Article

Preparation of Cordierite Monolith Catalysts with the Coating of K-Modified Spinel MnCo_2O_4 Oxide and Their Catalytic Performances for Soot Combustion

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Abstract: Diesel engines are important for heavy-duty vehicles. However, particulate matter (PM) released from diesel exhaust should be eliminated. Nowadays, catalytic diesel particulate filters (CDPF) are recognized as a promising technology. In this work, a series of monolith $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4$ catalysts were prepared by the simple citric acid method. The as-prepared catalysts displayed good catalytic performance for soot combustion and the $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ catalyst gave the best catalytic performance among all the prepared samples. The T_{10} and T_m of $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC catalyst for soot combustion are 310 and 439 °C, respectively. The physical and chemical properties of catalysts were characterized by means of SEM, XPS, H_2 -TPR, Raman and other techniques. The characterization results indicate that K substitution is favorable for the formation of oxygen vacancies, enhancing the mobility of active oxygen species, and improving the redox properties and so on. In-situ Raman results prove that the strength of Co-O bonds in the catalysts became weak during the reaction at high temperatures. In addition, SEM and ultrasonic test results show that the peeling rate of the coat-layer is less than 5%. The as-prepared catalysts can be taken as one kind of candidate catalyst for promising application in soot combustion because of its facile synthesis, low cost and high catalytic activity.

Keywords: cordierite monolith catalysts; MnCo_2O_4 spinel; K substitution; in-situ Raman; soot combustion

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1. Introduction

Diesel engines with excellent fuel efficiency have become the first choice for heavy-duty vehicles [1,2]. However, particulate matter (PM) released from diesel exhaust always threatens human health and environmental safety [3]. Because carbon is the main component of PM in diesel exhaust and its initiation temperature is higher than 450 °C, PM cannot be eliminated in the temperature range of diesel exhaust (150–450 °C) [4]. As the national emission standards become more stringent, it is necessary to develop catalytic purification technology to resolve the PM pollution. Nowadays, catalytic diesel particulate filters (CDPF) are considered a promising technology [5]. However, the design and preparation of high efficiency catalysts is still a difficult problem for the practical application of CDPF.

The catalytic combustion of PM is a solid–gas–solid heterogeneous catalytic reaction, and the diameter of PM is greater than 25 nm. Therefore, the catalytic performance of catalysts is influenced by two factors, including the redox property of catalysts and the contact efficiency between catalysts and PM. At present, the design and preparation of porous catalysts, especially three-dimensionally ordered microporous (3DOM) catalysts, contribute to significantly improving the contact between the soot and catalyst [6–10].

However, for CDPF, there are also two crucial aspects to improve the conditions of soot–catalyst contact in the filters [11,12]. The first one is the high dispersion and deep penetration of catalyst into the DPF walls by using suitable techniques; the second is how to avoid the cake layer by the accumulation of soot on the surface of DPF. To alleviate the contact problem, the design and preparation of high efficiency catalysts with the ability to activate oxygen at low temperatures is very important. In order to enhance the intrinsic activity and the ability to activate oxygen at low temperatures, a series of noble metals catalysts were also studied and they exhibit excellent catalytic performance for soot combustion, such as: Ag/Ce [13], Au–CoFe₂O₄ [14], Ag/Co–Ce [15], Pt/H-ZSM5 [16] and Ag/Al₂O₃ [17].

Solid solution with excellent oxidation performance is also a kind of catalyst for soot oxidation, such as perovskite (ABO₃) [18,19], spinel (AB₂O₄) [20–23] or mullite (AB₂O₅) [24,25]. In our previous work, a kind of novel catalyst, which combines the advantages of three-dimensional ordered macropores (3DOM) and noble metals, has been successfully synthesized and the as-prepared catalysts effectively reduce the ignition temperature of soot, such as 3DOM Au_{0.04}/Ce_{0.8}Zr_{0.2}O₂ [26], 3DOM Au_x/LaFeO₃ [27], 3DOM Pt@CeO_{2–x}/ZrO₂ [28]. In addition, previous researchers found that the contact efficiency could be improved when catalysts possess a low melting point or alkali metal components [29–31]. For example, K/La₂O₃, K/MgO, KNO₃/ZrO₂ catalysts have similar soot combustion temperatures under tight and loose contact conditions [32–35]. Moreover, the complex oxides of transition metal and alkali metals exhibit the ability for reduction of the loss of alkali elements due to the synergistic effect between transition metals and alkali metals [36,37].

At present, a variety of excellent powder catalysts have been successfully developed in the laboratory. However, it should not be neglected that conventional powder catalysts will sharply increase the back pressure of exhaust gas pipeline. Therefore, diesel particulate filter (DPF) or honeycomb ceramics (HC) with the ability to catalyze the oxidation of soot is very essential, that is also called monolith catalyst. For instance, 3DOM LaCoO₃/HC, LaKCoO₃/HC, Co₃O₄/OMS-2/HC and Ce_{0.6}Cu_{0.4}O₂/HC, these monolith catalysts displayed considerable performance for soot combustion [38–41]. Hernandez-Garrido prepared aluminum sols mixed with active components and studied the microscopic morphology of the slurry-coated honeycomb ceramics, revealing the interaction between them [42]. To make sure of the wide application of monolith catalyst, three factors for the preparation of monolith catalysts should be considered. The first is that the coating precursor liquid must have good fluidity, so that the honeycomb ceramics surface can be fully and evenly covered by the coating layer. The second is that inexpensive metals were used to prepare catalysts with good redox properties. The third is that honeycomb ceramics are used to ensure the smoothness of pipeline airflow to approximate the actual application situation.

Some researchers have studied the catalytic performance of alkali metals and spinel for soot combustion from the aspects of redox properties and intermediate products. However, the research on the effects between the structure and reactive oxygen species releasing, when the spinel A-site elements is substituted, especially the monolith spinel catalysts for soot oxidation are very few. Herein, a Co ion with good oxidizing ability is trivalent at the B position. The easily adjustable valence of Mn is beneficial to promoting the interaction between Mn and Co ions. In this work, MnCo₂O₄-HC spinel catalyst was synthesized and coated on honeycomb ceramics by the citric acid sol-solution method. To improve the catalytic performance of the as-prepared catalyst, the capacities for the adsorption and activation of oxygen of the MnCo₂O₄-HC catalyst were enhanced by introducing potassium, changing the unit cell structure of spinel and adjusting the valence of Mn and Co ions. At the same time, the catalyst coating can be more closely attached on the surface of honeycomb ceramics by citrate sol-solution, which is favorable for reducing the peeling rate of coating. In addition, the physical and chemical properties of catalysts were characterized successfully by SEM, XPS, H₂-TPR, Raman spectroscopy and other

techniques. The catalytic performances of the as-prepared monolith catalysts for soot combustion were also evaluated.

