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Synergistic Effects of Multicomponents Produce Outstanding Soot Oxidation Activity in a Cs/Co/MnO_x Catalyst

Meng Wang, Yan Zhang,* Yunbo Yu, Wenpo Shan, and Hong He



report a novel, non-noble metal catalyst for application in the catalytic combustion of soot with superb activity and resistance to H_2O and SO_2 . MnO_x oxide was prepared via a hydrothermal method, and then, Cs and Co were loaded on MnOx by impregnation. The 5%Cs/1%Co/MnO_x catalyst displayed excellent catalytic activity with values of T_{10} (332 °C), T_{50} (371 °C), and T_{90} (415 °C) under loose contact. The as-prepared catalysts were investigated by X-ray powder diffraction (XRD), transmission



electron microscopy (TEM), H₂ temperature-programmed reduction (TPR), O₂ temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption fine structure (XAFS). The results suggest that, after the introduction of Cs and Co into the MnO_x oxide, more NO_2 molecules take part in soot oxidation, exhibiting higher NO_2 utilization efficiency; this is due to the synergistic effects of multiple components (Cs, Co, and Mn) promoting the generation of more surface-active oxygen and then accelerating the reaction between NO₂ and soot. This study provides significant insights into the development of high-efficiency catalysts for soot oxidation, and the developed 5%Cs/1%Co/MnO_x catalyst is a promising candidate for application in diesel particulate filters.

1. INTRODUCTION

Particulate matter (PM, often called soot) emitted from diesel exhaust is one of the major environmental contaminants, which not only contributes to hazy weather but also causes severe public health problems such as bronchitis and lung cancers.^{1–4} Thus, control of the emission of soot produced by diesel engines is an urgent and significant requirement for environmental protection and human health. The diesel particulate filter (DPF) is one of the most efficient solutions for soot control.^{5,6} Yet, soot accumulates on the DPF, which needs periodic regeneration. Otherwise, the back pressure created by the loaded DPF could potentially have a negative influence on the efficiency of the engine. There are two kinds of regeneration methods, which are active and passive regeneration.⁸ At present, the combination of active and passive regeneration is the most popular regeneration method. A highefficiency catalyst is the key factor in passive regeneration.

Numerous catalytic materials have been studied for soot oxidation. For the most part, the noble metal-containing catalysts tend to be the most suitable candidates due to their excellent oxidation performance.9-12 For example, in Wu et al.'s work,^{13,14} when Pt was introduced into Mn-CeO₂/Al₂O₃ or H-ZSM-5 used for soot oxidation, a decrease in T_{50} of 51 or 123 $\,^{\circ}\text{C}$, respectively, was achieved. In the work of Chen's group,¹⁵ the noble metal Pt was added to $Ce_{0.64}Mn_{0.16}R_{0.2}O_x$ (R = Y, Zr, La, or Al) for which the T_{50} value was about 420–

468 °C, while after thermal aging at 800 °C for 12 h, the T_{50} value of $Pt/Ce_{0.64}Mn_{0.36}O_x$ was increased from 420 to 518 °C. The high price of noble metal catalysts as well as their weak resistance to sulfur poisoning and lack of thermal stability limits their commercial prospects.^{15,16} Therefore, transition metal oxides,^{17–19} perovskites,^{20,21} ceria-based oxides,^{22–27} and so forth have been also studied. Among these oxides, Mn oxides are applied in many gaseous heterogeneous catalytic reactions owing to their strong redox ability, low cost, and environmental benefits.²⁸ Bueno-López et al. investigated different Mn-based oxides for soot oxidation, and the results followed the trend birnessite > cryptomelane > Mn_3O_4 > $Mn_2O_3 > natural MnO_2 > MnO_2 = MnO.^{29}$ In addition, in Zhang et al.'s work, α -MnO₂ nanorod catalysts gave a decrease in the T_{50} value to 407 °C, suggesting that α -MnO₂ nanorods possessed excellent soot oxidation activity.³⁰ To further improve the catalytic performance of Mn-based oxides, doping with other metals could be a viable option. In Wu et al.'s

