cr helps to improve the redox capacity and the number of acid sites on the catalyst.

The composition of coal-fired flue gas in China is complex, often containing components such as SO\(_2\) and H\(_2\)O, which will seriously damage the activity and stability of the NH\(_3\)-SCR catalyst. Furthermore, the deactivation of the low-temperature DeNO\(_x\) catalyst was more severe when SO\(_2\) and H\(_2\)O were

Figure 1. NO conversion of (a) all catalysts, (b) CeCr/TiO\(_2\) and CeCrLa/TiO\(_2\) catalysts, (c) CeCrCu/TiO\(_2\) and CeCrLaCu/TiO\(_2\) catalysts, and (d) CeCrFe/TiO\(_2\) and CeCrLaFe/TiO\(_2\) catalysts. Reaction conditions: [NO] = [NH\(_3\)] = 1000 ppm, [O\(_2\)] = 5%, N\(_2\) balance, GHSV = 20,000 h\(^{-1}\).
2. RESULTS AND DISCUSSION

2.1. Performances of NH₃-SCR. NH₃-SCR performance of CeCr/TiO₂, CeCrCu/TiO₂, or CeCrFe/TiO₂ was measured using reaction temperatures of 650 and 769 °C. CeCrLa/Cu/TiO₂, CeCrLaFe/TiO₂, CeCrLaCu/TiO₂, and CeCrLaFe/TiO₂ catalysts were evaluated, and the results are illustrated in Figure 1. With the increase of temperature, the NO conversion of the catalysts increases, and CeCrM/TiO₂ (M = La, Cu, Fe) reaches the maximum NO conversion (98.9%) at 340 °C. Then, the NO conversion of the CeCrM/TiO₂ (M = Cu, Fe) catalyst decreases rapidly, while the NO conversion of the CeCrLa/TiO₂ catalyst remains stable in the temperature range of 340–420 °C. Compared with CeCrFe/TiO₂ catalysts, CeCrLa/TiO₂ catalysts have better high-temperature activity and a wider operating temperature window, which indicates that the addition of La is more favorable for the high-temperature activity (as shown in Figure 1a). And the addition of Cu, compared with Fe and La, produced a limited improvement in the low-temperature activity of the catalyst in the temperature range of 140–260 °C. However, the modification effects of La, Fe, and Cu are limited.

To further improve the low-temperature activity of the catalyst, considering the excellent redox performance of Cu and Fe, the CeCr/Ti catalyst was doped with LaCu and LaFe, respectively. As shown in Figure 1c, the NO conversion curve of CeCrLaCu/TiO₂ is shifted toward lower temperature by 80 °C compared to CeCrLa/TiO₂ (Figure 1b). In addition, 100% NO conversion is maintained until 420 °C, the temperature at which the conversion starts to decrease. The CeCrLaFe/TiO₂ catalyst (Figure 1d) reaches the maximum NO conversion (99%) at 300 °C. When the temperature exceeds 380 °C, the NO conversion drops rapidly to reach 70% at 460 °C. Consequently, the CeCrLa/TiO₂ and CeCrLaFe/TiO₂ catalysts effectively broadened the NO conversion at low temperatures. This indicates that the introduction of La can greatly improve the high-temperature catalytic activity of catalysts (Figure 1b–d), especially in the catalysts containing Cu and Fe. In addition, it was found that the interaction between La and Cu was more conducive to NH₃-SCR performance at low temperatures.

