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Cesium as a dual function promoter in Co/Ce-Sn catalyst for soot oxidation

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Keywords: Soot oxidation Cs Dual functional promoter Surface defects Contact	In this study, a 10 %Cs/3 %Co/Ce _{0.5} Sn _{0.5} O ₂ catalyst with outstanding soot oxidation performance was devel- oped, by doping Cs to 3 %Co/Ce _{0.5} Sn _{0.5} O ₂ . Remarkably, doping Cs lowered the T ₅₀ of the catalyst by 163 °C under a $H_2O/O_2/N_2$ atmosphere and loose contact. It was also noteworthy that the 10 %Cs/3 %Co/Ce _{0.5} Sn _{0.5} O ₂ catalyst exhibited excellent water and sulfur dioxide resistances. Characterizations indicated that the doping of Cs had dual functional effects on soot catalytic oxidation. On one hand, the introduction of Cs induced the formation of more oxygen defects, which was beneficial to the activation of surface chemisorbed oxygen. On the other hand, it also benefited the catalytic performance by increasing the mobility of the surface-active oxygen species, which favored the contact between soot and catalyst. Therefore, the alkali metal cesium was found to be an excellent promoter for soot catalytic oxidation, and the developed 10 %Cs/3 %Co/Ce _{0.5} Sn _{0.5} O ₂ catalyst is very promising for practical applications in diesel soot oxidation.		

1. Introduction

Soot particulates derived from diesel engines not only lead to environment pollution, such as haze, but also induce serious negative public health outcomes including lung cancer and cardiovascular diseases [1, 2]. Therefore, the elimination of diesel soot has attracted much attention over the last few years. The combination of a diesel particulate filter (DPF) with soot oxidation catalysts, named the catalytic diesel particulate filter (CDPF), is known as one of the most efficient techniques for soot purification, and highly active oxidation catalysts play a key role in CDPF [2,3].

Numerous catalysts have been reported for eliminating soot, including noble metal-based catalysts [3–6], perovskite or perovskite-related oxides [7,8], ceria-based oxides [9–11], and other mixed metal oxides [12,13]. Among them, ceria-based oxides have attracted wide attention owing to their excellent ability for oxygen storage and release [14–16]. To date, various types of ceria-based oxides had been reported. For instance, Reddy et al. found that a $COO_x/Sn-CeO_2$ hybrid material exhibited superior catalytic performance, with the T₅₀ decreased to 560 °C under loose contact [17]. Wu's group found that a Cu-Ce binary oxide could decrease the T₅₀ to 419 °C due to the strong

synergistic effect between Cu and Ce species [18]. Therefore, ceria-based oxide catalysts have shown great potential for lowering the temperature of soot combustion and need to be further explored to improve their soot oxidation performance.

Soot catalytic oxidation is a gas (O2/NO/NO2) - solid (catalyst) - solid (soot) heterogeneous catalytic reaction. To simulate the poor contact between soot and catalyst typically found in actual diesel particulate filters, the loose contact condition between soot and catalysts has often been employed for activity tests. Therefore, the contact efficiency between soot and the active sites plays a critical role in soot catalytic oxidation. For example, Zhao's group successfully fabricated a series of 3DOM catalysts to improve the contact efficiency between the catalysts and soot particles, and the catalysts exhibited excellent catalytic performance [8,19]. Besides, the addition of alkali metal is beneficial for improving the contact efficiency between catalyst and soot particles. Generally, it was thought that the high mobility of molten alkali metal can lead to the increase of contact efficiency between catalyst and soot particles [1,20]. For instance, Sun et al. found that the introduction of K to Co₃O₄ catalyst could improve the contact efficiency between catalyst and soot particles to promote soot oxidation [21]. Setiabudi et al. revealed that the catalyst with alkali metal could create a liquid

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catalyst-soot-gas interface, which is beneficial to soot oxidation [22]. Alkali metals can volatilize at high temperature inducing the deactivation of catalysts, thus the stability needs to be improved [23,24]. Neyertz et al. found a loss of potassium from K/CeO₂ catalysts after aging treatments at 800 °C, resulting in the decrease of soot oxidation activity [25]. Similarly, Cao's work reported that potassium species in the form of separate phases on the catalysts were unstable during soot oxidation [26]. Therefore, developing an excellent and stable soot oxidation catalyst and exploring the effects of alkali metal on soot oxidation catalysts were still of curial importance.