2. Results

2.1. Catalytic Performance of As-Prepared Monolith Catalysts for Soot Combustion

In order to explore the influence of K on the catalytic activity of MnCo_2O_4 -HC spinel, the catalytic performance of $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4$ -HC with different n values ($n = 0.1, 0.2, 0.3$) was evaluated and the results are shown in Figure 1. According to CO_2 concentration curves, the activities of catalysts sequentially increased in the following order, MnCo_2O_4 -HC < $\text{Mn}_{0.9}\text{K}_{0.1}\text{Co}_2\text{O}_4$ -HC < $\text{Mn}_{0.8}\text{K}_{0.2}\text{Co}_2\text{O}_4$ -HC < $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC. As shown in Table 1, when the n value is 0.3, the $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC catalyst has the lowest temperature of T_{10} , T_{50} and T_{90} among the as-prepared catalysts and the value are 310, 415 and 504 °C, respectively. Meantime, the selectivity of CO_2 for $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC catalyst is also higher than 99%. The above results indicate that potassium exhibits an obviously positive influence on catalytic performance for soot combustion. Compared with the case without a catalyst, the catalytic combustion temperature of soot on $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC is significantly reduced. Due to its simple preparation method, it is considered one of the candidate catalysts that has the potential for application.

Figure 1. The curves of CO_2 concentration and selectivity to CO_2 (a) and soot conversion curves (b) over as-prepared monolith catalysts.

Table 1. Catalytic performance, stability and tolerance of sulfur dioxide and water for soot combustion of as-prepared monolith catalysts.

Title 1	$T_{10}/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$	$T_m/^{\circ}\text{C}$	$S_{\text{CO}_2}^m/\%$
Soot (without catalyst)	451	562	607	588	38.9
MnCo_2O_4 -HC	336	451	538	489	98.2
$\text{Mn}_{0.9}\text{K}_{0.1}\text{Co}_2\text{O}_4$ -HC	320	428	511	436	97.3
$\text{Mn}_{0.8}\text{K}_{0.2}\text{Co}_2\text{O}_4$ -HC	313	424	508	442	99.4
$\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC	310	415	504	439	99.1
$\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC-cycle 2	311	415	503	429	98.9
$\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC-cycle 3	318	421	506	469	99.2
$\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC-cycle 4	311	423	516	453	98.2
$\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC-cycle 5	327	431	513	445	98.5
$\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC (SO_2)	312	414	496	438	99.3
$\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC (H_2O)	370	480	573	486	98.9

Reaction conditions: heating rate was 2 °C/min. The reaction atmosphere contained NO (2000 ppm), O_2 (10%) and argon gas as equilibrium gas, and the total flow rate was 50 ml/min.

2.2. Resistance versus Sulfur and Water and Stability Test on Monolith Catalysts

As one kind of monolith catalyst for practical application, the properties of stability, sulfur and water resistance are very important. As shown in Figure 2a, the similar CO₂ concentration curve indicated that the catalytic activity of the Mn_{0.7}K_{0.3}Co₂O₄-HC catalyst remained stable after five-cycle times. From Table 1, it can be seen that the catalytic activity of Mn_{0.7}K_{0.3}Co₂O₄-HC has remained stable until four-cycle times. The temperature of T₁₀ for cycle 3 is 318 °C and slightly higher than the T₁₀ of fresh Mn_{0.7}K_{0.3}Co₂O₄-HC (310 °C), while the T₁₀ for the cycle 4 is decreased to 311 °C again. The T₅₀ and T₉₀ for cycle 3 and cycle 4 are located at 421, 423 °C and 506, 516 °C respectively, and the changing of temperature is also not obvious. However, T₁₀, T₅₀ and T₉₀ of cycle 5 are located at 327, 431 and 513 °C, respectively, and the offset degree of T₁₀ and T₅₀ to higher temperature 15 °C than that of fresh Mn_{0.7}K_{0.3}Co₂O₄-HC. Figure 2b shows the catalytic activities of Mn_{0.7}K_{0.3}Co₂O₄-HC catalyst after pretreatment with SO₂ and water vapor. After treatment for 6 h by SO₂, the CO₂ concentration curve was sharper than that of the fresh catalyst and the peak temperature (T_m) was shifted from 423 °C to 439 °C. However, the values of T₁₀, T₅₀ and T₉₀ stayed the same as that of the fresh catalyst in Figure S1b. It perhaps means that SO₂ exhibits a weak influence on the catalytic activity of the Mn_{0.7}K_{0.3}Co₂O₄-HC catalyst. When the catalyst was treated with water, the catalytic activity was sharply decreased, and the values of T₁₀, T₅₀ and T₉₀ were shifted to the high temperature range of 370, 481 and 585 °C, respectively. The possible reason is that water vapor forms a competitive adsorption with NO on the surface of the catalyst, which hinders the path of NO participation in the reaction [43].

Figure 2. The CO₂ concentration curves of cycle test (a) and resistance versus sulfur and water (b) over Mn_{0.7}K_{0.3}Co₂O₄-HC monolith catalyst.

2.3. Morphologies of As-Prepared Monolith Catalysts

The photographs of the as-prepared catalysts are shown in Figure 3. From Figure 3a, it can be seen that the blank honeycomb ceramics monolith is white, and the channels are evenly and orderly distributed. When the Mn_{1-n}K_nCo₂O₄-HC active components were coated on the surface of blank honeycomb ceramics, the color of Mn_{1-n}K_nCo₂O₄-HC catalysts changed from white to black and was equally distributed (Figure 3b–e). Meanwhile, the channels were also well maintained. The above phenomena indicate that the Mn_{1-n}K_nCo₂O₄ active components are evenly coated on the honeycomb ceramics.