2.2. Physicochemical Properties. 2.2.1. XRD Analysis. The XRD patterns of the catalysts are shown in Figure 2. All samples display diffraction peaks at 25.3, 37.8, 48.1, 53.9, 55.1, 62.8, 68.7, 70.4, and 75.1°, which correspond to anatase TiO₂ phase peaks [PDF-ICPDS 89-4921]. No independent diffraction peaks related to CeO₂, Cr₂O₃, La₂O₃, CuO, and Fe₂O₃ were observed in samples. This indicates that the active components are in a highly dispersed state or the amount of active component is below the detection threshold. The good dispersion facilitated good contact of the active components with each other and led to strong interactions between Ti and other metal oxides. Compared with the diffraction peaks of CeCrFe/TiO₂, CeCrCu/TiO₂, and CeCrLa/TiO₂ catalysts, the weakened diffraction peak intensities of CeCrLaCu/TiO₂ and CeCrLaFe/TiO₂ catalysts indicate that the interaction of La and
Cu/Fe reduces the crystallinity of the catalysts, which is in agreement with the previous report. According to the Debye–Scherrer’s formula, the crystalline size is calculated and listed in Table 1. The crystal size increased in the following sequence:

Table 1. XRD and BET Results of All of the Samples

| samples          | crystal size (nm) | BET surface area (m²/g) | pore volume (cm³/g) | average pore diameter (nm) |
|------------------|-------------------|-------------------------|---------------------|---------------------------|
| CeCrCu/TiO₂      | 9.1               | 84.2                    | 0.24                | 11.1                      |
| CeCrFe/TiO₂      | 9.0               | 117.8                   | 0.28                | 10.1                      |
| CeCrLa/TiO₂      | 8.2               | 81.8                    | 0.20                | 9.1                       |
| CeCrLaCu/TiO₂    | 8.6               | 77.1                    | 0.19                | 9.7                       |
| CeCrLaFe/TiO₂    | 8.4               | 85.0                    | 0.20                | 9.1                       |

*Calculated by Debye–Scherrer.

CeCrLa/TiO₂ < CeCrLaFe/TiO₂ < CeCrLaCu/TiO₂ < CeCrFe/TiO₂ < CeCrCu/TiO₂. The particle size of the catalyst doped with La is smaller than without La, indicating that La doping inhibited the crystalline growth of anatase TiO₂. The CeCrCu/TiO₂ and CeCrFe/TiO₂ catalysts with lower NO conversion had larger crystallite size, while the CeCrLaCu/TiO₂ catalyst with the highest NO conversion had smaller crystallite size. The results show that the small crystallite size can promote the NO conversion of the catalyst, but it does not always increase with decreasing crystallite size.

2.2.2. N₂ Adsorption–Desorption Behavior. The N₂ adsorption–desorption isotherms of the catalysts are presented in Figure 3. As shown in Figure 3a, the samples showed isotherms of type III, which exhibited hysteresis loops mostly of type H3, indicating that these samples contained mesopores (2–50 nm). The specific surface area, pore volume, and pore size of all samples are summarized in Table 1. A larger surface area and smaller average pore size contribute to the higher physisorption ability of the catalyst. Compared with CeCrCu/TiO₂ and CeCrFe/TiO₂ catalysts, the CeCrLa/TiO₂ catalyst has a smaller specific surface area and average pore size, but the CeCrLa/TiO₂ catalyst has better NO conversion. The addition of composite metal oxides has little effect on the pore volume but has a greater effect on the specific surface area and average pore size. Compared with CeCrLa/TiO₂, the addition of the LaCu composite metal oxide leads to a decrease in the specific surface area of the catalyst, while the LaFe composite metal oxide increases the specific surface area of the catalyst. Furthermore, the CeCrLaCu/TiO₂ catalyst with the best catalytic activity has the smallest specific surface area and pore volume, indicating that the specific surface area is not the key factor limiting the catalytic activity.

2.2.3. SEM Analysis. SEM test was carried out to observe the morphology of all samples. It can be observed in Figure 4 that there is no significant difference in the morphology of the five catalysts. The catalysts are in the form of particles and they are aggregated. However, the surface of the CuCeCrLa/TiO₂ catalyst is relatively smooth compared to other catalysts. The results show that the addition of an appropriate amount of La and Cu improved the dispersity of the active components and reduced the agglomeration.