Received: September 9, 2020 November 5, 2020 Revised: Accepted: December 8, 2020 Published: December 18, 2020



work,³¹ Ce was introduced into MnO_x for use in soot oxidation, resulting in a further decrease of T_{50} by 11 °C because of the increase in NO oxidation and NO₂ storage capacity. Jampaiah et al.²⁸ found that the addition of Co and Cu to MnO_2 induced a decrease in T_{50} of 116 °C due to the formation of more oxygen vacancies. In addition, it is well known that alkali metals added to catalysts can activate O_2 and improve the contact between soot and the catalyst, which are beneficial for soot catalytic oxidation.^{32,33} For instance, in Guo et al.'s work,³⁴ after K was introduced into Co_3O_4 , the T_{50} was dramatically lowered from 490 to 417 °C. Thus, the introduction of transition metals and alkali metals into Mn oxide catalysts offers an efficient strategy to improve the soot catalytic oxidation activity.

In this study, MnO_x nanorods were successfully fabricated *via* a hydrothermal method. Cs and Co were introduced into the MnO_x nanorods by simple impregnation. It was found that the $5\%Cs/1\%Co/MnO_x$ catalyst gave the best soot oxidation activity. Furthermore, the $5\%Cs/1\%Co/MnO_x$ catalyst also exhibited excellent resistance toward H₂O and SO₂. Finally, the effects of Co and Cs on the MnO_x oxide were analyzed *via* a series of characterization techniques, including XRD, Brunauer–Emmett–Teller (BET), X-ray photoelectron spectroscopy (XPS), TEM, and X-ray absorption fine structure (XAFS).

2. EXPERIMENTAL SECTION

2.1. Materials Preparation. In this work, MnO_x was synthesized *via* a hydrothermal method, which is similar to the method reported in previous works.^{35,36} KMnO₄ (10.84 g) was dissolved in deionized water, which was then added to a solution containing 18.34 g of $MnAC_2$ ·4H₂O, deionized water (40 mL), and 12.5 mL of glacial acetic acid with agitation upon which a mixed solution was obtained. Subsequently, the mixed solution was placed into a 500 mL Teflon-lined autoclave and maintained at 100 °C for 24 h. The obtained black slurry was filtered, further washed with distilled water, and dried at 110 °C overnight. Finally, the sample was calcined in a furnace at 700 °C for 3 h and then kept at 500 °C for 3 h, as reported in a previous study.

Different concentrations of cobalt ions (0.5, 1, 3, and 5% are the theoretical Co loadings with regard to the weight of the MnO_x oxide) were loaded *via* wetness impregnation. Then, the obtained fluid was ultrasonicated for 30 min, stirred for 1 h, and then water was removed by a rotary evaporation process. Finally, calcination at 700 °C for 3 h led to the formation of 0.5, 1, 3, and 5%Co/MnO_x.

The alkali metal-containing catalysts (different alkali metals Li, Na, K, and Cs with the same mole ratio) were also prepared *via* wetness impregnation, and a detailed description is recorded in the Supporting Information.

2.2. Materials Characterization. X-ray powder diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), an X-ray fluorescence spectrometer (Axios-MAX), and N₂ adsorption-desorption analysis were applied to explore the structural properties of the catalysis. XPS and XAFS technologies were used to study the surface chemical state of the catalysts. H₂ temperature-programmed reduction (H₂-TPR) and O₂ temperature-programmed desorption (O₂-TPD) were carried out to analyze the reducibility and desorption of oxygen species for the catalysts. The detailed characterization section is described in the Supporting Information.

2.3. Catalytic Activity Measurement. Catalytic activity measurements were evaluated *via* TPO (temperature-programmed oxidation), which was carried out in a fixed-bed tubular quartz microreactor under the following reaction conditions: 0.1% NO (when used), 50 ppm SO₂ (when used), 5% H₂O (when used), and 10% O₂ balanced by N₂. A soot–catalyst mixture (100 mg of the catalyst and 10 mg of soot) was prepared with loose contact. The outlet gases were monitored by using an Antaris IGS gas analyzer (Thermo Fisher).

