Efficient Catalysts of K and Ce Co-Doped LaMnO$_3$ for NO$_x$–Soot Simultaneous Removal and Reaction Kinetics

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ABSTRACT: Presently, the treatment of four-way catalysts is important for reducing pollutant emissions from diesel engine exhaust, which is a major cause of urban haze. In this study, we prepared perovskite-type catalysts via the citric acid sol–gel method. Experiment results showed that K substitution at site A in LaMnO$_3$ decreased the agglomeration of the catalysts effectively, increased the contact with the reaction gas, promoted the conversion of Mn$^{3+}$ → Mn$^{4+}$, and reduced the ignition temperature of soot. Ce substitution at the B-site in La$_{0.8}$K$_{0.2}$Mn$_{1-x}$O$_3$ produced a CeO$_2$ phase and decreased the Mn$^{3+}$/Mn$^{4+}$ ratio to 0.49, which is conducive to improving the catalytic oxidation performance. The K and Ce co-doping had the best activation effect, which showed a low activation energy (10.87 KJ mol$^{-1}$) and a high simultaneous removal rate of NO$_x$ (reaching 90% at 275 °C) and soot ignition at 250 °C under lean conditions.

1. INTRODUCTION

Because of their high combustion efficiency, low fuel consumption, high power, and good economy, diesel engines have been widely used; however, their exhaust emissions cannot be underestimated.$^{1,2}$ According to the China Mobile Source Environmental Management Annual Report (2020),$^3$ CO, HC, NO$_x$, and PM emitted by diesel vehicles in 2019 accounted for 18.5, 12.5, 88.9, and more than 99%, respectively, of the total vehicle emissions—a major contribution to vehicle pollution. Nitrogen oxides (NO$_x$)$^{4-6}$ are one of the main causes of acid rain and photochemical smog, which lead to lung and respiratory diseases. Soot particles (PM)$^{7,8}$ are one of the main causes of haze formation, and their surfaces can easily adsorb various toxic and harmful substances; thus, upon entering a human body, the soot can cause lung and respiratory diseases and even cancer. Therefore, diesel exhaust emissions have attracted attention globally, and more stringent emission regulations have been constituted; this makes developing an effective purification technology for diesel exhaust an urgent need. Meanwhile, the four-way catalytic technology is being studied as one of the potential strategies to treat exhaust pollutants of diesel vehicles. However, limitations such as high cost, large area occupation, and poor simultaneous removal efficiency of NO$_x$ and PM remain unresolved.

A perovskite-type catalyst (ABO$_3$) is a promising four-way catalyst for diesel exhaust control owing to its relatively low price and high thermal stability and catalytic activity.$^{9-11}$ To improve the catalytic activity, chemical tailoring is the main characteristic used for perovskite-type oxides. Usually, an alkali metal, an alkaline earth metal, or a rare earth metal is doped in site A, and a transition metal is doped in site B. Among these, the transition metal in site B plays a paramount role in the catalytic action, and site A, as a part of the lattice, is responsible for support and stabilization.$^{12}$ A previous study focused on four categories of perovskite-type catalysts—Co, Mn, Fe, and Cu—in which Mn-based and Co-based catalysts were used to purify diesel exhausts.$^{13}$ Moderate amounts of alkali metals substituted for La at site A increase the mobility of oxygen in the lattice and enhance the oxygen adsorption on the surface of the catalyst. Patel et al. reported that the catalytic activity increased remarkably by the substitution of La$^{3+}$ with Sr$^{2+}$ and Ce$^{4+}$ in LaMnO$_3$ perovskites. The catalyst (SrKTiO$_3$) exhibited a high activity after K doping, which decreased the soot ignition temperature to 350 °C.$^{14}$ Peng et al.$^{15,16}$ prepared La$_{0.8}$K$_{0.2}$Mn$_{1-x}$Cu$_x$O$_3$ catalysts and found that simultaneous A and B partial substitution can not only transform Mn$^{3+}$ to the high price of Mn$^{4+}$ but also produce more oxygen vacancies, which can improve the activity of the catalyst. Ce is not only a rare earth metal but also a transition metal.$^{17,18}$ Ce-containing catalysts possess large specific surface areas, high oxygen storage capacity, and high removal efficiency of soot and CO.