2.2.4. XPS Analysis. The O 1s, Ti 2p, Ce 3d, Cr 2p, Cu 2p, and Fe 2p photoelectron profiles of all samples are shown in Figure 5, and their relative atomic concentrations are listed in Table 2. The O 1s XPS spectra of all catalysts are shown in Figure 5A. The spectra of O 1s could be split into two peaks: lattice oxygen (BE = 530.0–530.4 eV, denoted as Oₐ) and chemisorbed oxygen (BE = 531.6–532.2 eV, denoted as Oₐ). The content of surface adsorbed oxygen over these catalysts is calculated as Oₐ/(Oₐ+Oₐ) and listed in Table 2. The mobility of the surface chemisorbed oxygen is stronger than the lattice oxygen; thus, it is easier to participate in the NH₃-SCR reaction. In general, the high Oₐ/Oₐ relative concentration ratio on the catalyst surface could be related to excellent SCR activity. However, it is obvious from Table 2 that there is a slight difference in Oₐ over catalysts. The chemical adsorption oxygen species on the CeCrLaCu/TiO₂ surface were the most, indicating that the doping of LaCu was more conducive to the generation of chemical adsorption oxygen sites on the catalyst surface. As shown in Figure 5A, according to (c, d, e), the peaks of Oₐ and Oₐ over CeCrLaCu/TiO₂ and CeCrLaFe/TiO₂ catalysts shifted to lower binding energy compared to the CeCrLa/TiO₂ catalyst, suggesting the strong interaction among La and Cu/Fe. According to (b, c, e), the peak of Oₐ over CeCrLaFe/TiO₂ catalysts shifted to lower binding energy compared to CeCrLa/TiO₂ and CeCrFe/TiO₂ catalysts, indicating that there is some kind of synergy between La and Fe. According to (a, c, d), the peaks of Oₐ and Oₐ over CeCrLaCu/TiO₂ catalysts shifted to lower binding energy compared to CeCrLa/TiO₂ and CeCrFe/TiO₂ catalysts, indicating that there is a certain kind of synergy between La and Fe. This is consistent with previous studies.

XPS of Ti 2p can be fitted into two peaks (Figure 5B). The peaks located at around 458.9 and 464.7 eV could be the result of the orbitals of Ti 2p₃/2 and Ti 2p₁/2 respectively. This indicated

Figure 3. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distributions of the samples.
that Ti existed in the Ti$^{4+}$ oxidation state.$^{47,48}$ Compared to other catalysts, the Ti 2p peak position of the CeCrLaFe/TiO$_2$ catalyst was shifted to the right by approximately 0.2 eV, indicating that some of the Ti$^{4+}$ ions were reduced to Ti$^{3+}$ ions. The redox cycle of Ti$^{4+}$/Ti$^{3+}$ is hypothesized to be another reason for the high SCR performance.$^{49}$

Figure 4. SEM images obtained for (a) CeCrCu/TiO$_2$, (b) CeCrFe/TiO$_2$, (c) CeCrLa/TiO$_2$, (d) CeCrLaCu/TiO$_2$, and (e) CeCrLaFe/TiO$_2$.

Figure 5. (A) O 1s, (B) Ti 2p, (C) Ce 3d, (D) Cr 2p, (E) Cu 2p, (F) Fe 2p, and (G) La 3d XPS spectra of the samples (a) CeCrCu/TiO$_2$, (b) CeCrFe/TiO$_2$, (c) CeCrLa/TiO$_2$, (d) CeCrLaCu/TiO$_2$, and (e) CeCrLaFe/TiO$_2$. 
The Ce 3d XPS spectra of the catalysts are presented in Figure 5C. The Ce 3d bands are deconvoluted by the curve-fitting procedure,\(^5,48,50\) and the Ce 3d XPS spectra could be separated into seven peaks and "u" and "v" were attributed to Ce 3d\(_{5/2}\) and Ce 3d\(_{3/2}\), respectively. The two peaks labeled "u'" and "v'" could be assigned to Ce\(^{3+}\), with the remaining peaks of "u", "v" and "v" belonging to Ce\(^{4+}\).\(^5,51\) It is generally believed that Ce\(^{3+}\) is related to the appearance of oxygen vacancies. One electron lost by Ce\(^{3+}\) combines with O\(_2\) to form O\(^{2-}\) (eq 1), which oxidizes NO to NO\(_2\) (eq 2). Therefore, the more Ce\(^{3+}\), the more NO\(_2\) is produced, providing the possibility of a low-temperature L─H mechanism.