Soot conversion and CO_2 selectivity were determined as follows

sootconversion =
$$\frac{A_i}{A_t} \times 100\%$$
 (1)

 T_{10} , T_{50} , and T_{90} are defined as the temperatures of 10, 50, and 90% of soot conversion, respectively.

$$CO_2 \text{ selectivity} = \frac{A_{iCO_2}}{A_{iCO_2} + A_{iCO}} \times 100\%$$
(2)

where A_i is the total peak areas of CO₂ and CO at a given temperature, A_t is the total peak areas of CO₂ and CO, A_{iCO2} is the total peak areas of CO₂ at a given temperature, and A_{iCO} is the total peak areas of CO at a given temperature.³⁷

The details of the experiment are shown in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Catalytic Activity. 3.1.1. Soot Oxidation Activity over Co (or Cs and Co)/ MnO_x . The soot conversion over all the catalysts is described in Figure 1. For comparison, pure



Figure 1. Soot conversion of the 5%Cs/1%Co/MnO_x, 1%Co/MnO_x, and MnO_x catalysts and pure soot during temperature-programmed oxidation. Reaction conditions: 0.1% NO, 10% O₂ balanced by N₂ under loose contact mode, GHSV = 300,000 mL·g⁻¹·h⁻¹, and heating rate = 10 °C/min.

soot oxidation without a catalyst was also performed and the results revealed that the values of T_{10} , T_{50} , and T_{90} were 538, 607, and 648 °C, respectively. It can be clearly seen that the addition of the MnO_x catalyst effectively lowered the soot ignition temperature, with the T_{10} , T_{50} , and T_{90} values decreased by about 169, 176, and 166 °C, respectively. After Co was added into MnO_x, the T_{10} , T_{50} , and T_{90} values of the 1%Co/MnO_x catalyst (from Figure S1, the optimal load of Co is 1%) were lowered to 345, 396, and 447 °C, respectively. To further improve the activity, 5% Cs (from Figures S2 and S3,

the optimal alkali metal was Cs and the optimal load of Cs was 5%) was introduced into the 1%Co/MnO_x oxide, and the results showed that the T_{10} , T_{50} , and T_{90} values were further lowered to 332, 371, and 415 °C, respectively. The CO₂ selectivity for all the catalysts was nearly 100% (Figure S4), avoiding the generation of CO. It was worth noting that both Cs and Co were beneficial to lowering the temperature of soot combustion, which could be due to the synergistic effects among Cs, Co, and Mn. Moreover, the soot oxidation performance of a commercial precious metal catalyst (0.76wt %Pt-0.26wt%Pd-based catalyst) was evaluated as a contrast, and the results are shown in Figure S5. The 5%Cs/1%Co/ MnO_x catalyst exhibited higher soot oxidation activity than the commercial precious metal catalyst under the same conditions, suggesting that a cheap and effective catalyst for soot oxidation could be obtained.

3.1.2. The Activity of the As-Prepared Catalysts under Different Reaction Conditions. The oxidation performance of the prepared catalysts under different conditions is shown in Figure 2. In the absence of NO, the catalytic activities of all the



Figure 2. Soot conversion of the as-prepared catalysts during temperature-programmed oxidation of soot in different reactant gases, GHSV = 300,000 mL·g⁻¹·h⁻¹, and heating rate = 10 °C/min.

catalysts were similar. When 0.1% NO was introduced into the reaction feed, all the catalysts exhibited outstanding catalytic activity for soot oxidation. For example, the T_{90} values of the 5%Cs/1%Co/MnO_x, 1%Co/MnO_x, and MnO_x catalysts were lowered to 415, 447, and 482 °C, giving decreases of 159, 141, and 93 °C compared with those obtained in 10% O₂ balanced by a N₂ atmosphere, respectively. The CO₂ selectivity for all the catalysts was still close to 100% (Figure S6).

Additionally, the soot oxidation performance was also evaluated in different reaction conditions (heating rates and tight contact conditions). As shown in Figure S7, the soot oxidation performance over all the catalysts decreased with the increase of the heating rate. However, the 5%Cs/1%Co/MnO_x catalyst still exhibited the best catalytic activity among all the catalysts under different heating rates (5, 10, and 15 °C/min). Similarly, the 5%Cs/1%Co/MnO_x catalyst possessed the most excellent activity under tight contact conditions (Figure S8).