In this study, we developed an excellent Cs/Co/Ce_{0.5}Sn_{0.5}O₂ catalyst for soot oxidation, and the effects of the alkali metal Cs on a 3 %Co/Ce_{0.5}Sn_{0.5}O₂ (3 % was the weight ratio of Co to carrier) catalyst were investigated. It was found that Cs is an excellent promoter with dual functional effects on soot catalytic oxidation: improving soot-catalyst contact and promoting the generation of more surface oxygen defects. The dual positive effects of Cs assured the high soot combustion activity of the 10 %Cs/Co/Ce_{0.5}Sn_{0.5}O₂ catalyst.

2. Experimental

2.1. Catalyst preparation

The Ce-Sn mixed oxide (denoted as Ce_{0.5}Sn_{0.5}O₂) used as the support for the catalyst was synthesized by a co-precipitation method. Ce $(NO_3)_3$ ·6H₂O and SnCl₄·5H₂O (Ce/Sn molar ratios = 1:1) were dissolved together in deionized water. Then, the above aqueous solution was added dropwise into another mixed solution consisting of H₂O : NH₃·H₂O : H₂O₂ = 4:4:1 under vigorous mixing. Next, the obtained suspension was ultrasonicated for 30 min, stirred for 1 h, and washed. The obtained precipitate was dried at 110 °C for 12 h, and finally calcined at 700 °C for 3 h in air.

3 % Co (3 % = the weight ratio of Co to carrier) was loaded on the Ce_{0.5}Sn_{0.5}O₂ via impregnation method. 2 g Ce_{0.5}Sn_{0.5}O₂ was added into 50 mL aqueous solution of Co(NO₃)₂·6H₂O. The obtained mixture was ultrasonicated for 30 min and stirred for 1 h. Then, the mixture was subjected to a rotary evaporation process to remove water. Finally, the obtained powders were dried at 110 °C overnight and then calcined at 700 °C for 3 h in air.

After that, 5,10 and 20 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalysts (5, 10 and 20 % represent the weight ratios of Cs to 3 %Co/Ce_{0.5}Sn_{0.5}O₂ were prepared by impregnation of 3 %Co/Ce_{0.5}Sn_{0.5}O₂ with aqueous CsNO₃. The obtained turbid fluid was ultrasonicated for 30 min and stirred for 1 h. Then, the mixture was subjected to a rotary evaporation process to remove water. Finally, the obtained samples were dried at 110 °C for 12 h and calcined at 700 °C for 3 h in air.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the catalysts were obtained on a X'Pert PRO instrument with a Cu target operated at 40 kV and 40 mA ($\lambda = 1.5418$). The measurements were taken with a 2 θ range from 10–90° and a scan step of 0.07°.

The morphologies and element mapping of the as-prepared catalysts were obtained with a high-resolution transmission Tecnai FEI-F20 electron microscope.

 $\rm N_2$ adsorption isotherms were carried out at $-196~^{\circ}\rm C$ using an ASAP 2020 N Autoscore surface analyzer. Prior to the test, all of the catalysts were degassed at 300 $^{\circ}\rm C$ under vacuum for 1 h. The specific surface area and pore volume were obtained with the BET and BJH models, respectively.

The actual Cs and Co contents in the catalysts were determined by inductive coupled plasma optical emission spectrometry (ICP-OES) using an Agilent 5110 apparatus.

 $H_2\text{-}TPR$ was performed with a Micromeritics Auto Chem II 2920 automatic chemical adsorption analyzer. After pre-treatment under 5 %

 O_2 balanced by He at 500 °C for 1 h, the 100 mg sample was heated from room temperature to 900 °C at a constant rate (10 °C/min) in a U-shaped quartz reactor under 10 % H₂/Ar mixture gas (30 mL/min). The hydrogen consumption was monitored with a TCD detector calibrated by the signal generated by the introduction of the known amounts of hydrogen.

O₂-TPD was tested in the same apparatus as H₂-TPR. A 100 mg sample was pre-treated in He at 300 °C for 1 h, then cooled down to room temperature, and treated with 5 % O₂/He mixture gas (30 mL/min) for 1 h. Finally, the temperature was raised in He flow at a rate of 10 °C/min to 900 °C. The outlet exhaust was detected by TCD.

A Soot-TPR test was performed involving the thermal reduction of soot without gaseous oxygen in the same apparatus as that used for H₂-TPR. The mixture of 10 mg soot and 100 mg catalyst under loose contact mode was pre-treated in He at 300 °C for 1 h, and then heated up from 30 to 950 °C in Ar atmosphere. The productions of CO₂ and CO were detected on-line by a mass spectrometers (MS) with a quadrupole-type detector.