\[
\text{Ce}^{3+} + \text{O}_2 \rightarrow \text{Ce}^{4+} + \text{O}^{2-} \quad (1)
\]

\[
\text{NO} + \text{O}^{2-} \rightarrow \text{NO}_2 \quad (2)
\]

where "☐" represents an empty position originating from the removal of O\(^{2-}\) from the lattice.\(^5,52\) The ratio of Ce\(^{3+}\)/Ce for the samples could be calculated from the results of XPS analysis, and the results are listed in Table 2. Obviously, the Ce\(^{3+}\)/Ce ratio of the CeCrLa/TiO\(_2\) catalyst is higher than that of the CeCrM/TiO\(_2\) (M = Cu, Fe) catalyst, which indicates that the introduction of La promotes the conversion of Ce\(^{3+}\) to Ce\(^{3+}\). However, the doping of bimetallic oxides led to the increase of Ce\(^{3+}\)/Ce ratio in CeCrLaCu/TiO\(_2\) and CeCrLaFe/TiO\(_2\) catalysts, indicating that the synergistic effect of LaCu or LaFe played an important role in the formation of Ce\(^{3+}\).

The XPS spectra for Cr 2p of all samples are given in Figure 5D and show that two distinct peaks correspond to Cr\(^{3+}\) (577.6─578.8 eV) and Cr\(^{6+}\) (579.8─581.0 eV).\(^14,15\) It has been reported that the addition of Cr could facilitate the SCR performance by the valence change between Cr\(^{6+}\) and lower oxidized states (Cr\(^{3+}\), Cr\(^{3+}\), and Cr\(^{2+}\)).\(^16,53\) It is obvious that most Cr species in catalysts exist in the form of Cr\(^{6+}\). It is noteworthy that the Cr\(^{6+}\)/Cr ratio (Table 2) of CuCrLaCu/TiO\(_2\) (68%) is higher than those of CeCrCu/TiO\(_2\) (54%) and CeCrLa/TiO\(_2\) (61%). The Cr\(^{6+}\)/Cr ratio of CeCrLaFe/TiO\(_2\) (63%) was similar to those of CeCrLa/TiO\(_2\) (61%) and CeCrFe/TiO\(_2\) (63%), indicating that the doping of LaCu was conducive to the formation of Cr\(^{6+}\) and the synergistic effect of LaCu was stronger than that of LaFe.

The XPS spectra for Cu 2p of the catalysts are shown in Figure 5E. Both peaks of 932.2 eV and 952.1 eV ought to be attributed to Cu\(^{2+}\) species, and the peaks at 953.1 eV and 933.1 eV should be ascribed to Cu\(^{3+}\).\(^54\) As shown in Table 2, the ratio of Cu\(^{2+}\)/Cu on the surface of the CeCrLaCu/TiO\(_2\) catalyst is slightly higher than that of the CeCrLa/TiO\(_2\) catalyst. The doping of La leads to the increase of the Cu\(^{2+}\)/Cu ratio on the surface, indicating that the synergistic effect of LaCu contributes to the formation of surface Cu\(^{2+}\).