Figure 3. The photographs of as-prepared monolith catalysts. Blank honeycomb ceramics monolith (a), $\text{MnCo}_2\text{O}_4\text{-HC}$ (b), $\text{Mn}_{0.9}\text{K}_{0.1}\text{Co}_2\text{O}_4\text{-HC}$ (c), $\text{Mn}_{0.8}\text{K}_{0.2}\text{Co}_2\text{O}_4\text{-HC}$ (d), $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ (e).

To more deeply investigate the morphologies of $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4\text{-HC}$ catalysts, the representative $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ catalyst was characterized by SEM and the results are shown in the Figure 4. The views for the plane surface of blank honeycomb ceramics are shown in Figure 4a,b. The surface of the blank honeycomb ceramics is very rough. There are many irregular macropores on the surface under high resolution. Figure 4c,d shows that the surface of honeycomb ceramics was covered by the $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-P}$ active component based on the difference of plane and section. The image in Figure 4d indicates that the catalyst coat-layer exhibits lamellar appearance on the surface of the honeycomb ceramics with a large number of irregular macropores. Compared with the blank honeycomb ceramics, Figure 4d exhibits that the interface between the catalyst coat-layer and honeycomb ceramics was very clear. The thickness of the coating is $25.7\ \mu\text{m}$. Additionally, the adhesion stability of the $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-P}$ active component on the surface of the honeycomb ceramics was also tested with the ultrasonic vibration test and the result is shown in Figure 4e. Based on the previously reported calculation method, the shedding rate of the $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ catalyst is lower than 3.5%, indicating that the $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-P}$ active component can be well coated on the honeycomb ceramics [39]. $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ displayed good cycle stability and adhesion, which meant that the catalyst possessed a longer lifetime.

2.4. EDS Mapping and X-ray Fluorescence of As-Prepared Monolith Catalysts

To obtain the distribution and content of elements for the prepared monolith catalysts, EDS mapping and X-Ray Fluorescence were carried out and the results are shown in Figure 5 and Table 2. The elemental mapping of Mg, Al, Si and active components on the ceramics and monolith catalysts are displayed in Figure 5. Mg, Al and Si are the main elements in ceramics and are distributed evenly. The elements of Mn and Co in MnCo_2O_4 have good dispersion on the surface of $\text{MnCo}_2\text{O}_4\text{-HC}$. For the $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ catalyst, there is no obvious aggregation of K, indicating that K is homogeneously doped into the $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ spinel.

Figure 4. SEM images of blank honeycomb ceramics monolith (a,b), Mn_{0.7}K_{0.3}Co₂O₄-HC (c,d) and ultrasonic vibration test (e).

Figure 5. EDS result of elemental distribution on monolith catalysts and blank ceramics.

Table 2. XRF results of oxide content on monolith catalysts and blank ceramics.

Element	Blank Ceramics (wt %)	MnCo ₂ O ₄ -HC (wt %)	Mn _{0.7} K _{0.3} Co ₂ O ₄ -HC (wt %)
MnO	–	0.64	0.44
Co ₃ O ₄	–	0.96	0.91
K ₂ O	0.21	0.23	0.42
SiO ₂	45.71	48.23	45.71
Al ₂ O ₃	35.24	34.79	35.24
MgO	16.82	13.44	16.83
other	2.02	1.71	0.45

As shown in Table 2, the XRF results indicate that the elements of Si, Al, and Mg are the main components for the blank ceramics, and their contents are 45.71%, 35.24% and 16.82%, respectively. Meanwhile, the blank ceramics also have little K element (0.21%) and others (2.02%). Because of the low loading amount of MnCo₂O₄, Si, Al, Mg and O elements of ceramics are still the main components in the MnCo₂O₄-HC catalyst. Due to a small amount of K in blank ceramics, the ratio of Mn to K is about 2.7 when the content of K in blank ceramics is deducted. The result is close to the theoretical stoichiometric ratio of Mn_{0.7}K_{0.3}Co₂O₄.

2.5. XRD Patterns of As-Prepared Monolith Catalysts

To deeply study the crystal structure of as-prepared catalysts, the monolith and corresponding powder Mn_{1–n}K_nCo₂O₄-HC catalysts were evaluated by the XRD technique and the results are shown in Figure 6. Figure 6a shows that the blank honeycomb ceramics, which are constituted by alumina, silica and magnesia, has very high crystallinity and very strong diffraction peaks. When Mn_{0.7}K_{0.3}Co₂O₄-P active components are coated on the surface of honeycomb ceramics, a weak characteristic peak, which belongs to the Mn_{1–n}K_nCo₂O₄-P spinel and is located at $2\theta = 37^\circ$, can be observed. However, the characteristic peak of Mn_{1–n}K_nCo₂O₄-P in Figure 6a is so week that the crystal structure of the Mn_{1–n}K_nCo₂O₄-P spinel cannot be well identified. To more clearly explain the characteristic peaks, the XRD diffraction peaks of Mn_{1–n}K_nCo₂O₄-P spinel catalysts were also characterized (Figure 6b). The characteristic peaks of the samples at $2\theta = 18.8^\circ$, 30.8° , 36.5° , 44.3° , 58.9° and 64.9° correspond to the crystal planes of (111), (220), (311), (400), (511), (440) for the spinel [44]. Figure 6b also indicates that the substitution of K metal can enhance the crystallinity of sample. As shown in the insert of Figure 6b, it can be seen that the diffraction peaks are shifted to high angle with increasing substitution amount of K in the 2θ range of $30\text{--}40^\circ$. This phenomenon indicates that K ions are successfully entered into the interior of the MnCo₂O₄-P spinel and cause lattice distortion [45].

Figure 6. XRD of Mn_{1–n}K_nCo₂O₄-HC monolith catalysts (a) and the corresponding powder catalysts (b).