X-ray photo electron spectroscopy (XPS) of the catalysts were measured on a scanning X-ray micro probe (ESCALAB250I, Thermo Fisher scientific) using Al K α radiation. All of the binding energies were calibrated using the C 1s peak (BE = 284.8 eV) as standard.

Cs L₃-edge and Co and Sn K-edge XAFS were collected on the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). All the data analysis of the Cs-L₃ edge, Co-K edge and Sn-K edge for both XAFS and EXAFS was carried out by the Athena analysis package.

2.3. Catalytic activity measurement

Catalytic activity tests were performed in a fixed-bed reactor, which was equipped with a quartz tube of 5 mm inner diameter. Printex-U carbon black produced by Degussa AG was used as model soot, with the particle size and specific surface area being 25 nm and 100 m^2/g , respectively. To make the evaluation conditions similar to practical conditions, loose contact was employed, which involved using a spatula to mix the catalyst with soot for 2 min. In addition, tight contact condition was also implemented for comparison by mixing the catalyst and soot in an agate mortar for 10 min. Thereafter, the mixture including 10 mg soot, 100 mg catalyst, and 300 mg quartz sand (40-60 mesh, for the purpose of reducing air resistance) was put into the quartz tube. The reactor feed was composed of 1000 ppm NO (when needed), 50 ppm SO₂ (when needed), 5 % H₂O, and 10 % O₂, with N₂ as balance gas at a total flow rate of 500 mL/min. The water vapor was fed into the airflow system via passing N₂ into the water in a thermostatic water bath (with the theoretical amount of water being 5 % in this work). All the pipelines were covered with a heating strip to make sure that the reactants were vaporized completely. The reaction temperature was increased from room temperature to 700 °C at a heating rate of 10 °C/min, which was measured by a K-type thermocouple in the fixed bed reactor. The concentrations of outlet gases from the soot catalytic oxidation process, such as CO₂, CO, NO and NO₂, were analyzed by an Antaris IGS (Thermo Fisher) gas analyzer equipped with a heated, low-volume multiple-path gas cell (2 m).

Soot conversion and CO_2 selectivity play an important role in evaluating catalyst activity. They are calculated by the following formulas (1) and (2), respectively:

$$Soot \ conversion = \frac{A_i}{A_t} \times 100\% \tag{1}$$

Where A_i is the total peak areas of CO_2 and CO at a certain temperature, and A_t is the total peak areas of CO_2 and CO during the whole reaction. The catalytic activity was described by the values of T_{10} , T_{50} , and T_{90} , which were defined as the temperatures corresponding to 10 %, 50 %, and 90 % soot conversion, respectively [27].



Fig. 1. Soot conversion of the as-prepared samples during temperatureprogrammed oxidation (TPO) of soot (a) and the stability of 10 %Cs/3 %Co/ Ce-Sn in five soot-TPO cycles (b) in 5 % H₂O and 10 % O₂ balanced by N₂ under loose contact mode, heating rate =10 °C/min.

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

where $A_{i\ CO2}$ is the total peak area of CO_2 at a certain temperature, and $A_{i\ CO}$ is the total peak area of CO at a certain temperature.

3. Results and discussion

3.1. Soot oxidation performance

The alkali metal Cs (Cs is the optimal alkali metal as shown in Fig. S1a) was used to improve soot oxidation performance, and the optimal loading amount of Cs was about 10 % (Fig. S1b). The soot conversion and CO_2 selectivity of the 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O_2 and 3 $Co/Ce_{0.5}Sn_{0.5}O_2$ catalysts are shown in Fig. 1 and S2, at a heating rate of 10 °C/min, under O2/H2O/N2 atmosphere and loose contact. For a comparative study, the combustion of soot in the absence of catalyst was implemented, and the T10, T50 and T90 were 540, 616 and 663 °C, respectively. When soot was mixed with 3 %Co/Ce_{0.5}Sn_{0.5}O₂, the T₅₀ was lowered from 616 °C to 556 °C, and the CO2 selectivity was increased to nearly 100 %. Remarkably, the Cs loading dramatically improved soot oxidation activity, which further decreased the T₅₀ by 163 °C in comparision with the 3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst. As shown in Fig. S2, the CO₂ selectivity was still close to 100 %, revealing that there was almost no CO generation with Cs-containing catalyst. In addition, the impacts of NO, H2O and SO2 on the 10 %Cs/3 %Co/ $\mathrm{Ce}_{0.5}\mathrm{Sn}_{0.5}\mathrm{O}_2$ catalyst were also tested, and the results are shown in

Table 1

fextural properties of the catalysts.	
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Catalyst	$S_{BET}(m^2/g)^{a}$	$V_p(cm^3/g)^b$	D _p (nm) ^c
10 %Cs/3 %Co/Ce _{0.5} Sn _{0.5} O ₂	11.89	0.04	12.50
3 %Co/Ce _{0.5} Sn _{0.5} O ₂	23.95	0.125	19.29

^a BET surface area.