The Fe element was present in the catalyst mainly in two valence states, Fe\(^{2+}\) and Fe\(^{3+}\), and was attributed to BE = 702.9 eV, 716.1 eV and BE = 711.6 eV, 733.8 eV, respectively, in Figure 5F. The content of Fe\(^{3+}\) and Fe\(^{3+}\) in the catalysts was closely related to the formation of oxygen vacancies in the catalyst. From reactions (3, 4), it is known that Fe\(^{2+}\) and Fe\(^{3+}\) produce O\(^{2-}\) during the mutual conversion process. The effect is the same as that of Ce\(^{3+}\). Therefore, the greater the Fe\(^{3+}\) content, the more the oxygen adsorption site, and the better the denitration activity of the catalyst.

\[
\text{Fe}^{2+} + \text{O}_2 + \square \rightarrow \text{Fe}^{3+} + \text{O}^{2-} \quad (3)
\]
NO + O^{2-} \rightarrow NO_2 \tag{4}

The relative contents of Fe^{2+}/Fe were calculated and are listed in Table 2. Compared with the CeCrFe/TiO_2 catalyst, the CeCrLaFe/TiO_2 catalyst has lower Fe^{2+}, but its catalytic performance is better than the CeCrFe/TiO_2 catalyst. Due to the lower ionization energy of La^{3+} \rightarrow La^{5+}, electrons are easy to be lost and may be more easily transferred from La to the active component. The incorporation of La facilitates the transformation from low-valence species (Fe^{2+}) to the stable high-valence species (Fe^{3+}).

**Figure 6.**

That Fe/Cu promotes the electron supply of O_2p. The electron catalysts have stronger companion peak intensities, indicating have double peaks, which meant that companion peaks appear. The electron transfer on the catalyst surface is of great significance for NH_3d

was determined by H_2-TPR Analysis. The H_2-TPR profiles of the catalysts. From the XPS analysis in this paper, it is known that the incorporation of La facilitates the transformation from low-valence species (Fe^{2+}) to the stable high-valence species (Fe^{3+}).

**Figure 5G** shows the La 3d spectra. Both La 3d_{5/2} and La 3d_{3/2} have double peaks, which mean that companion peaks appear. Due to the ionization of electrons in the inner shell layers of La 3d_{5/2} and La 3d_{3/2}, the transfer of 2p valence electrons from the La-coordinated oxygen to the 4f vacant orbital of La results in the splitting of the La 3d characteristic peak and the resultant vibrational companion peaks of La 3d_{5/2} and La 3d_{3/2}. So, the change in the intensity of the companion peak can reflect the ability of the 2p electrons of oxygen to give La. Compared with CeCrLa/TiO_2 catalysts, CeCrLaFe/TiO_2 and CeCrLaCu/TiO_2 catalysts have stronger companion peak intensities, indicating that Fe/Cu promotes the electron supply of O 2p. The electron transfer on the catalyst surface is of great significance for NH_3-SCR. From the XPS analysis in this paper, it is known that the incorporation of La promotes the electron transfer between the active components. Doping of LaFe/LaCu is by surface charge transfer doping. And the LaCu/LaFe dopant is in surface contact with the TiO_2 carrier, and the former is used to transfer charges to the carrier based on the difference in the ability of the former to gain and lose electrons.

**2.2.5. H_2-TPR Analysis.** The redox property of the samples was determined by H_2-TPR analysis, and the results are shown in Figure 6. The H_2 consumption values of all samples are shown in Table 2. Five peaks appear from 250 to 750 °C in the H_2-TPR profile of CeCrCu/TiO_2. It has been reported that CuO species have a great degree of reduction capacity at lower temperatures. Thus, two reduction peaks of CuO could be seen at 339 and 422 °C, respectively, which are due to two reduction steps, that of CuO into Cu_2O and Cu_2O into Cu_6+.