In this study, we consider the simultaneous substitution of K at site A and Ce at site B in a LaMnO$_3$ lattice prepared using a
citric acid sol–gel method. Increasing the number of oxygen vacancies can effectively enhance the sample catalytic activity. To improve the redox activity, we attempted to improve the mobility of the catalyst lattice oxygen and the generation of oxygen vacancies through K and Ce doping. We examined the K and Ce co-doped catalysts to determine their effects on the catalytic activity for NOx capture and soot combustion.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. We prepared the catalysts needed in the experiment using the citric acid sol–gel method. The reagents La2O3, HNO3 solution, Mn(NO3)2·6H2O, KNO3, and Ce(NO3)3·6H2O were weighed in stoichiometric amounts (La1−xKxMn1−yCyO3x = 0, 0.5; y = 0, 0.3 M ratio) and dissolved in deionized water to prepare a precursor solution. Then, according to the proportion of citric acid and the sum of metal ions (molar ratio) = 1.2:1, citric acid was weighed, dissolved in deionized water, and added in the abovementioned solution. The mixture was stirred and heated to a temperature of 80 °C in a constant-temperature oil bath pot, and then, the wet gel was obtained after most of the initial water had evaporated. After being heat-treated at 120 °C for 24 h in a constant-temperature drying box, the sample was placed into a muffle burner at a temperature of 400 °C for 2 h with a heating rate of 3 °C·min−1. Then, it was calcined at 700 °C for 6 h; thus, LaMnO3, La0.5K0.5MnO3, and La0.5K0.5Mn0.7Ce0.3O3 perovskite composite oxides, labeled as LMO, LKMO, and LKMCO, respectively, were obtained.

2.2. Catalyst Characterization. X-ray diffraction (XRD) patterns were recorded on an automated powder XRD instrument operating at 100 mA and 40 kV using Cu Kα radiation. The data of 2θ from 5 to 90° were collected with a step scan of 8°. The Brunauer–Emmett–Teller (BET) surface area, pore volume, and pore size distribution were tested by determining nitrogen adsorption and desorption using a NOVA4000 surface area analyzer (Quantachrome). Scanning electron microscopy (SEM) was performed on a HITACHI S4800 field-emission SEM instrument operated at 20 kV. Fourier transform infrared (FTIR) spectra were collected on a NICOLET iS10 using anhydrous KBr as the dispersing agent. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250XI spectrometer using Mono Al Ka (1486.6 eV) radiation as the excitation source. The materials’ peak positions were corrected by setting the binding energy of adventitious carbon (C 1s) at 284.6 eV.

2.3. Reactivity Tests. The catalytic activities of the prepared samples were evaluated using a temperature-programmed reaction (TPR) on a fixed-bed tubular quartz system. Printex-U from Degussa was used as a model diesel soot, whose diameter size and specific surface area were 25 nm and 100 m2/g, respectively. The mass ratio of the catalyst and soot particles was 9:1. For conducting the TPR experiment, we took 0.5 g of mixed samples of the mixture of the catalyst and carbon particles uniformly and filled them in a constant-temperature quartz tube. During each TPR, the reaction temperature ranged from 30 to 500 °C, the heating rate was 3 °C·min−1, the equilibrium gas was argon, and the exhaust gas flow rate was 250 mL·min−1. Figure 1 shows the reaction device. The length of the reaction furnace is 350 mm, the quartz tube filled with the catalytic material is 400 mm long, and the quartz tube’s outer diameter is 20 mm.