^b BJH desorption pore volume.

^c BJH adsorption pore radius.

Fig. S3. After introducing NO, the T_{50} value was further decreased by about 26 °C, which could be due to that NO was oxidized to NO₂ and then promoted soot oxidation (Fig. S4), consistent with other previous studies [28,29]. To explore the catalytic stability of the 10 %Cs/3 % Co/Ce_{0.5}Sn_{0.5}O₂ catalyst, five soot-TPO cycles were performed, and the results are shown in Fig. 1b and Fig. S5. It is evident that the composition of 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst is stable for soot oxidation. It is noteworthy that the 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst exhibited superior H₂O and SO₂ resistances (as shown in Fig. S3), suggesting that it is very promising for practical application in the oxidation of diesel soot.

3.2. Textural properties of the as-prepared catalysts

The XRD patterns of the catalysts are shown in Fig. S6. The pattern of the 3 $(Co/Ce_{0.5}Sn_{0.5}O_2)$ catalyst mainly showed the typical peaks of CeO₂ with the cubic fluorite structure (PDF#43-1002). In addition, diffraction peaks of SnO₂ (PDF#41-1445) were also observed for the 3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst. Yet, no Co species were detected, indicating that the Co species were well dispersed on the catalyst surface [13,30]. Compared with 3 %Co/Ce_{0.5}Sn_{0.5}O₂, the XRD patterns of 10 %Cs/3 % $Co/Ce_{0.5}Sn_{0.5}O_2$ showed similar peaks, which were mainly the typical peaks for CeO₂ and SnO₂. Cs and Co species were still not observed. This may be due to the fact that these species were highly dispersed on the catalyst surface and below the detection limit of the XRD technique. In order to prove that the oxides of Cs and Co were highly dispersed on the catalyst surface, elemental mapping of the catalysts was conducted via EDS (Fig. S7). Fig. S7a shows the distribution of Cs relative to other elements for the 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ sample. Fig. S7b presents the Co distribution of the 3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst. Based on a comparative analysis, it can be concluded that the oxides of Cs and Co were well dispersed on the catalyst surface, consistent with the results of XRD.

Nitrogen physisorption analysis was carried out to determine the BET specific surface areas and total pore volumes of the samples, and the results are shown in Table 1. After the impregnation of 3 %Co/Ce_{0.5}Sn_{0.5}O₂ with Cs oxide, some changes in textural properties



Fig. 2. H₂-TPR profiles of the as-prepared catalysts.



Fig. 3. O₂-TPD profiles (a) and O₂ desorption amount (b) of the as-prepared catalysts.

appeared. The 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ sample had lower surface area in comparison to the 3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst, which is associated with blockage of part of the inter-particle mesopores and part of the pores by the supported Cs species. In addition, according to the ICP results (Tables S1 and S2), the amounts of Cs and Co on the catalysts were very similar with their theoretical values. The spent 10 %Cs/3 % Co/Ce-Sn catalyst also showed almost the same contents of Cs and Co as the fresh catalyst, indicating that alkali metal Cs species and transition metal Co species are stable in the catalyst for soot oxidation.