3.1.3. Resistance to H_2O and SO_2 . As we all know, real diesel exhaust includes some harmful components such as H_2O and SO_2 , which could have an influence on the performance of catalysts. Therefore, excellent H_2O and SO_2 resistance are required for the catalysts in practical application. To explore the effects of SO_2 and H_2O on soot catalytic activity, Figure 3



Figure 3. T_{50} values of the as-prepared catalyst under conditions of 0.1% NO + 10% O₂ + N₂, 5% H₂O + 0.1% NO + 10% O₂ + N₂, 50 ppm SO₂ + 0.1% NO + 10% O₂ + N₂, and 5% H₂O + 50 ppm SO₂ + 0.1% NO + 10% O₂ + N₂.

shows the T_{50} values of the catalysts for soot-TPO tests under different reaction atmospheres. In the presence of $H_2O(5\%)$, O_2 (10%), and NO (0.1%), all the catalysts showed activities similar to those obtained without water vapor in the reaction feed, showing that all the Mn oxide catalysts possessed excellent H₂O tolerance. After introducing 50 ppm SO₂ or 50 ppm SO_2 and 5% H_2O into the reaction gas, the temperature of soot combustion for the Mn oxides catalysts increased slightly, which could be due to the formation of MnSO₄. Yet, the 5%Cs/1%Co/MnO_x catalyst still showed the highest catalytic activity among all the catalysts, even in the $H_2O/SO_2/$ NO/O_2 atmosphere. Additionally, the introduction of H₂O or SO_2 had no influence on the CO_2 selectivity, which remained close to 100% (shown in Figure S9). To study the stability of the 5%Cs/1%Co/MnO_x catalyst, five soot-TPO cycles were performed in the H₂O/SO₂/NO/O₂ atmosphere, and the results are shown in Figure S10. It is evident that the 5%Cs/1% Co/MnO_x catalyst was stable for soot oxidation. Therefore, the 5%Cs/1%Co/MnO_x catalyst shows good prospects for practical application.

3.2. Structural Properties of the Catalysts. To investigate the effect of Cs and Co on the MnO_x phase structure, X-ray diffraction patterns of the catalysts were measured, and the results are shown in Figure 4A. For the MnO_x oxide, it can be seen from Figure 4A that the XRD patterns mainly show the characteristic peaks of MnO₂ (PDF #44-0141). Additional peaks centered at 23.13 and 32.95° were assigned to Mn_2O_3 (PDF #41-1442). With the addition of Co and Cs, the diffraction peaks were similar to those of MnO_x oxide, indicating that the supported Co and Cs catalysts still maintained the MnO_x phase structure. Yet, no diffraction peaks of Co and Cs species were observed, which could be due to the high dispersion of Co and Cs on the surface of MnO_x oxide.^{28,37} The crystallite size of as-prepared catalysts calculated by the Scherrer formula (in Table S1) was almost the same. In addition, the XRD experiment of the spent 5%Cs/ 1%Co/MnO_x catalyst in the stability test was carried out. It is clear to see in Figure S11 that, after five soot-TPO tests, the 5%Cs/1%Co/MnO_x catalyst exhibited almost the same diffraction peaks and crystallite size with the fresh catalyst. The peaks of SiO₂ centered at 20.89 and 26.74° for the spent 5%Cs/1%Co/MnO_x catalyst were also detected because the



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Figure 4. (A) XRD patterns of the as-prepared catalysts and (B) elemental mapping results of the (a) 5%Cs/1%Co/MnO_x, (b) 1%Co/MnO_x, and (c) MnO_x catalysts.



Figure 5. (A) Mn 3s XPS spectra, (B) linear combination fitting of the XANES spectra, and (C) curve-fitting spectra of the Mn-K EXAFS for the as-prepared catalysts.

quartz sand could not been completely separated from the mixture after five soot-TPO cycle tests.

The morphologies of the catalysts were obtained by highresolution TEM (HRTEM) characterization. As shown in Figure S12, the 5%Cs/1%Co/MnO_x, 1%Co/MnO_x, and MnO_x oxides present similar nanorod morphologies. In addition, the HRTEM images presented in Figure S12 also reveal that all the materials exhibit well-defined lattice fringes. The lattice spacing for all catalysts is about 0.309 nm, corresponding to the diffraction pattern of the (310) zone axis of MnO₂, which is consistent with the results of XRD. In addition, energydispersive X-ray spectroscopy (EDS) mapping of Co and Cs was carried out; the results are presented in Figure 4B. It can be clearly seen that Co or Cs and Co are well dispersed on the MnO_x oxide, further verifying the results of XRD.