Temperature programmed reaction was conducted with a GSVH of 20000 h-1. The catalysts were directly exposed to reaction gas containing NO (0.1%), C3H6 (0.05%), CO (0.5%), O2 (10%), and SO2 (0.3%), which has been shown in Table 1. In the activity evaluation of the catalysts, gas conversion (X) and soot ignition temperature (Tig) were the evaluation indices. The gas conversion rate used is given by Formulas 1–3. The activity of the catalyst Tig is the

Table 1. Experimental Parameters of the Gases

| constituents | SO2 | NO | CO | C3H6 | O2 | Ar | Flow (mL·min−1) |
|--------------|-----|----|----|------|----|----|----------------|
| content      | 14.7| 0.25| 1.25| 0.125| 25 | 208.7| 250            |
temperature level response curve of CO$_2$ concentration that increased to the maximum tangential curvature intersected with the temperature line.

$$X_{\text{CH}_3} = \frac{[\text{CH}_3\text{H}_3]}{[\text{CH}_3\text{H}_2]}$$

$$X_{\text{CO}} = \frac{[\text{CO}]}{[\text{CO}_2]}$$

$$X_{\text{NO}} = \frac{[\text{NO}]}{[\text{NO}_2]}$$

where $X$ is the conversion of a component in the reaction process, $i$ is the concentration of a component in the reaction, and $o$ is the outlet concentration of a component in the reaction (obtained by chromatographic analysis).

### 3. RESULTS AND DISCUSSION

#### 3.1. XRD Analysis.

Figure 2 shows the XRD patterns of the catalysts: (a) LaMnO$_3$, (b) La$_{0.5}$K$_{0.5}$MnO$_3$, and (c) La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$.

Table 2. Lattice Parameters, BET Surface Areas, and Pore Sizes of Catalysts

| composition               | $a$   | $b$   | $c$   | crystallite size (nm) | surface area (m$^2$ g$^{-1}$) | pore size (nm) |
|---------------------------|-------|-------|-------|-----------------------|-------------------------------|----------------|
| LaMnO$_3$                 | 19.12 | 19.05 | 25.26 | 14.2                  | 35                            | 3.1            |
| La$_{0.5}$K$_{0.5}$MnO$_3$| 14.39 | 12.58 | 15.74 | 20.0                  | 4                             | 4.3            |
| La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$ | 20.05 | 8.36  | 15.43 | 18.1                  | 18                            | 3.8            |

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La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$ has diffraction peaks at 28 and 56$^\circ$, which are characteristic of CeO$_2$. This is because Ce$^{3+}$ partially replacing Mn$^{2+}$ causes the average radius of site B of the perovskite to increase. In addition, the crystal lattice is distorted, causing the partial collapse of the perovskite structure to produce CeO$_2$. However, after Ce doping, the characteristic diffraction peak of the La$_{0.5}$K$_{0.5}$MnO$_3$ catalyst shifted to a large angle because the Ce doping produced more Mn$^{3+}$, Mn$^{4+}$, or oxygen vacancies with an ionic radius smaller than that of Ce$^{3+}$; therefore, the diffraction peak shifts from 32.50$^\circ$ to a larger angle of 32.63$^\circ$. These results indicate that Ce doping can improve the catalytic activity.
The particle sizes and lattice parameters of the catalyst were calculated and analyzed using Bragg’s equation and Jade software, and the specific surface area of the catalyst was characterized. Table 2 summarises the changes in cell parameters, grain size, and surface area before and after doping. Notably, the radial parameters $a$, $b$, and $c$ of LaMnO$_3$ changed after the K doping, which were smaller than the cell parameters of LaMnO$_3$. This is because although the radius of K$^+$ (1.33 Å) is larger than that of La$^{3+}$ (1.06 Å), the radius of Mn$^{4+}$ (0.39 Å) is much smaller than that of Mn$^{2+}$ (0.66 Å); therefore, the lattice parameter of LaMnO$_3$ is smaller after doping, indicating that after the K doping, a part of Mn$^{2+}$ is converted into Mn$^{4+}$ to maintain the charge balance of the catalyst. Moreover, the crystallite sizes of La$_{0.5}$K$_{0.5}$MnO$_3$ and La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$ increased, which was attributed to the distortion of the crystal after doping. The specific surface area and pore size of LaMnO$_3$, La$_{0.5}$K$_{0.5}$MnO$_3$, and La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$ increased, which was attributed to the distortion of the crystal after doping. Table 2 lists the specific surface area and pore size of LaMnO$_3$, La$_{0.5}$K$_{0.5}$MnO$_3$, and La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$; the larger pore size corresponds to the smaller surface area in general. LaMnO$_3$ has the largest surface area, 35.05 m$^2$ g$^{-1}$, and the pore diameter is 3.06 nm. However, the surface areas of the doped catalysts La$_{0.5}$K$_{0.5}$MnO$_3$ and La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$ both decreased and the pore sizes increased, which were 4.21 and 17.49 nm$^2$ g$^{-1}$ and 4.31 and 3.77 nm, respectively. This is because the excessive amount of substitution of K causes lattice distortion and the perovskite structure collapses and piles up, thereby forming clumps. The BET characterization of the catalysts is consistent with the crystallite size change in XRD; a smaller grain size corresponds to a larger specific surface area, indicating that the Ce doping significantly improved the catalyst dispersibility.