2.6. Raman Spectra of As-Prepared Monolith Catalysts

Figure 7a,b shows the Raman spectra of $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4\text{-HC}$ catalysts with 532 nm and 325 nm laser wavelengths, respectively. As shown in Figure 7a, the catalysts exhibit obvious Raman vibration peaks in the two regions of $434\text{--}543\text{ cm}^{-1}$ and $625\text{--}709\text{ cm}^{-1}$. The peaks at low wavenumber are related to the spinel E_g mode, and the peaks at high wavenumber are belonged to the overlap peaks of the two vibration modes of F_{2g} and A_{1g} [46]. The Raman vibration peaks show significant shift under 532 nm laser wavelength when Mn ion is substituted by K in $\text{MnCo}_2\text{O}_4\text{-HC}$. The A_{1g} vibration peak is shifted from 665 cm^{-1} to 673 cm^{-1} for $\text{Mn}_{0.9}\text{K}_{0.1}\text{Co}_2\text{O}_4\text{-HC}$ catalyst. While the corresponding vibration peak of $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ is continually shifted to 679 cm^{-1} . The introduction of potassium element into the spinel structure makes $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$'s vibration peak intensity higher than $\text{MnCo}_2\text{O}_4\text{-HC}$ but lower than Co_3O_4 at the octahedral position of 679 cm^{-1} , indicating that both the Co^{3+} cation-anion bond length and the coordination environment of the octahedral position have changed in the spinel lattice [47]. However, there is no corresponding vibration peak of manganese species in the Raman spectra [48].

Figure 7. Raman spectra of as-prepared monolith catalysts under different laser wavelength of 532 nm (a) and 325 nm (b).

Figure S2a shows the Raman spectrum of Co_3O_4 under 532 nm laser wavelength. There were five vibration peaks appeared in the detection range, which located at 191, 469, 512, 607 and 673 cm^{-1} . These vibration peaks correspond to different vibration modes of Co_3O_4 , such as, the vibration peak at 191 cm^{-1} belonging to the F_{2g}^1 vibration mode of the cobalt tetrahedron (CoO_4). The vibration peaks at 469 and 512 cm^{-1} are attributed to the vibrations of E_g and F_{2g}^2 modes, respectively. The weak peak at 607 cm^{-1} is related to the F_{2g}^2 symmetrical vibration mode. The strong vibration peak at 673 cm^{-1} ascribed to A_{1g} symmetrical vibration mode, which typically correlated with the octahedral point (CoO_6) in the cobalt oxide spinel structure [49]. Different with cobalt oxide, manganese oxide only shows three Raman vibration peaks under laser wavelength of 532 nm. Raman band at 202 cm^{-1} can be attributed to external vibration, originating from the translational motion of MnO_6 octahedron. The weak peak at 305 cm^{-1} may be related to the local crystal defect. The peak at 630 cm^{-1} can be assigned to symmetric stretch of Mn-O, which is perpendicular to the MnO_6 octahedral [50].

The Raman spectra under 325 nm of $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4\text{-HC}$ catalysts are also provided in Figure 7b and Figure S2b,d. As shown in Figure S2b, the cobalt oxide calcined under the same conditions has five vibration peaks at 184, 468, 497, 606 and 661 cm^{-1} , which belong to the F_{2g}^1 vibration mode, E_g , F_{2g}^2 , F_{2g}^2 symmetrical vibration mode, and A_{1g} symmetrical vibration mode of the surface cobalt species, respectively. Generally, manganese oxide is mainly composed of MnO_2 and Mn_2O_3 . MnO_2 exhibits Raman vibration peaks at 512, 645 and 739 cm^{-1} , while Mn_2O_3 has Raman peaks at 302 and 690 cm^{-1} [51]. The

crystal structure of metal formed during calcination and intrinsic electronic properties can significantly affect the Raman signal [52]. The curve of pure manganese oxide displays weak vibration peaks located at 501, 635 and 701 cm^{-1} in Figure S2d [53]. As shown in Figure 7b, the Raman peaks at 463(468) and 497 cm^{-1} can be recognized as the E_g and F_{2g}^2 vibration modes and 606 cm^{-1} is the F_{2g}^2 symmetric vibration of Co-O bands. Compared with pure cobalt oxide and manganese oxide, no detection of vibration peak of Mn-O bands was observed and the vibration peaks at 184 and 661 cm^{-1} for Co-O bands disappeared in the Raman spectra of $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4$ -HC catalysts.

2.7. Soot-TPR

To deeply investigate the type of oxygen species in the $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4$ -P catalysts, soot-TPR for as-prepared powder catalysts were carried out and the results are shown in Figure 8a. During the soot-TPR process no gaseous oxygen was present in the reactant gas atmosphere. The oxygen species reacted with soot comes from the catalyst, including the adsorbed oxygen and lattice oxygen from the catalyst. The weak peak of CO_2 at 200–300 °C is corresponded to the physical adsorption oxygen on the catalyst surface, namely $\alpha\text{-O}_{\text{ads}}$ (superoxide, O_2^-). The amount of such oxygen species is little; as a result, the amount of CO_2 produced is also very little. The peak in the range of 490–670 °C for MnCo_2O_4 -P is corresponded to the chemical adsorption state oxygen species $\beta\text{-O}_{\text{ads}}$ (per-oxygen, O_2^{2-}), namely superoxide or peroxide. The peaks are the range of 379–670 °C for $\text{Mn}_{0.9}\text{K}_{0.1}\text{Co}_2\text{O}_4$ -P are also attributed to the chemisorbed oxygen on the catalyst surface. From the Figure 8, it can be concluded that the temperature range of chemisorbed oxygen peak is shifted to low temperature with increasing of K substitution. This phenomenon is well agreed with the rule of catalytic activity. In addition, the peak at 700–800 °C corresponded to the surface lattice oxygen O_{lat} of MnCo_2O_4 -P [54,55]. Due to the K substitution, $\text{Mn}_{0.8}\text{K}_{0.2}\text{Co}_2\text{O}_4$ -P and $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -P exhibit the ability to release more active oxygen species at relatively low temperatures. Deconvolution of soot-TPR curves obtained by Gaussian Fitting are shown in the Figure 8b, based on the integrating results for peaks, the integral areas of $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4$ -P catalysts are about twice as long as that of MnCo_2O_4 -P. The corresponding amounts of reactive oxygen species $[\text{O}^*]$, which are involved in the catalytic oxidation of soot, are listed in Table 3. The results indicate that the K substitution in the MnCo_2O_4 -P spinel has changed the surface structure of catalysts and increased the number of surface oxygen species. These surface oxygen species are mainly derived from the bulk phase lattice oxygen of the catalyst subsurface. In addition, the increasing content of K substitution also enhances the mobility of these oxygen species.