3.3. Redox properties

3.3.1. H2-TPR

H₂-TPR was applied to evaluate the reducibility of all the catalysts, and the results are shown in Fig. 2. The H2-TPR profile of the 3 %Co/ Ce0.5Sn0.5O2 catalyst contained two minor peaks at 304 °C and 377 °C, respectively, and a major broad reduction peak at 506 °C. According to previous studies [21,31,32], the first reduction peak below 350 °C could be attributed to the reduction of Co^{3+} to Co^{2+} in cobalt oxide dispersed on the Ce0.5Sn0.5O2, the second minor peak centered at 377 °C was related to the reduction of Co^{2+} ions to Co, and the last broad reduction peak observed above 400 $^{\circ}$ C may include the reduction of Ce⁴⁺ to Ce³⁺ in the range of 425–665 $^\circ C$ [33] and Sn^{4+} to Sn^{2+} or Sn in the range of 400-675 °C [33,34]. After introducing Cs into 3 %Co/Ce_{0.5}Sn_{0.5}O₂, the three reduction peaks shifted towards lower temperatures, indicating that doping with Cs had a positive effect on the redox ability of the 3 % Co/Ce_{0.5}Sn_{0.5}O₂ catalyst. In addition, H₂-TPR could also reflect the oxygen reduction processes in the sample. With the addition of Cs, the reduction peaks shifted towards lower temperatures, indicating that the 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst possessed more mobile oxygen species, which would be beneficial for soot combustion.

3.3.2. O2-TPD

O₂-TPD experiments were carried out to demonstrate the activation capability and adsorption behavior of the 3 %Co/Ce_{0.5}Sn_{0.5}O₂ and 10 % Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalysts towards oxygen species, and the results are shown in Fig. 3. The desorption peaks between 150 and 450 °C were assigned to chemisorbed active oxygen species, such as O_2^{2-}/O_2^{-} , and the peak above 450 °C belonged to lattice oxygen [35–37]. For the 3 % Co/Ce_{0.5}Sn_{0.5}O₂ catalyst, the desorption of active oxygen species started at 303 °C and centered at 432 °C. With the addition of Cs, the desorption peak of active oxygen species shifted to the low temperature range (started at 280 °C and centered at 396 °C), indicating that the introduction of Cs species enhanced the mobility and activation of the chemisorbed oxygen. The addition of Cs species greatly promoted the activation of the surface lattice oxygen, with the desorption peak of surface lattice oxygen species desorbed included the chemisorbed the chemisorbed oxygen species desorbed included the chemisorbed



Fig. 4. Soot-TPR-MS profiles of the catalysts with and without alkali metal Cs. Reaction conditions: catalyst : soot = 10 : 1, purity Ar atmosphere, from 30 to 950 °C, heating rate =10 °C/min.

oxygen species, and surface lattice oxygen plays a key role in promoting soot combustion [39]. From Fig. 3b, it could be seen that the desorption amount of surface-active oxygen species increased more than a factor of ten with the addition of Cs. Therefore, it is likely that the enhanced



Fig. 5. Cs 3d XPS spectra (a), normalized absorption of Cs L_{III} edge XANES spectra (b) and first-order derivatives (c) of 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ and CsNO₃.



Fig. 6. Co 2p XPS spectra (a), Ce 3d XPS spectra (b), Sn 3d XPS spectra (c), and O 1s XPS spectra (d) of the as-prepared catalysts.



Fig. 7. Normalized absorption of Co K edge XANES spectra (a), normalized absorption of Sn K edge XANES spectra (b), EXAFS spectra of Co K-edge (c), and EXAFS spectra of Sn K-edge (d) of the as-prepared samples.

activation of chemisorbed oxygen and the surface lattice oxygen due to Cs addition lead to the excellent activity of the 10 %Cs/3 % $Co/Ce_{0.5}Sn_{0.5}O_2$ catalyst.

3.3.3. Soot-TPR

Generally, surface-active oxygen species play a significant role in oxidation reactions [29]. Soot-TPR experiments on the as-prepared catalysts were carried out in a high-purity He atmosphere, and the profiles are shown in Fig. 4. With soot as the reductant, it was believed that more direct information could be obtained with better correlation to the reaction performance of the catalysts [28,39]. According to the CO2 and CO peak positions, the profiles could be divided into two temperature regions, which were in accordance with the O_2^- and O_2^{2-} species (320–500 $^{\circ}$ C) and lattice oxygen (> 450 $^{\circ}$ C), including surface lattice (450-680 °C) oxygen and bulk lattice oxygen (> 680 °C), respectively [7,27,31]. In light of the temperature range of soot combustion (< 700 °C) in Fig. 1, the surface adsorbed and surface lattice oxygen species are the main active oxygen species for soot combustion. By comparing the profiles in Fig. 4, it is clear that after the addition of Cs a larger number of active oxygen species were observed. Notably, the addition of Cs also caused a shift in the peak for desorption of lattice oxygen to the lower temperature, revealing that Cs species addition enhanced the mobility of surface-active oxygen, and the results were in accord with the results of O2-TPD.