The chemical compositions, pore volumes, and surface area values of the 5%Cs/1%Co/MnO_x 1%Co/MnO_x and MnO_x catalysts are presented in Tables S1 and S2. The XRF results in Table S2 show that Co and Cs had been introduced to MnO_x and were close to the theoretical value. In comparison with the MnO_x catalyst, the catalysts with loadings of Co or Co and Cs metal oxides showed lower surface areas, following the order 5%Cs/1%Co/MnO_x (19.57 m²/g) < 1%Co/MnO_x (22.90 m²/g) < MnO_x (30.72 m²/g). This was most likely due to the blockage of part of the inter-particle mesopores by the supported Co or Co and Cs metal oxides during the calcination.³⁸

3.3. Characterization of Mn 3s, Mn 2p XPS, and Mn-K XAFS. The XPS technique was applied to investigate the influence of Co and Cs on the surface chemical state of the MnO_x catalyst. Figure 5A illustrates the Mn 3s XPS spectra of the prepared catalysts, which could be used to verify the manganese oxidation state. The spectrum of Mn 3s exhibits two peaks due to the coupling of a nonionized 3s electron with 3d valence band electrons. It is reported that the average oxidation state (AOS) of manganese represents the oxidation state of the Mn skeleton in the MnO_x oxide, which can be calculated via the formula AOS = $8.956 - 1.126\Delta Es$, where ΔEs represents the binding energy difference between the two Mn 3s peaks.^{28,39–41} The AOS of the MnO_x catalyst is 3.8 (shown in Figure 5A), while after introducing Co into the MnO_x catalyst, the AOS was decreased to 3.76. Interestingly, with the addition of Cs to the 1%Co/MnO_x catalyst, the AOS was further lowered to 3.66. Based on the results of XRD, it can be concluded that Mn⁴⁺ is dominant in MnO_{x*} According to previous research, 42-45 the reduction in the AOS could be due to an increase in the amount of Mn³⁺. For further exploring the chemical state of Mn, the results of Mn 2p spectra are shown in Figure S13. Figure S13A exhibits two peaks at about 641.8 and 653.4 eV binding energies relating to Mn $2p_{3/2}$ and Mn $2p_{1/2}\text{,}$ respectively. Mn $2p_{3/2}$ could be divided into Mn⁴⁺ (642.8 eV) and Mn³⁺ (641.5 eV) species.^{28,46} The relative contents of Mn species are also calculated in Figure S13B, revealing that the introduction of Cs and Co is beneficial to promoting the generation of more

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Figure 6. (A) H2-TPR, (B) O2-TPD profiles, and (C) O 1s XPS spectra of the as-prepared catalysts.

 Mn^{3+} . Even more exciting, the Mn 3s and Mn2p XPS results of the spent 5%Cs/1%Co/MnO_x catalyst in the stability test (Figure S14) were similar to the fresh 5%Cs/1%Co/MnO_x catalyst, revealing its high surface chemical stability.

To distinguish the subtle differences in the valence of manganese among the as-prepared catalysts, the Mn-K X-ray absorption near-edge structure (XANES) of samples is illustrated in Figure 5B. The MnO_x oxide and Mn₂O₃ were used as reference materials. Increments of Mn³⁺ in 1%Co/MnO_x and 5%Cs/1%Co/MnO_x catalysts calculated by the Rex2000 analysis package were 0.6 and 17.1%, respectively, revealing that the introduction of Cs and Co led to an increase in the amount of Mn³⁺. Previous studies^{28,35} revealed that the presence of Mn³⁺ was related to the generation of oxygen vacancies, which played a key role in accelerating the adsorption and dissociation of oxygen molecules.

To further explore the defects in the crystal structures, curve fitting was carried out on the R space profiles of the extended XAFS (EXAFS) Mn-K edge for all the catalysts. The reference material was α -MnO₂, which included three coordination shells (Mn–O, Mn–Mn₁, and Mn–Mn₂) with coordination numbers of 6, 4, and 4.^{35,36} The curve-fitted data are recorded in Figure 5C and Table S3. It can be concluded that 5%Cs/1% Co/MnO_x and 1%Co/MnO_x possessed a relatively small coordination number for the Mn-O coordination shell, revealing that more crystalline defects such as oxygen vacancies are produced.^{35,36,45} The 5%Cs/1%Co/MnO_x catalyst had the smallest coordination number for the Mn-O coordination shell (3.94) and the best soot oxidation performance, in contrast with 1%Co/MnO_x (4.45) and MnO_x (4.49). These results reveal that oxygen defects play a significant role in soot oxidation.