Figure 8. Soot-TPR curves (a) and peak fitting (b) of as-prepared catalysts: MnCo_2O_4 -P (1), $\text{Mn}_{0.9}\text{K}_{0.1}\text{Co}_2\text{O}_4$ -P (2), $\text{Mn}_{0.8}\text{K}_{0.2}\text{Co}_2\text{O}_4$ -P (3), $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -P (4).

Table 3. The temperature of each peak in the Soot-TPR and H₂-TPR curves over as-prepared monolith catalysts.

Catalyst	Soot-TPR ^a				H ₂ -TPR ^b			
	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)	R ₁ (mol × 10 ^{−5})	Peak 1 (°C)	Peak 2 (°C)	Peak 3 (°C)	R ₂ (mmol/g)
MnCo ₂ O ₄	533	687	-	8.81	350	509	-	0.165
Mn _{0.9} K _{0.1} Co ₂ O ₄	426	594	734	14.7	350	428	491	0.204
Mn _{0.8} K _{0.2} Co ₂ O ₄	473	-	-	16.9	240	331	483	0.180
Mn _{0.7} K _{0.3} Co ₂ O ₄	407	435	-	15.1	215	318	401	0.214

R₁ is the amount of active [O*] consumed by Mn_{1−n}K_nCo₂O₄-P catalysts to generate CO₂ in the soot-TPR reaction; R₂ is the amount of hydrogen consumed by Mn_{1−n}K_nCo₂O₄-HC catalysts in H₂-TPR reaction; Soot-TPR ^a: the reaction was carried out on a powder catalyst; H₂-TPR ^b: The reaction was carried out on fragments of the monolithic catalyst.

2.8. H₂-TPR of As-Prepared Monolith Catalysts

Figure 9 shows the H₂-TPR results of as-prepared catalysts. The MnCo₂O₄-HC catalyst exhibits two distinct reduction peaks. The reduction peak in the temperature range of 250–400 °C is attributed to the reduction of the Mn and Co metal cations to the intermediate state. The high temperature of 400–650 °C belongs to the intermediate state to the low valence state [56]. Because the reduction of K⁺ ions cannot be achieved at 800 °C, the reduction peaks of Mn_{0.9}K_{0.1}Co₂O₄-HC are still attributed to the reduction of Mn and Co species [57]. However, compared with the MnCo₂O₄-HC catalyst, the intensity of the reduction peak at 350 °C for k-substituted samples has a significant improvement and the reduction peak at 491 °C obviously shifts to a low temperature. In addition, the Mn_{0.9}K_{0.1}Co₂O₄-HC catalyst has a new weak reduction peak at 428 °C. The changes indicate that the surface and internal oxygen species of the Mn_{0.9}K_{0.1}Co₂O₄-HC catalyst were activated by K substitution, which is beneficial to soot combustion. When the amount of the K substitution was increased, Mn_{0.8}K_{0.2}Co₂O₄-HC shows a weak reduction peak at 200–300 °C, which is belonged to the weak adsorption of oxygen on the catalyst surface [58]. Compared with Mn_{0.9}K_{0.1}Co₂O₄-HC, the temperatures for reduction peaks of Mn_{0.8}K_{0.2}Co₂O₄-HC are shifted to low temperatures of 331 and 483 °C. For the Mn_{0.7}K_{0.3}Co₂O₄-HC catalyst, the reduction peaks are obviously different than with other catalysts. It has three reduction peaks, which are located at 215, 318 and 401 °C, respectively. Compared with other catalysts, the lowest reduction temperature indicates that the metal cations in Mn_{0.7}K_{0.3}Co₂O₄-HC can be easily reduced demonstrating that oxygen species were easy to move and participate in the soot combustion. To deeply illustrate the results of H₂-TPR, the H₂ consumption amounts of as-prepared catalysts were calculated by the integral peak area. As shown in Table 3, the total H₂ consumption amounts for as-prepared catalysts are similar to each other. However, due to K substitution, the reduction temperature ranges and H₂ consumption for each reduction peak are different from each other.

Figure 9. H₂-TPR curves of as-prepared catalysts: MnCo₂O₄-HC (a), Mn_{0.9}K_{0.1}Co₂O₄-HC (b), Mn_{0.8}K_{0.2}Co₂O₄-HC (c), Mn_{0.7}K_{0.3}Co₂O₄-HC (d).

2.9. XPS Results of As-Prepared Monolith Catalysts

To more clearly study and obtain high accuracy data for the composition and valence state of each element, the XPS of $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4\text{-HC}$ were characterized and the results are exhibited in Figure 10. As shown in Figure 10a, the survey spectra clearly exhibit the difference in surface elements among $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4\text{-HC}$. The potassium element doped inside the spinel lattice shows a distinct XPS peak, and the C, O, Mn, and Co elements contained on the catalyst's surface also show clear peaks in the spectrum.

Figure 10. XPS Spectra of $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4\text{-HC}$ catalysts: surface wide spectrum (a), Co 2p (b), Mn 2p (c) and O 1s (d).

Figure 10b exhibits the results of Co 2p XPS. There are two main peaks located at 780.0 and 795.1 eV, respectively, which can be assigned to Co $2p_{3/2}$ and Co $2p_{1/2}$ and the electron spin splitting energy is 15.2 eV [59]. Meanwhile, the satellite peak located at 784–792 eV also can be observed. Generally speaking, $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4$ spinel oxides contain two valence states of Co^{3+} and Co^{2+} , and the binding energies of Co $2p_{3/2}$ and Co $2p_{1/2}$ in mixed valence states are in the range of 779.5–780.3 eV and 795.0–795.5 eV, respectively. Because the binding energy difference defining the spin-orbit splitting of Co $2p_{3/2}$ and Co $2p_{1/2}$ is 15.2 eV, Co 2p can be divided into two sets of doublet peaks by deconvolution. The peaks located at 780.1 and 795.2 eV belong to Co^{3+} , while the peaks located at 781.6 and 796.2 eV belong to Co^{2+} , respectively.