The reduction peak appearing at 483 °C belongs to the reduction of Cr^{3+} \rightarrow Cr^{2+}; the peak at 550 °C is attributed to Ce^{4+} \rightarrow Ce^{3+}; and the peak at 631 °C is attributed to crystal lattice CeO_2/Ce_2O_3 and Cr^{3+} \rightarrow Cr^{2+}. For the CeCrFe/TiO_2 catalyst, the reduction peaks appearing at 570 °C belong to the reduction of Cr^{6+} \rightarrow Cr^{3+} and Fe_{0.1}O_1 \rightarrow Fe_{0.9}. The reduction peak at 630 °C belongs to the reduction of FeO \rightarrow Fe^0 and the transformations of surface CeO_2/Ce_2O_3. The H_2 reduction peaks at 695 °C may be due to overlapping of transformations of surface CeO_2/Ce_2O_3 and Cr^{3+} \rightarrow Cr^{2+}. The reduction peaks at 763 °C were attributed to lattice oxygen contained in bulk CeO_2. As for CeCrLa/TiO_2, the reduction peak can be divided into four peaks. The reduction peaks appearing at 565 °C belong to the reduction of Cr^{3+} \rightarrow Cr^{2+}, the peaks at 617 and 707 °C are respectively attributed to transformations of surface CeO_2/Ce_2O_3 and crystal lattice CeO_2/Ce_2O_3; and the peak at 664 °C might be assigned to Cr^{3+} \rightarrow Cr^{2+}. After the introduction of La, the peak positions move to a higher temperature and the peak area gradually decreases, indicating that the reducibility of the CeCrLa/TiO_2 catalyst decreases.

The reduction profiles of the CeCrLaCu/TiO_2 catalyst are composed of five main hydrogen consumption steps. Compared with the CeCrCu/TiO_2 catalyst, the reduction peak position of the CeCrLaCu/TiO_2 catalyst is basically unchanged. And compared with the CeCrLa/TiO_2 catalyst, the reduction peak position of the CeCrLaCu/TiO_2 catalyst shifted to a lower temperature, such as the reduction temperature of Ce^{4+} \rightarrow Ce^{3+} and Cr^{6+} \rightarrow Cr^{3+} decreases. This indicates that Ce and Cr become more reducible, which can be attributed to the synergetic effect of LaCu. At the same time, the introduction of La increases the hydrogen consumption of Cu and Cr, indicating that the synergetic effect of LaCu is more conducive to improving the redox performance of the catalyst. Similarly, compared with CeCrLa/TiO_2 and CeCrFe/TiO_2 catalysts, the reduction peak position of CeCrLaFe/TiO_2 catalysts shifted to lower temperatures, and the introduction of La increases the reduction peak area of Fe (321 and 424 °C) and Cr (523 and 672 °C), indicating that the synergetic effect between LaFe is beneficial to improve redox performance of catalysts, which is consistent with the result of the improved low-temperature activity of CeCrLaFe/TiO_2.

**2.2.6. NH_3-TPD Analysis.** NH_3-TPD tests were performed, and the results are shown in Figure 7. The total NH_3 adsorption capacity is summarized in Table 3. From Figure 7, three peaks appear from 100 to 500 °C in the NH_3-TPD profile of each catalyst. The peaks at the range of 150–250, 250–400, and 400–550 °C refer to weak acid, medium-strength acid, and high-strength acid, respectively. According to the literature, the medium-strength and high-strength acid sites are effective for NO reduction at moderate to high temperature. The NH_3
uptake of these catalysts in descending order is CeCrLaCu/TiO$_2$ > CeCrLaFe/TiO$_2$ > CeCrLa/TiO$_2$ > CeCrFe/TiO$_2$ > CeCrCu/TiO$_2$. The NH$_3$ adsorption capacity of the catalyst is proportional to the catalytic performance, indicating that the NH$_3$ adsorption capacity plays an important role in the catalytic system. Compared with CeCrLa/TiO$_2$ and CeCrCu/TiO$_2$ catalysts, the NH$_3$ adsorption capacity of CeCrLaCu/TiO$_2$ and CeCrLaFe/TiO$_2$ catalysts was significantly improved, indicating that the synergistic effect of LaCu/Fe promoted the surface acidity of the catalysts, which could provide more ad-NH$_3$ species for the NH$_3$-SCR reaction. Compared with the CeCrLaFe/TiO$_2$ catalyst, the CeCrLaCu/TiO$_2$ catalyst has stronger NH$_3$ adsorption capacity, so it is more conducive to NH$_3$-SCR performance.