3.4. Characterization of H₂-TPR, O₂-TPD, and O 1s XPS. The reducibility of the catalysts plays a significant role in soot catalytic combustion. Therefore, H₂-TPR measurements were carried out to evaluate the reducibility of the catalysts, and the results are shown in Figure 6A. It is found that the MnO_x catalyst exhibits a broad reduction peak centered at around 297.2 °C, indicating that different reduction routes are included in the broad peak. According to previous reports, ^{35,45} there could be three reduction processes occurring, including MnO₂ to Mn₂O₃, Mn₂O₃ to Mn₃O₄, and then to MnO in the broad reduction peak. With the addition of Co and Cs, all the reduction peaks had similar reduction patterns and the peaks appeared in similar locations. Yet, it is worth noting that the amount of H₂ consumed increased dramatically with the

introduction of Co and Cs and followed the order 5%Cs/1% Co/MnO_x (9301 umol/g) > 1%Co/MnO_x (8649 umol/g) > MnO_x (8336 umol/g). According to Zhao et al.'s research,⁴⁷ the temperature range from 200 to 500 °C is related to the process of surface oxygen extraction by H₂. Thus, the H₂ consumption could be assigned to the consumption of surface oxygen in the range of 200–500 °C. There is a good correlation between the total H₂ consumption and T_{10} , T_{50} , and T_{90} values (Figure S15), revealing that soot oxidation activity over the catalysts strongly relies on oxygen species.

The O₂-TPD technique was used to investigate the oxygen species in the catalysts, and the obtained profiles are presented in Figure 6B. Jampaiah et al. reported that the desorption peak centered at temperatures below 506 °C could be attributed to surface oxygen species (denoted as α).²⁸ According to previous research,^{48,49} the surface oxygen is the key active oxygen species for soot oxidation. As shown in Figure 6B, it can be clearly seen that, after loading Co and Cs, the catalyst possesses a larger number of active oxygen species than the MnO_x oxide. Yet, the desorption peak of surface-active oxygen shifts to higher temperature, which could be due to the strong interaction with the surface defects.⁵⁰ The amounts of active oxygen were the highest for the 5%Cs/1%Co/MnO_x sample (93 umol/g), which is in agreement with the soot oxidation performance results.

The O 1s spectrum, which could be deconvoluted into three peaks, is presented in Figure 6C. According to the literature, $^{19,51-53}$ the binding energy peak around 532 eV is assigned to the hydroxyl oxygen species (O_{γ}) . The surfaceadsorbed oxygen species (O_{α}) and lattice oxygen species (O_{β}) appear at 530–531 and 528–529 eV, respectively. According to previous reports, 37,47 surface oxygen plays an important role in soot oxidation. The 5%Cs/1%Co/MnO_x catalyst possesses the highest amount of O_{α} (shown in Figure 6C) and thus exhibits the highest catalytic activity for soot oxidation. Even after five soot-TPO tests, O 1s XPS results show that the O_{α} amount of spent 5%Cs/1%Co/MnO_x catalyst presented is similar to the fresh sample, indicating its high stability for soot oxidation (Figure S14C).

3.5. Relationship between the Properties of the Catalysts and Catalytic Activity. To gain further insight into the relationship between the properties and catalytic activity of the catalysts, the correlations between the properties of the catalysts and their soot oxidation activity were investigated. According to previous research, ^{12,48,54} NO₂ plays a crucial role in soot oxidation due to being more active



Figure 7. (A) Relationship between the utilization efficiency of NO_2 and soot oxidation activity and (B) relationship between surface-active oxygen and the NO_2 utilization efficiency.

than gaseous O_2 . Yet, NO is the major NO_x species emitted in diesel exhaust. Therefore, it is commonly believed that the higher its ability for oxidation of NO to NO₂, the better the catalytic activity. However, the as-prepared catalysts in this work did not fit this pattern. Figure S16 shows that all the catalysts had similar ability for oxidation of NO to NO₂ while showing wide differences in soot oxidation activity (shown in Figure 1), which could be related to the NO_2 utilization efficiency. For a comparative analysis and to make sure that enough soot takes part in NO2 oxidation, the NO2 utilization efficiency for these catalysts is calculated via eq S1 below the temperature of 50% soot conversion (T_{50} , 371–431 °C), and the results are shown in Table S4. Interestingly, there is a good close linear correlation between the NO2 utilization efficiency and the soot oxidation activity for the as-prepared catalysts (shown in Figure 7A), which indicates that Cs and Co addition are beneficial to the NO₂ utilization efficiency.