3.2. SEM Analysis. Figure 3 shows the SEM images of the catalysts: (a) LaMnO$_3$, (b) La$_{0.5}$K$_{0.5}$MnO$_3$, and (c) La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$. Although there are small spherical particles in the LaMnO$_3$ catalyst, the agglomeration phenomenon is still serious, which may influence the activity of the catalyst. The image of the La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$ catalyst shows that the sample surface is loose while the particle diameter increases; this characterization result corresponds to the calculation results of the lattice parameters in Table 2. Moreover, simultaneous doping of sites A and B in the La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$ catalyst makes the particle size reduce to 25 nm, thereby forming a honeycomb structure, which can provide a better access channel for the reaction gases and promote catalytic reactions.

3.3. FTIR Analysis. To further analyze the effect of K and Ce doping on the valence bond structure of the LaMnO$_3$ catalyst, we performed FTIR characterization of LMO, LKMO, and LCMO.
and LKMCO (Figure 4). The absorption peaks of the catalysts at 606, 595, and 617 cm$^{-1}$, respectively, are attributed to the skeletal vibration peak of the perovskite, which indicates that the prepared catalysts maintain a good perovskite structure of ABX$_3$. This result is consistent with those of the XRD analysis. In the perovskite structure, the intensity of the absorption peaks in the FTIR spectrum is mainly determined by the vibrational strength of the three pairs of B–O bonds in BO$_6$. For LMO, two strong absorption bands at 606 cm$^{-1}$ and around 441 cm$^{-1}$ can be observed. The band at 606 cm$^{-1}$ is the stretching vibration peak of the B–O bond in the BO$_6$ octahedron, while the 441 cm$^{-1}$ band is the bending vibration peak of B–O. When the BO$_6$ structure is highly symmetric, its characteristic peak intensity decreases, but the peak intensity increases. In the IR spectrum of LKMO, the peak shifts from 606 cm$^{-1}$ to a lower wavenumber of 595 cm$^{-1}$, and the peak at 441 cm$^{-1}$ disappears, indicating that K ion substitution at the A-site would improve the symmetry of MnO$_x$ and induce some of the Mn$^{3+}$ ions to be oxidized into Mn$^{4+}$. Moreover, there is no characteristic infrared peak of CeO$_2$ in LKMCO, and compared with that of LKMO, the peak intensity becomes weaker, the width becomes larger, and the peak positions of the LKMCO catalyst shift to 617 and 445 cm$^{-1}$. The result shows that the Ce ion was successfully doped into the perovskite crystal lattice, resulting in a different bonding length of the BO$_6$ octahedral and improving the symmetry of the perovskite crystal. The distortion of the BO$_6$ lattice structure leads to high-valence Mn$^{4+}$ products, and surface oxygen vacancy changes. When Ce is doped into LKMO, the peak intensity is further weakened, and the peak position shifts, indicating that the oxygen vacancy amount in the Mn$^{3+}$–Mn$^{4+}$ system increased, improving the catalytic activity. Formulas 4–6 show the reaction process.