3.4. Surface chemical states and defects of the as-prepared catalysts

3.4.1. XPS and XAFS analysis of Cs

XPS measurement was employed to explore the states of the Cs species in the as-prepared catalyst, and the results are described in Fig. 5a. Two Cs 3d peaks at 724.43 and 738.34 eV were observed for the 10 %/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst, which were the typical peaks for Cs⁺ cations [40]. According to previous studies [41–44], the Cs⁺ cations can

be regarded as active electronic promoters because they can donate electrons to other metal oxides. In order to further understand the chemical state of the Cs species, XAFS measurement was carried out for the 10 %/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst and a CsNO₃ sample. Fig. 5b and c display the normalized absorption of Cs L_{III} edge XANES spectra and first-order derivatives for the as-prepared samples. As shown in Fig. 5b, the Cs species were in the Cs⁺ state. Yet, the first-order derivative spectrum for the 10 %/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst showed a shift to higher energy in comparation to CsNO₃ (Fig. 5c). It could be due to the Cs⁺ transferring negative charge density to oxide anions and then affect other metal cations such as Co, Ce and Sn.

3.4.2. The effect of Cs on the surface chemical states and defects of Co/Ce-Sn $\,$

XPS and XAFS measurements were used to explore the surface chemical state of Co for the catalysts with and without added Cs. As shown in Fig. 6a, deconvolution of the Co 2p spectra of the as-prepared catalysts displayed four peaks. The peaks centered at 780.09 eV and 795.09 eV of Co 2p could be assigned to Co^{3+} and the others corresponded to Co^{2+} on the 3 %Co/Ce_{0.5}Sn_{0.5}O₂ sample [40,45,46]. After the addition of Cs, the peaks of Co 2p shifted to lower energies by about 0.9 eV, suggesting that electrons were transferred from the Cs dopant (electron donor) to the Co species. Therefore, the ratio of Co^{2+}/Co^{3+} species would increase from 1.02 to 1.33 with the loading of Cs (Fig. 6a). Co^{2+} ions were associated with a neighboring oxygen defect, which easily reacted with gaseous O_2 to produce adsorbed oxygen species [29, 46], consistent with the results of O₂-TPD. To further explore the chemical state of the Co species before and after Cs addition, XAFS measurements were conducted. Fig. 7a shows that the Co-K edge XANES spectra for the 3 %Co/Ce $_{0.5}$ Sn $_{0.5}$ O₂ and 10 %Cs/3 %Co/Ce $_{0.5}$ Sn $_{0.5}$ O₂ catalysts were similar to that of Co₃O₄, which suggested that the Co species of the as-prepared catalysts existed as Co₃O₄. Fig. 7c illustrates the EXAFS R space profiles of the Co-K edge for all the catalysts. Three



Fig. 8. Ozawa plots for soot conversion of 10 % with varying temperature increase rates of 2, 5, 10, 15 and 20 °C/min under loose contact mode, GHSV 300,000 mL g^{-1} h⁻¹. Feed composition: 5 % H₂O, 10 % O₂, and N₂ balance.

peaks centered at 1.91, 2.85 and 3.35 Å can be attributed to backscattering from the first Co-O shell, the first Co-Co₁ shell and the second Co-Co₂ shell [47]. As can be seen, the 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst exhibited a relatively small coordination number for the first coordination shell of Co-O, compared with the 3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst (Table S3), indicating that Cs species could be beneficial to the formation of surface oxygen defects.

XPS was also used to investigate the effect of supported Cs on the surface Ce species of the as-prepared catalysts, which was correlated with the catalytic performance for soot oxidation. As shown in Fig. 6b, Ce 3d deconvolution spectra of the catalysts were identified into the ten classical peaks, namely v_0 , v, v_1 , v_2 , v_3 , u_0 , u, u_1 , u_2 and u_3 . The v_0 , v_1 , u_0 and u_1 were ascribed to the reduced cerium species Ce³⁺, while the rest peaks were ascribed to Ce⁴⁺ species [48–50]. Fig. 6b shows the ratio of Ce³⁺/Ce⁴⁺. It was clear that Cs doping significantly increased the ratio of Ce³⁺/Ce⁴⁺ from 0.384 to 0.526, suggesting that Cs species were beneficial to production of Ce³⁺. As is well known, the higher the Ce³⁺ concentration in these samples, the more oxygen defects are generated [51], which would beneficial for the adsorption and activation of O₂.