Figure 10c shows the XPS spectra of Mn 2p. It can be seen that Mn $2p_{3/2}$ and Mn $2p_{1/2}$ are located in the two intervals of 638–647 eV and 650–659 eV, respectively. According to the previous literature and standard oxides, the binding energy difference between the two spin peaks is fixed at 11.3 eV [60]. The valence states of Mn in spinel are mainly divalent and trivalent [60–62]. The binding energies of the two groups of sub-peaks are 642.0, 653.3 eV and 643.8, 655.1 eV, which are attributed to Mn^{2+} and Mn^{3+} , respectively. Their ratios are listed in Table 4. The proportion of Mn^{2+} rose slightly with the increasing of the amount of potassium substitution.

Table 4. XPS results for transition metal valence and surface oxygen species of as-prepared monolith catalysts.

Catalysts	Mn Species			Co Species			O Species		K Species
	Atomic ^a	Mn ²⁺ ^b	Mn ³⁺ ^b	Atomic ^a	Co ²⁺ ^c	Co ³⁺ ^c	O ₂ ⁻ + O ₂ ²⁻ ^d	O ₂ ²⁻ ^d	Atomic ^a
MnCo ₂ O ₄ -HC	15.3%	62.2%	37.8%	15.9%	48.5 %	51.5%	17.1%	82.9%	
Mn _{0.9} K _{0.1} Co ₂ O ₄ -HC	14.3%	62.7%	37.3%	15.2%	41.9%	58.1%	20.6%	79.4%	2.2%
Mn _{0.8} K _{0.2} Co ₂ O ₄ -HC	17.3%	63.7%	36.3%	17.0%	34.6%	65.4%	21.3%	78.7%	3.1 %
Mn _{0.7} K _{0.3} Co ₂ O ₄ -HC	14.7%	64.1%	35.9%	15.4%	30.9%	69.1%	25.8%	74.2%	4.3%

^a: The data of atomic (%) came from XPS Survey; ^b: The sub-peaks were deconvoluted by XPS peak with deviation value less than 6 and the ratio was calculated according to formula $\frac{Mn^{n+}}{Mn^{2+}+Mn^{3+}}$; ^c: The sub-peaks were deconvoluted by XPS peak with deviation value less than 6 and the ratio was calculated according to formula $\frac{Co^{n+}}{Co^{2+}+Co^{3+}}$; ^d: The sub-peaks were deconvoluted by XPS peak with deviation value less than 6 and the ratio was calculated according to formula $\frac{O_2^-+O_2^{2-}}{O_2^-+O_2^{2-}+O^{2-}}$.

The XPS spectra of O1s are shown in Figure 10d. The O1s XPS peaks centered at 530, 531.9 and 533.1 eV can be assigned to lattice oxygen (O²⁻), adsorbed oxygen species (O₂²⁻, O₂⁻) and hydroxyl, and surface adsorbed water of catalysts, respectively [62]. The ratio of adsorbed oxygen species in the surface oxygen species have an important impact on catalytic performance. The amount of oxygen species adsorbed by the oxygen vacancies surface is fixed under static conditions. Therefore, analyzing the ratio of adsorbed oxygen can infer the state of oxygen vacancies. The ratio of adsorbed oxygen is listed in Table 4. As the amount of potassium substituted for manganese increased, the proportion of adsorbed oxygen species also showed an upward trend, and this trend was also consistent with the gradual increase in catalytic performance, which meant that more oxygen vacancies were generated on the surface after potassium substitution.

Table 4 listed the content of each element on the surface of Mn_{1-n}K_nCo₂O₄-HC catalysts. With the increasing of substitution amount of K, the K species content on the surface of the catalysts also gradually increased. Based on the data of atomic ratios in Table 4, the ratio of manganese to cobalt species on the surface is close to 1:1, indicating that manganese species were more easily enriched on the catalyst surface. Meanwhile, the proportion of Mn²⁺ species is slightly raised. Interestingly, the content of Co³⁺ species rapidly increased correspondingly. The results of Table 4 illustrate that the spinel structure of as-prepared catalysts is not changed when K is partially replaced by manganese. However, the K substitution indeed causes lattice distortion and imbalance of the charge of the spinel oxide. To maintain the overall charge balance of the catalyst, there may occur two cases, including loss of electrons to form Mn^{2+δ} or Co³⁺ increases the valence states of cations at A or B sites, reducing the oxygen coordination number in the spinel lattice and forming Mn_{1-n}K_nCo₂O_{4-δ}. In this work, the K substitution can easily result in the transformation of Co²⁺ to Co³⁺ and reduce the amount of coordinated oxygen and form oxygen vacancies. In addition, the H₂-TPR results also prove that the distorted crystal lattices can create more oxygen vacancies on the catalyst's surface and the ability for the adsorption of oxygen species is also improved. The effect of oxygen deficiency caused by potassium substitution and the change in the valence of metal cations on activity will be further described in following Section 3.

2.10. In-Situ Raman Results of As-Prepared Monolith Catalysts

The in-situ Raman results mainly reflect the changes of the metal-oxygen bonds between the surface and sub-surface layers in different reaction environments during the reaction, which should be mainly attributed to the change of coordination oxygen in the catalyst. Therefore, the in-situ Raman experiments for TPO of the mixture of Mn_{0.7}K_{0.3}Co₂O₄-HC catalysts and soot particles under a laser wavelength of 532 nm were carried out. Figure 11 exhibits the Raman spectra for a mixture of Mn_{0.7}K_{0.3}Co₂O₄-HC catalyst and soot under a 532 nm wavelength laser. Compared with the Raman spectrum of pure soot (Figure S3), the Raman peaks for soot particles do not overlap with the peaks of in-situ Raman for Mn_{0.7}K_{0.3}Co₂O₄-HC catalyst. Therefore, the vibrational peak of a cobalt octahedron A_{1g} at

697 cm^{-1} is still obvious at room temperature. With the increasing temperature, the A_{1g} vibration peak shifted to low wavenumber and peak intensity decreased. A_{1g} vibration peak shifted to 667 cm^{-1} when the temperature was increased to $450\text{ }^{\circ}\text{C}$ and the peak intensity of the vibration peak reached the lowest value at $350\text{ }^{\circ}\text{C}$. At high temperature, the shift of the main peak to the lower wave number and the widening of the spectral peak are generally considered to be the increase of the lower lattice disorder, while the intensity decrease is attributed to the degradation of CoO_6 octahedron [63].