\[
\text{La}_{1-x}\text{K}_x\text{Mn}_{1-2x}\text{Mn}_x\text{Mn}_3\text{O}_4(s) \\
\rightarrow \text{LaMnO}_3(s) + x\text{La}^{3+}\text{K}^+(e) + 2x\text{Mn}^{2+}\text{Mn}^{3+}\text{Mn}^{4+}\text{I}
\]

(4)

\[
\text{La}_{1-x}\text{K}_x\text{Mn}_{1-2x}\text{O}_{3-y}(e) \\
\rightarrow \text{LaMnO}_3(s) + x\text{La}^{3+}\text{K}^+(e) + y\text{IOl}
\]

(5)

\[
\text{La}_{1-x}\text{K}_x\text{Ce}_{2x}\text{Mn}^{(x-1)+}\text{O}_{3-y}(e) \\
\rightarrow \text{LaMnO}_3(s) + x\text{La}^{3+}\text{K}^+(e) + 2x\text{Ce}^{3+}(e) + \text{Mn}^{x+}(e) + y\text{IOl}
\]

(6)

Figure 4. FTIR spectra of the catalysts (LMO: LaMnO$_3$, LKMO: La$_{0.5}$K$_{0.5}$MnO$_3$, and LKMCO: La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$).

Figure 5. XPS spectra of the catalysts (LMO: LaMnO$_3$, LKMO: La$_{0.5}$K$_{0.5}$MnO$_3$, and LKMCO: La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$).
where $\gamma$/OI is the oxygen vacancy, s is the solid solution, and e denotes an electron.

In Figure 4, the peaks at 3436 and 1636 cm$^{-1}$ correspond to the stretching vibration peak of liquid water O−H and the variable angle vibration peak of crystallization water, respectively. The characteristic peak of the LMO catalyst appearing at 1512 cm$^{-1}$ corresponds to the nitrate antisymmetric stretching vibration peak. The bands at 1388, 902, and 848 cm$^{-1}$ are ascribed to the adsorption of CO$_2$, which are the characteristic peaks of atmospheric carbonate from the atmosphere. Meanwhile, the peak height and area of the characteristic peaks of atmospheric carbonate from the catalyst at 1388 cm$^{-1}$ exhibited different degrees of increase with the K doping and K and Ce co-doping, which is conducive to the storage of NO$_x$.

3.4. XPS Analysis. The surface element valence state changes were obtained via XPS analyses (Figure 5). From the total element spectrum of Figure 5 (Survey) on the left, we can see that the LaMnO$_3$ catalyst doped with K shows K 2p peaks, while the K and Ce co-doped catalysts show K 2p and Ce 3d peaks, which indicates that the doping element has entered the crystal lattice of the catalyst. From the full element spectrum on the left, we can see that the LaMnO$_3$ catalyst doped with K shows K 2p peaks, while the K and Ce co-doped catalysts show K 2p and Ce 3d peaks, indicating that the doping elements entered the lattice of the catalyst. This is consistent with the conclusion of the XRD characterization that K and Ce co-doping formed a good perovskite crystal phase. From the XPS spectra of Mn 2p in catalysts a, b, and c, we can see that the content of Mn$^{2+}$ in catalyst b decreased after doping with K, while the content of Mn$^{3+}$ and Mn$^{4+}$ increased. After the replacement of La$^{3+}$ by low-value K$^+$, part of the Mn$^{2+}$ ions in site B were converted into high-valent manganese ions to maintain the electrical neutrality of the catalyst. When K and Ce were co-doped, the ratio of Mn$^{3+}$/Mn$^{4+}$ decreased; the presence of Mn$^{3+}$ and reduction of Mn$^{4+}$ mean that the generation of oxygen vacancies contributes to the improvement of the catalytic performance. Based on the XPS spectrum of Mn 2p, we calculated the relative percentages of Mn ions in different valence states. Table 4 summarises the results.