The Sn species states on the surface of the samples were analyzed by XPS and XAFS. Fig. 6c showed the Sn 3d XPS results, in which the 486.00 eV and 494.44 eV peaks were ascribed to Sn²⁺, and the others were Sn⁴⁺, for the 3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst [52,53]. It was noteworthy that the addition of Cs induced a shift in the peaks of Sn 3d spectra to lower binding energy by about 0.37 eV, and the ratio of Sn²⁺/Sn⁴⁺ increased to 1.31 [54]. Sn²⁺ could promote the increase in surface

defects by synergetic interaction with other metal oxides. Fig. 7b describes the Sn-K edge XANES spectra for the as-prepared samples, in which the profiles of Sn for both 3 %Co/Ce_{0.5}Sn_{0.5}O₂ and 10 %Cs/3 % Co/Ce_{0.5}Sn_{0.5}O₂ catalysts were similar to that of SnO₂, revealing that the Sn species predominantly exist in the form of SnO₂. The EXAFS data fitting results are displayed in Fig. 7d and Table S4. The reference sample (SnO₂) was shown to possess Sn-O, Sn-Sn₁ and Sn-Sn₂ coordination shells located 2.05, 3.19 and 3.72 Å with the coordination numbers being 6.33, 1.35 and 5.63, respectively. As can be seen, the 3 % Co/Ce_{0.5}Sn_{0.5}O₂ catalyst showed a relatively small coordination number for Sn-Sn1 and Sn-Sn2 coordination shell in comparison with the reference sample, suggesting that the catalyst possessed more abundant crystalline defects [55]. Interestingly, after Cs addition, the coordination numbers for the Sn-O coordination shell was further decreased, indicating that doping with Cs was beneficial to inducing surface oxygen defects.

Fig. 6d shows the O 1s XPS spectra of all catalysts, containing two kinds of O species. In general, the high intensity peaks in the binding energy range of (531–532.08 eV) were assigned to be the surface adsorbed oxygen species (O_{α}) and the band at lower binding energy (528.90–530.48 eV) was ascribed to the lattice oxygen species (O_{β}) [56]. With the addition of Cs, the binding energies of the oxygen species decreased, which could be because of the strong electro-positivity of the Cs⁺ dopant [38]. As shown in Fig. 6d, it was noticeable that the proportion of O_{α}/O_{β} on the surface of 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst increased to 0.508, which could be due to the induction of more abundant surface oxygen defects by Cs doping. The surface oxygen molecules to produce surface-active oxygen species, which was consistent with the results of O₂-TPD and Soot-TPR.

3.5. Activation energy measurements

Measurement of the apparent activation energy, an effective method to disclose catalytic reaction kinetics, was also employed in evaluating the soot catalytic oxidation processes [27,31,57]. Fig. 8 shows the Ozawa plots and the Ea values of 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ and 3 % Co/Ce_{0.5}Sn_{0.5}O₂ catalysts for 10 % soot conversion, with varying temperature increase rates of 2, 5, 10, 15 and 20 °C/min. For the 3 % Co/Ce_{0.5}Sn_{0.5}O₂ catalyst, the apparent activation energy was reduced to 143.28 kJ/mol. Remarkably, with Cs doping, the Ea value was lowered to 96.08 kJ/mol, revealing that the introduction of Cs caused a significant reduction in the energy barrier. Thus, Cs could be used as promoter to improve the performance of the soot oxidation catalysts.

3.6. Contact efficiency during the reaction process



The contact efficiency also plays a key role in soot catalytic oxidation, due to the poor contact between soot and diesel filters in practical

Fig. 9. Soot conversion (a) and the contact efficiency of T_{50} and T_{90} (b) of the as-prepared catalysts. Reaction conditions: T = tight contact mode, L = loose contact mode, and 5 %H₂O and 10 % O₂ balanced by N₂, heating rate =10 °C/min.



Fig. 10. Schematic illustration of soot oxidation process. A: $3 \ \%$ Co/Ce_{0.5}Sn_{0.5}O₂; B: 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂.

application. For a comparative study, the concept of degree of contact (DC) was proposed, as recently used by Liu et al. [39] for reporting the degree of relative contact. It was defined as:

$$DC_i = \frac{T_i(L) - T_i(T)}{T_i(T)}$$

where $T_i(L)$ and $T_i(T)$ represent the temperature of i % soot conversion under loose and tight contact. Fig. 9a shows the soot conversion under tight and loose contact models to illustrate the effects of Cs on the contact efficiency. There was a great difference of the soot oxidation activity between tight and loose contact models for the 3 %Co/ Ce_{0.5}Sn_{0.5}O₂ catalyst. Yet, interestingly, after the introduction of Cs, the difference was clearly decreased. To compare the temperature differences for catalysts with or without Cs doping, DC₅₀ and DC₉₀ were calculated, and the results are shown in Fig. 9b. With the addition of Cs, the DC was improved, for example DC₅₀ increased from 0.61 to 0.83, which revealed that the addition of Cs was beneficial for improving the contact between soot and catalyst.