Figure 11. In-situ Raman spectra of $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ catalyst under laser wavelength of 532 nm . Reaction conditions: heating rate was $2\text{ }^{\circ}\text{C}/\text{min}$. The reaction atmosphere contained NO (2000 ppm), O_2 (10%) and He as equilibrium gas, and the total flow rate was $50\text{ mL}/\text{min}$. Monolith catalyst maintains loose contact with soot.

Compared with visible laser Raman spectra (532 nm), ultraviolet Raman spectra (UV) laser (325 nm) can reflect better surface sensitivity [64]. Therefore, the in-situ Raman for mixture of $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ catalyst and soot particles under the soot-TPO reaction atmosphere were tested and the results are shown in Figure 12. From the spectra, it can be seen that soot particles also exhibit obvious Raman peaks and its peak positions are located at about 1590 cm^{-1} . With the increasing of reaction temperature, the Raman peak intensity for soot gradually decreased and the peaks basically disappeared when the temperature rose to $400\text{ }^{\circ}\text{C}$. It is worth noting that the intensity of the F_{2g}^2 vibration mode for Co-O at 606 cm^{-1} gradually decreased with increasing temperature. This may be because that the cobalt oxide species on the outer surface participated in the catalytic reaction and was partially reduced by the soot, but it was oxidized by the reaction atmosphere after the soot was reacted, which indicated that the absence of alkali metal potassium made the cobalt-oxygen bond in $\text{MnCo}_2\text{O}_4\text{-HC}$ difficult to participate in the oxidation reaction of soot.

Figure 12. In-situ Raman spectra of $\text{MnCo}_2\text{O}_4\text{-HC}$ (a) and $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ (b) catalysts under laser wavelength of 325 nm. Reaction conditions: heating rate was $2^\circ\text{C}/\text{min}$. The reaction atmosphere contained NO (2000 ppm), O_2 (10%) and He as equilibrium gas, and the total flow rate was 50 mL/min. Monolith catalyst maintains loose contact with soot.

3. Discussion

3.1. Influencing Factors of Structure for Monolith Catalytic Activity

Catalytic combustion of soot particles in the diesel vehicles exhausts gas occurs on the surface of monolith catalyst, which is a typical solid–gas–solid multi-phase catalytic reaction. The oxidation property and ability to adsorb and activate the gas phase reactants determine the activity of catalysts. Based on the characterization results, K-substitution has a significant impact on the structure, coordination bond and oxygen vacancy of the $\text{MnCo}_2\text{O}_4\text{-HC}$ catalysts. It is known that the radius of K ion is 0.133 nm, which is much larger than that of Mn^{2+} ($r = 0.080$ nm) and Co^{3+} ($r = 0.063$ nm). The diffraction peaks of $\text{MnCo}_2\text{O}_4\text{-HC}$ in the XRD shifted to high angle with the increasing of K content, and the peak intensity also increased. The Raman spectra 532 and 325 nm for $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ and $\text{MnCo}_2\text{O}_4\text{-HC}$ (Figure 7) indicate that the coordinated oxygen environment of $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ is significantly different from that of $\text{MnCo}_2\text{O}_4\text{-HC}$. The Co–O bond of CoO_6 in the bulk phase is affected by K^+ substitution and the Raman band moves to high wavenumber. The above results indicate that K has successfully entered the unit cell structure of MnCo_2O_4 spinel. Due to this influence, the Co–O bonds in CoO_6 were weakened, and more structural defects and lattice distortions were generated in the bulk phase of catalyst [46]. That is, $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4\text{-HC}$ will generate more oxygen vacancies than $\text{MnCo}_2\text{O}_4\text{-HC}$, indicates that more adsorbed oxygen species can be generated on $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ surface. Moreover, some amounts of Co^{2+} transformed into Co^{3+} . The relationship of these factors has been displayed in Figure 13.

Figure 13. The relationship between in-situ Raman vibration peak intensity and ratio of O_2^- and O_2^{2-} for as-prepared catalysts under laser wavelength of 532 nm.

The in-situ Raman spectra under 532 and 325 nm clearly show the different changes in the bulk and surface phases of $Mn_{1-n}K_nCo_2O_4-HC$ catalyst under the reaction conditions. On the one hand, the in-situ Raman under 532 nm is sensitive to bulk (subsurface layer) [60]. On the other hand, the catalytic oxidation of soot is closely related to the oxygen species in the catalysts, which can affect the lattice structure of catalysts when they migrate in different environments. The structure changing regular of $MnCo_2O_4-HC$, $Mn_{0.9}K_{0.1}Co_2O_4-HC$ and $Mn_{0.7}K_{0.3}Co_2O_4-HC$ under different atmospheres (NO, NO+O₂ and O₂) were studied and the results are shown in Figure S4. It can be seen that Raman peak of CoO_6 at 679 cm^{-1} shifts to low wavenumber and its intensity decreases, which indicates that the adsorption and activation of NO and O₂ in the gas phase is related to the symmetric stretching vibration of CoO_6 , and $O-Co^{3+}-O$ is the main active site. Figure S4 also exhibits that the peaks at 679 cm^{-1} of $MnCo_2O_4-HC$ and $Mn_{0.9}K_{0.1}Co_2O_4-HC$ shift to low wavenumbers more obviously than that of $Mn_{0.7}K_{0.3}Co_2O_4-HC$, which means that the A_{1g} vibrational mode of the Co-O bonds was changed in the $MnCo_2O_4-HC$ and $Mn_{0.9}K_{0.1}Co_2O_4-HC$ catalysts. When K is enriched on the surface, this negative impact can be effectively alleviated. It may speculate that the presence of K is beneficial to maintaining the kind of $O-Co^{3+}-O$ bonds in CoO_6 , and promotes the activation of oxygen species during the process of soot combustion [65]. From the in-situ Raman spectra of Figure S4, the vibration peak intensity ratio of (CoO_6) at 25 °C and 350 °C, which can be abbreviated as $I^{350/25}$, changes regularly with the increase of K content. Based on the results above, it can be concluded that the regular is related to the proportion of reactive oxygen species. The results are shown in Figure 13. As the K content increased, $I^{350/25}$ gradually decreased while the content of reactive oxygen species gradually increased over the monolith catalysts.