3. CATALYTIC HYDROTHERMAL AGING

As shown in Figure 8, when the temperature is less than 300 °C, the activities of all catalysts have a sharp decrease; this may be due to the reduction of catalyst active sites due to hydrothermal aging. It can be concluded that hydrothermal aging has a great influence on low temperature catalysts. CeCrLaCu/TiO$_2$-H and CeCrLaFe/TiO$_2$-H still maintain good activity while the temperature is greater than 300 °C, and the NO conversion drops from 99.5 to 95%, which shows that the synergistic effect of LaCu and LaFe is better for hydrothermal stability. In general, hydrothermal aging has an acceptable effect on catalysts in this article (Figure 8).

4. CONCLUSIONS

In this paper, a series of CeCrM/TiO$_2$ (M = Cu, Fe, La, LaCu, LaFe) catalysts were prepared. By mixing low-dose components, a good low-temperature denitrification catalyst CeCrLaCu/TiO$_2$ was selected. The catalyst has excellent NH$_3$-SCR performance in a wide temperature window. XRD analysis showed that the synergistic effect of LaCu and LaFe could effectively reduce the aggregation of active species and promote the high dispersion of active components on the surface of TiO$_2$. The addition of LaCu and LaFe changed the redox state and surface species concentration of the catalysts. The synergistic effect of LaCu/Fe promoted the formation of Ce$^{3+}$/Ce$^{6+}$ and the synergistic effect of LaCu was stronger. The CeCrLaCu/TiO$_2$ catalyst has the highest relative atomic ratio (Ce$^{3+}$/Ce$^{6+}$, Cr$^{6+}$/Cr, Cu$^{2+}$/Cu, and O$_2$/O$_3$). It is beneficial for redox of reactive gas on the catalyst surface. The results of H$_2$-TPR and NH$_3$-TPD showed that the synergistic effect of LaCu improved the redox capacity and surface acidity of the catalyst, which was an important reason for the excellent performance of the NH$_3$-SCR catalyst.

5. EXPERIMENTAL SECTION

5.1. Catalyst Preparation. 5.1.1. Preparation of Supports. A certain amount of metatitanic acid (TiO(OH)$_2$, Xiya Reagent, China, 98%) was calcined at 500 °C for 3 h in air.

5.1.2. Preparation of Catalysts. The catalyst was prepared by the impregnation method. TiO$_2$ powder and specific amounts of Ce(NO$_3$)$_3$·6H$_2$O, Cr(NO$_3$)$_3$·9H$_2$O, La(NO$_3$)$_3$·6H$_2$O, Cu(NO$_3$)$_2$·6H$_2$O, and Fe(NO$_3$)$_3$·9H$_2$O were mixed together in absolute ethanol, and the mixture was stirred in a magnetic stirrer at room temperature for 6 h. The mixture was aged at room temperature for 24 h and then dried at 80 °C for 12 h, followed by calcination at 450 °C for 4 h in a muffle furnace. CeO$_2$, CrO$_3$, La$_2$O$_3$, and CuO (FeO$_2$) mixed metal oxides are obtained after calcination. The solid sample was crushed and sieved to 40–60 mesh and was recorded as CeCrM$_x$/TiO$_2$ (M = La, Cu, Fe, LaCu, LaFe). The active ingredient ratio of catalysts Ce/Cr/La/Fe/Cu was 4:3:2:8:8.