Table 4. Percentages of Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ in La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$

| catalysts         | Mn$^{2+}$ | Mn$^{3+}$ | Mn$^{4+}$ | Mn$^{4+}$/({Mn$^{2+} + $Mn$^{3+}$}) |
|-------------------|-----------|-----------|-----------|-----------------------------------|
| LaMnO$_3$         | 0.32      | 0.33      | 0.34      | 0.52                              |
| La$_{0.5}$K$_{0.5}$MnO$_3$ | 0.31      | 0.33      | 0.36      | 0.56                              |
| La$_{0.5}$K$_{0.5}$Mn$_{0.3}$Ce$_{0.3}$O$_3$ | 0.32      | 0.35      | 0.33      | 0.49                              |

There are two forms of oxygen in the XPS peak spectrum of O 1s, which are lattice oxygen O$_{\text{l}}$ at 528.5−530.2 eV and high-binding oxygen O$_{\text{hl}}$ at 530.2−531.9 eV, assigned to the adsorbed oxygen species of the defect or hydroxyl group. Figure 5 (4) reveals that after the K and Ce co-doping, the ratio of the peak area of high-binding O$_{\text{h}}$ and low-binding energy peak O$_{\text{l}}$ of the catalyst increased significantly. To clarify the content changes of the lattice oxygen and adsorbed oxygen in the catalyst before and after doping, we performed a semiquantitative analysis of the O 1s spectrum. Table 5 summarises the analysis results, revealing that the content of lattice oxygen and adsorbed oxygen did not change significantly after K doping; however, the lattice oxygen content decreased and the adsorbed oxygen increased significantly after the K and Ce co-doping. The catalyst is partially replaced by low-cost K$^+$, and site-B Mn$^{3+}$ is forced to convert into the high-valent state of the Mn$^{4+}$ ion to maintain the catalyst’s electrical neutrality, while after the Ce doping, the ratio of Mn$^{4+}$/Mn$^{3+}$ decreased, indicating that more oxygen vacancies are generated to maintain the charge balance, and the mobility of the lattice oxygen is enhanced, which can be inferred from the characterization of XRD, XPS, and FTIR. The presence of oxygen vacancies promotes the adsorption of active oxygen and the formation of nitrate and nitrite. Finally, NO$_3^-$ desorbed by the nitrate and activated oxygen atom generated by the oxygen vacancy react with the soot particles to generate CO$_2$, H$_2$O, and N$_2$, thereby completely the purification of NO and soot.

3.5. Catalytic Activity for NO$_x$−Soot Removal. We investigated the catalytic performance of LMO, LKMO, and LKMCO via the TPR. Figure 7 reveals that the removal rate of CO for the three catalysts increased with the increase in the temperature and the catalysts co-doping with K and Ce had
higher conversion rates for CO than undoped LMO. When the conversion rate of CO reached 50%, the temperatures of the LKMO and LKMCO catalysts were 322 and 490 °C, respectively, while the maximum conversion of the undoped LMO catalysts was only 24%. For the removal of C₃H₆, the conversion rate of LMO, LKMO, and LKMCO catalysts also increased with an increase in the temperature, which is the same as the removal rate of CO. However, the catalytic oxidation ability of LMO for C₃H₆ was the worst among the three catalysts.

In contrast to the conversion of CO, the three types of catalysts for NO catalytic reduction showed a downward trend under 150 °C. NO may react mainly with O₂ to produce NO₂ at low temperatures, the oxidized and adsorbed NO₂ is stored in the catalyst, and the adsorption reaches saturation so that the conversion rate tends to zero. When the temperature continues to rise, the stored NOₓ begins to desorb and react with soot, CO, and C₃H₆, which again increases the removal rate of NO. Among the three catalysts, the K and Ce co-doped catalyst, LKMCO, reached the NOₓ storage equilibrium at 110 °C, and the NO conversion rate reached more than 90% at 275 °C with the temperature increase. The results indicate that the K and Ce co-doping significantly improved the NOₓ removal performance of the catalyst.