3.7. The dual functions of Cs

Fig. 1 shows that with Cs addition, the soot oxidation performance was dramatically improved and CO₂ selectivity was still close to 100 %. On the basis of the above analysis and experimental results, it is evident that the addition of Cs has dual positive effects on soot catalytic oxidation. On one hand, the added Cs could donate electrons to the 3 % $Co/Ce_{0.5}Sn_{0.5}O_{2}$ catalyst, inducing the formation of more surface oxygen defects. XPS and XAFS results (as shown in Figs. 6 and 7) confirmed that the 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst possessed more surface oxygen defects than the catalysts without Cs doping. In addition, the O₂-TPD, Soot-TPR, and XPS of O1 s analysis (described in sections 3.3.2, 3.3.3 and 3.4.2) further indicated that the Cs dopant was beneficial for the generation of surface-active oxygen, which could be due to the formation of more surface oxygen defects. On the other hand, doping Cs to the 3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst was also beneficial for improving the activity of the surface-active oxygen species and then favoring the contact between soot and catalyst. According to previous reports [1,22], the alkali oxides could favor soot-catalyst contact due to the formation of low melting point compounds or eutectics with other catalyst components to improve the surface mobility of the active species. Fig. 9b showed that with the addition of Cs, the DC_{50} was increased from 0.61 to 0.83, which revealed that Cs was beneficial for improving the contact between soot and catalyst. As shown in Fig. 9a, the 3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst performed worse soot oxidation activity under loose contact in comparation with tight contact, which could be due to most active

oxygen species being depleted, yielding stable gas molecules before reaching the soot particles. With the addition of Cs, the T_{10} , T_{50} and T_{90} values were lowered by about 103, 163 and 195 °C, which was due to that the contact efficiency was improved; thus, more surface-active oxygen could take part in soot oxidation, under loose contact.

Based on the above discussions, Fig. 10 displays the functions of Cs on the catalyst. On one hand, the addition of Cs increased the surface oxygen defects, which was beneficial for the generation of surface-active oxygen. On the other hand, the addition of Cs could improve the contact efficiency, and thus favor more active species taking part in soot oxidation instead of yielding stable gas molecules, under loose contact. Therefore, the dual functions of Cs endowed the 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst with outstanding soot oxidation activity.

4. Conclusions

In this work, Cs was added to a 3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst using a facile impregnation method, which led to a sharp decrease of T₅₀ to 393 °C under H₂O/O₂/N₂ atmosphere, loose contact, and a high GHSV of 300,000 mL g⁻¹ h⁻¹. Characterization results indicated that Cs addition had dual effects on soot catalytic oxidation. The Cs dopant was not only beneficial for facilitating the generation of more surface oxygen defects and the activation of surface chemisorbed oxygen, but also greatly improved the mobility of the surface-active oxygen species and then favored the contact between soot and catalyst. Thus, the addition of Cs made the T₅₀ decreased by 163 °C. The obtained 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst also exhibited excellent H₂O and SO₂ tolerances, which is a very promising catalyst for the application in diesel soot combustion.

CRediT authorship contribution statement

Meng Wang: Investigation, Formal analysis, Writing - original draft, Writing - review & editing. Yan Zhang: Formal analysis, Data curation, Supervision, Writing - review & editing, Project administration. Yunbo Yu: Data curation, Writing - review & editing. Wenpo Shan: Formal analysis, Supervision, Writing - review & editing, Project administration, Funding acquisition. Hong He: Resources, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

The following files are available free of charge.

Summary of Soot conversion and CO₂ selectivity of 3 %Co/Ce_{0.5}Sn_{0.5}O₂ supported different alkali metals and different loading weights of Cs, CO₂ selectivity of the as-prepared samples, T₅₀ values of the 10 %Cs/3 %Co/Ce_{0.5}Sn_{0.5}O₂ catalyst in different reaction conditions, NO₂/(NO + NO₂) profiles, XRD results, Element mapping results from EDX, ICP results and Curve-Fitting results of Co-K EXAFS and Sn-K EXAFS.

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