5.1.3. Preparation of Hydrothermal Aging Catalysts. The hydrothermal aging conditions are as follows: 5% CO$_2$, 5% H$_2$O, 5% O$_2$, and N$_2$ as equilibrium gases, 700 °C for 12 h.

5.2. Catalyst Characterization. 5.2.1. X-ray Diffraction (XRD). An X-ray diffractometer (Rigaku Ultima IV) was used in determining the catalyst crystal structures using these parameters: scanning at 2θ range from 10 to 80° and radiation at 40 mA and 40 kV with Cu Kα ($\lambda = 0.15406$ nm).

5.2.2. Brunauer–Emmett–Teller (BET) Surface Area Analysis. A Micromeritics ASAP 2460 was used to perform the test of N$_2$ adsorption–desorption for the measurement of the textural characteristics of the catalysts at a liquid nitrogen temperature of −196 °C. To remove physically adsorbed species, the catalysts were pre-degassed for 10 h at 200 °C before each analysis. The pore size distribution and specific surface area of the catalysts were calculated using the Barrett–Joyner–Halenda (BJH) method and the Brunauer–Emmett–Teller (BET) equation.

5.2.3. Scanning Electron Microscopy (SEM). An FEI Apreo was used to examine the morphology of the catalysts. The sample was dispersed on the conductive adhesive and then sprayed gold to observe.

5.2.4. X-Ray Photoelectron Spectroscopy (XPS). An Escalab 250Xi with a monochromatic Al-Kα target ($h\nu = 1486.6$ eV) was used to obtain X-ray photoelectron spectroscopy (XPS) of the
samples. Before the test, the samples were outgassed in a UHV chamber (<10⁻⁷ Pa). The calibration of binding energies of O 1s, Ti 2p, Ce 3d, Cr 2p, Cu 2p, and Fe 2p were obtained using the C 1s peak (284.8 eV). Peak fitting is done using XPSPEAK 4.1 with a Shirley background.

5.2.5. Temperature-Programmed Reduction by Hydrogen (H₂-TPR). A chemisorption apparatus (Micromeritics ChemiSorb 2720) with 0.2 g of catalyst was used to collect H₂-TPR profiles. Before that, the samples were pretreated in a pure Ar atmosphere for 1 h at 300 °C and then cooled to 50 °C for half an hour to mix the gas 10% H₂/Ar. The TPR profiles of the catalysts were collected when the baseline remained unchanged by heating the samples from 50 to 800 °C at a rate of 10 °C/min, with an aggregation rate of 25 mL/min with 10% H₂/Ar. Thermal conductivity detectors were taken in continuously monitoring H₂ consumption.

5.2.6. Temperature-Programmed Desorption by Ammonia (NH₃-TPD). A chemisorption apparatus (Micromeritics Auto Chem II 2920) with 0.2 g of catalyst was used to collect NH₃-TPD profiles. Before that, the catalysts were preheated for 1 h at 300 °C in a helium flow and then cooled to 100 °C for 5% NH₃/He 1 h. The physically adsorbed NH₃ was removed by purging He for another 1 h. When the samples were heated at a rate of 10 °C/min from 100 to 500 °C, with an aggregation rate of 50 mL/min with He, the profiles of the catalysts were recorded.

5.3. Catalytic Performance Measurement. In this work, a fixed-bed flow reactor containing 3 mL of catalyst of 40–60 mesh was taken for testing SCR activities. The reaction condition was controlled as follows: 1000 ppm NO, 1000 ppm NH₃, 5% O₂, and the balance gas N₂. The gas hourly space velocity (GHSV) was approximately 20,000 h⁻¹ with a sum rate of 1000 mL/min of the feed gas. The NO concentration was measured with a signal NO analyzer (KM94S, KANE, U.K.). The following equation was used to calculate NO conversion:

\[ \text{NO conversion (\%) } = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \] (5)

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Notes
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