Figure 7 reveals that the K doping can significantly improve the yield of N₂; the highest N₂ yield of the undoped catalyst LMO is 26.39%. The N₂ yields of both LKMO and LKMCO catalysts increased gradually as the temperature increased. The N₂ yield of the LKMO catalyst doped with K reached 50% at 250 °C, while Pd and K co-doped LKMCO had a N₂ yield of 50% at 221 °C. Notably, Pd and K co-doping increased the low-temperature reduction performance of the catalyst effectively.

By calculating the ignition temperature, we found that the catalyst modified by K effectively reduced the ignition temperature of soot, which is consistent with the results of Li. The soot ignition temperatures of LaMnO₃, La₀.₅K₀.₅MnO₃, and La₀.₅K₀.₅Mn₀.₇Ce₀.₃O₃ were 380 °C, 268, and 252 °C, respectively. After the K and Ce co-doping in LaMnO₃, the ignition temperature of soot decreased by 128 °C, which was lower than that of undoped LaMnO₃. This is because the K and Ce co-doping improved the structure and oxygen vacancies of the catalysts, which effectively increased the contact with soot and promoted the catalytic reaction.

4. KINETICS OF THE LKMCO CATALYST ON NOₓ–SOOT REMOVAL

Kinetic factors affect the conversion efficiency of the catalyst for NO and soot particles in diesel exhaust. In addition, the process of component change of the reaction system follows the conservation of surface components, conservation of active sites, and conservation of gas-phase components. During the specific reaction kinetics process, CO, HC, NO, and other pollutants in the exhaust gas will be adsorbed on the surface of the catalyst and then diffused from the surface into the interior. In this study, we calculated the activation energy of the CO₂ and N₂ formation reaction over the catalysts using the Arrhenius equation and then investigated if K and Ce doping could effectively improve the catalytic activity.

The equation for the rate of the catalytic reaction between O₂, NO, and soot can be written as follows

\[ v = kC_A^{a}C_B^{b}C_C^{c} \]  (7)

where \( k \) is the rate constant; \( c \) is the reactant or product concentration; and \( a, b, \) and \( c \) denote the reaction levels.
Considering the complex heterogeneous catalytic reaction environment of soot, NO, and the catalyst, we calculated the relationship between the rate constant $K$ and temperature $T$ in the temperature range of 35–280 °C using the first-order reaction model of the Arrhenius equation in macroscopic reaction kinetics.\textsuperscript{36–38} The formula for the catalytic reaction rate equation can be written as

$$K = A \exp \left( - \frac{E_a}{R T} \right)$$

(8)

where $K$: response constant, mol g\textsuperscript{-1} s\textsuperscript{-1}; $A$: pre-exponential factor; $E_a$: apparent activation energy (J mol\textsuperscript{-1} K\textsuperscript{-1}); $R$: universal gas constant (8.314 J mol\textsuperscript{-1} K\textsuperscript{-1}); and $T$: temperature (K)

$$v = A \exp \left( \frac{E_a}{R T} \right) C_{PM}^{n_1} C_{NO}^{n_2} C_{O_2}^{n_3}$$

(9)

Taking the logarithm of both sides of Formula 8, we have

$$\ln v = \ln A + n_1 \ln C_{PM} + n_2 \ln C_{NO} + n_3 \ln C_{O_2}$$

(10)

which can be rewritten as

$$\ln v = \frac{E_a}{RT} + \ln \epsilon A \left( \epsilon = C_{PM}^{n_1} C_{NO}^{n_2} C_{O_2}^{n_3} \right)$$

(11)

where $\epsilon A$: pre-exponential factor; $\epsilon$: apparent activation energy; $C$: reactant concentration; $n$: reaction order, and $E_a$ and $A$: constants that do not change with $T$.

According to eq 11, the linear regression equation is drawn with ln$v$ as the ordinate and $1/T(10\textsuperscript{-3})$ as the abscissa. Then, the activation energy $E_a$ can be calculated from the slope of the line and $\epsilon A$ can be calculated from the intercept of the abscissa axes.