An interesting question arose: how does doping with Cs and Co improve the utilization efficiency of NO_2 under loose contact and a $NO/O_2/N_2$ atmosphere? Based on the previous

reports,^{7,55–57} NO₂ could interact with soot to generate surface oxygen complexes (SOCs) at the catalyst-soot interface (NO₂ + soot \rightarrow SOCs + NO or soot + catalyst-NO₃ \rightarrow SOCs + catalyst-O + NO). Then, the generated SOCs are oxidized to CO_2 by reacting with surface-active oxygen (SOCs + O* (surface-active oxygen) \rightarrow CO₂). Figure 7B reveals that there is a linear relationship between the surface-active oxygen calculated by O 1s XPS results and the NO₂ utilization efficiency, suggesting that surface-active oxygen has a positive effect on the utilization efficiency. In addition, to further illustrate the relationship between surface-active oxygen and NO₂ utilization efficiency, the surface-active oxygen species obtained by O2-TPD results are also analyzed. It is found that it also exists in a linear relationship between surface-active oxygen calculated by O2-TPD results and NO2 utilization efficiency (Figure S17). As reported in the previous studies,^{35,49} surface defects are beneficial for activating gaseous O₂ to form surface-active oxygen. The XPS and XAFS results (shown in Figure 5) showed that the 5%Cs/1%Co/MnO_x catalyst possessed the most oxygen defects of all the catalysts.

In summary, the 5%Cs/1%Co/MnO_x catalyst was found to exhibit excellent soot oxidation activity, with T_{10} , T_{50} , and T_{90} values of 332, 371, and 415 °C under loose contact and a high heating rate of 10 °C/min, respectively. The introduction of Co and Cs can be beneficial to the formation of more surface oxygen defects, which results in the generation of more surface-active oxygen species and then improvement of the NO₂ utilization efficiency. In addition, the 5%Cs/1%Co/ MnO_x catalyst also exhibited outstanding resistance to H₂O and SO₂. All in all, this work provides a facile strategy for improving soot oxidation *via* synergistic effects among the catalyst components (Co, Cs, and Mn).

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c06082.

Summary of characterization and catalytic activity tests of catalysts: soot oxidation activity; XRD results of the spent 5%Cs/1%Co/MnO_x catalyst; HRTEM images and Mn 2p XPS of the as-prepared catalysts; Mn 3s, Mn 2p, and O 1s XPS results of the spent 5%Cs/1%Co/MnO_x catalyst; relationship between the H₂ consumption amounts and T_{50} ; NO₂ profiles; relationship between surface-active oxygen obtained from O₂-TPD and the NO₂ utilization efficiency; BET surface areas, XRF, and curve-fitting results of Mn-K EXAFS for different samples; and the NO₂ utilization efficiency(PDF)

■ AUTHOR INFORMATION

Corresponding Author

Yan Zhang – Center for Excellence in Regional Atmospheric Environment and Ningbo Urban Environment Observation and Research Station, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China;
orcid.org/0000-0002-5423-8255; Phone: +86 574 86085855; Email: yzhang3@iue.ac.cn; Fax: +86 592 6190990

Authors

- Meng Wang Center for Excellence in Regional Atmospheric Environment, Chinese Academy of Sciences, Xiamen 361021, China; University of Chinese Academy of Sciences, Beijing 100049, China
- Yunbo Yu Center for Excellence in Regional Atmospheric Environment, Chinese Academy of Sciences, Xiamen 361021, China; State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; University of Chinese Academy of Sciences, Beijing 100049, China; ◎ orcid.org/0000-0003-2935-0955
- Wenpo Shan Center for Excellence in Regional Atmospheric Environment and Ningbo Urban Environment Observation and Research Station, Institute of Urban Environment,

Chinese Academy of Sciences, Xiamen 361021, China; orcid.org/0000-0003-2818-5708

Hong He – Center for Excellence in Regional Atmospheric Environment, Chinese Academy of Sciences, Xiamen 361021, China; State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; University of Chinese Academy of Sciences, Beijing 100049, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.0c06082

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Key R&D Program of China (2017YFC0212502), the National Natural Science Foundation of China (51908532), and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA23010201).

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