Figure 8 shows the Arrhenius function curve of the LaMnO$_3$, La$_{0.5}$K$_{0.5}$MnO$_3$, and La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$ catalysts simultaneously removing soot particles and nitrogen oxides between 35 and 280 °C. Figure 8C shows that the La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$ linear regression equations of CO$_2$ and N$_2$ are $y = 6.60898 - 1.9561x$ and $y = 7.04854 - 2.00437x$, respectively, and after the K and Ce co-doping, the linear fitting degree $R^2$ of the catalyst increases significantly. The slopes of the two equations are similar, which indicate that their activation energies are also similar.

Table 6 lists the kinetic parameters $E_a$ and ln$A$ in the catalytic reaction. The activation energies of the LaMnO$_3$, catalyst for CO$_2$ and N$_2$ were 16.26 and 16.66 kJ mol\textsuperscript{-1}, respectively, and after the K doping, the apparent activation energy $E_a$ of CO$_2$ and N$_2$ decreased. Moreover, the least activation energies of CO$_2$ and N$_2$ were for the K–Ce co-doped catalyst, La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$, at 8.15 and 10.87 kJ mol\textsuperscript{-1}, respectively. The activation energies decreased by 8.11 and 5.79 kJ mol\textsuperscript{-1}, respectively, compared with that of the undoped LaMnO$_3$ catalyst. The kinetic analysis results established that K and Ce co-doping effectively improved the capture performance of NO$_x$ promoted the combustion of soot, and enhanced the catalytic activity.

### Table 6. Kinetic Parameters of Pyrolysis

| Catalysts          | $E_a$ (kJ mol\textsuperscript{-1}) $\pm 0.1$ | $\ln \epsilon A$ | $R^2$ |
|--------------------|------------------------------------------|------------------|------|
| LaMnO$_3$          | 16.26 & 16.66                           | 6.61 & 7.05      | 0.95 & 0.95 |
| La$_{0.5}$K$_{0.5}$MnO$_3$ | 8.87 & 15.89                          | 4.22 & 5.64      | 0.93 & 0.95 |
| La$_{0.5}$K$_{0.5}$Mn$_{0.7}$Ce$_{0.3}$O$_3$ | 8.15 & 10.87                          | 3.76 & 5.46      | 0.93 & 0.94 |

5. CONCLUSIONS

After the co-doping of K and Ce, the perovskite-type catalyst prepared via the citric acid sol–gel method can still be formed when calcined at 700 °C, and it has good stability at high temperature. The K and Ce co-doping effectively improved the catalytic activity, where the activation energies of CO$_2$ and N$_2$ were only 8.15 and 10.87 kJ mol\textsuperscript{-1}, respectively. Moreover, the removal rate of NO$_x$ reached 90% at 275 °C and soot ignition occurred at 250 °C under lean conditions.

K doping partially replaced La in LaMnO$_3$, which can improve the agglomeration of particles in the LaMnO$_3$ catalyst, make the catalyst loose and porous, increase the contact with the reaction gas, increase the adsorption of NO, and improve the catalytic activity. Simultaneously, the addition of K leads to the transition of Mn$^{2+}$ → Mn$^{4+}$ and the generation of oxygen vacancies, which can effectively improve the removal rate of CO and the conversion rate of NO at high temperatures, considerably reduce the ignition temperature of carbon smoke, and increase the activity of catalytic soot.

Ce doping partially replaced Mn in La$_{0.5}$K$_{0.5}$MnO$_3$ and formed a honeycomb structure, which provided an effective...
channel for the reaction gas and thus improved the catalytic activity. Because of the excellent oxygen storage performance of CeO₂, Ce doping decreased the ratio of Mn⁴⁺/Mn³⁺ and promoted the oxidation of CO effectively.

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Conceptualization, L.Y. and J.H.; methodology, L.Y.; formal analysis, L.Y. and Q.S.; investigation, J.Z., G.T., and H.W.; and writing—original draft preparation, L.Y. All authors have read and agreed to the published version of the manuscript.

**Notes**

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