The symmetrical vibration peak of catalyst $Mn_{0.7}K_{0.3}Co_2O_4-HC$ at 606 cm^{-1} gradually decreases during the reaction in the 325 Raman result, while the peak for $MnCo_2O_4-HC$ has almost no change, as shown in Figure 12, which further illustrates the positive effect of surface potassium in promoting soot combustion.

3.2. The Influence of K Substitution on Monolith Catalytic Performance and Physicochemical Properties

The physicochemical properties and oxygen species are important for the enhancement of catalytic performance. To more deeply study the nature of high activity, the TPR temperature, active oxygen, H₂ consumption, K content and catalytic performance for as-prepared monolith catalysts are summarized in Figures 14 and 15. As shown in the Figure 14, it can be obtained that the peak temperature of H₂-TPR over monolith catalysts decreases with increasing K content. Similarly, the peak temperature of soot-TPR also has the same tendency (Figure 15). The temperatures for T₁₀ and T₅₀ of as-prepared monolith

catalysts are decreased with increasing K content, which means the catalytic activity is enhanced.

Figure 14. The relationships among catalytic performance, K content, peak temperature of H₂-TPR and active oxygen in as-prepared monolith catalysts.

Figure 15. The relationships among catalytic performance, K content, peak temperature of soot-TPR and active oxygen in as-prepared monolith catalysts.

Based on the XPS results for Co³⁺ content in Table 4, because of the K substitution, the charge imbalance caused by the low charge of K can promote the production of more Co³⁺ and improve the oxidation ability of catalysts. The mobility of oxygen species in the lattice increased and the formation of active oxygen species easily occurred. The reduction peaks shifted to low temperature in soot-TPR and H₂-TPR verifying this viewpoint. From Figures 14 and 15 and Table S1, it can be observed that the amounts of active oxygen for as-prepared monolith catalysts obtained by soot-TPR follow the order: MnCo₂O₄-HC < Mn_{0.9}K_{0.1}Co₂O₄-HC ≈ Mn_{0.8}K_{0.2}Co₂O₄-HC ≈ Mn_{0.7}K_{0.3}Co₂O₄-HC. However, the amounts of active oxygen obtained by H₂-TPR follow the order: MnCo₂O₄-HC < Mn_{0.8}K_{0.2}Co₂O₄-HC < Mn_{0.9}K_{0.1}Co₂O₄-HC ≈ Mn_{0.7}K_{0.3}Co₂O₄-HC.

The essence of soot-TPR and H₂-TPR reaction is as follows:

As we all know, hydrogen can react with subsurface or bulk lattice oxygen. However, due to a lack of K, oxygen species in MnCo₂O₄-HC is difficult to release from the (CoO₆) octahedral unit and react with soot. The K substitution can change the coordination

environment in the $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4$ catalysts and part of the lattice oxygen can transform into active oxygen and move to the surface. Moreover, the metal-oxygen bond interaction is further weakened with increasing of K content and the mobility of active lattice oxygen also gradually increased. Therefore, the active oxygen species in the subsurface layer can be easily desorbed because of K substitution and the reduction peaks gradually shifted to low temperature.

As a result, T_{10} and T_{50} of $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ are significantly lower than other catalysts. In summary, the replacement of potassium for Mn leads to the enhancements of Co^{3+} and defect sites, the mobility of oxygen species and the increase of active lattice oxygen which can participate in the reaction, and thus the temperature for catalytic combustion of soot decreases.

4. Materials and Methods

4.1. Catalyst Preparation

4.1.1. Materials

The chemical reagents used in this article are all standard reagents. The name and purity information of the reagents involved in the preparation are as follows: manganese nitrate $\text{Mn}(\text{NO}_3)_2$ (50%), AR), cobalt nitrate ($(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR), potassium nitrate (KNO_3 , AR), anhydrous ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, AR), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, AR). The above reagents are all from Sinopharm Chemical Reagent Co., Ltd. The honeycomb ceramics for preparing monolith catalyst was a conventional commercial cylindrical ceramic with 400 mesh. The diameter and height of ceramics were 50×50 mm.

4.1.2. Synthesis of Honeycomb Ceramics Monolith Catalysts with the Coating of $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4$

The honeycomb ceramics monolith catalysts with the coating of $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4$ were prepared by the citric acid complexation method. The potassium nitrate, manganese nitrate and cobalt nitrate were weighed according to the nominal composition of the spinels of MnCo_2O_4 , $\text{Mn}_{0.9}\text{K}_{0.1}\text{Co}_2\text{O}_4$, $\text{Mn}_{0.8}\text{K}_{0.2}\text{Co}_2\text{O}_4$, $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$, respectively. The molar ratio of citric acid to total metal cation was 1:1. The weighed metal salts and citric acid were dissolved in ethanol and the concentration of metal cations was 2 mol/L in the solution. Then, the solution was slowly stirred for 3 h to form a homogenous purple solution. After that, the pretreated cylindrical honeycomb ceramics monolith (high $\times$ diameter = 50×50 mm, calcined at 600°C) was repeatedly immersed in the above purple sol to ensure the sol can be coated on the inner wall of the honeycomb ceramics. The excess solution in the channel was removed by purge gas, and then dried in an oven at 80°C for 24 h. The dried samples were heated to 550°C at $2^\circ\text{C}/\text{min}$ in a muffle furnace for 6 h. Finally, the honeycomb ceramics monolith catalysts with the coating of K-modified MnCo_2O_4 spinel were obtained. The as-prepared monolith catalysts were named as $\text{MnCo}_2\text{O}_4\text{-HC}$, $\text{Mn}_{0.9}\text{K}_{0.1}\text{Co}_2\text{O}_4\text{-HC}$, $\text{Mn}_{0.8}\text{K}_{0.2}\text{Co}_2\text{O}_4\text{-HC}$ and $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-HC}$ for the sake of clarity. In addition, to more clearly study the physicochemical properties of as-prepared catalysts, the corresponding $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4$ powder samples were also prepared by the drying and calcination of the remaining impregnation purple solution and the powder were named $\text{MnCo}_2\text{O}_4\text{-P}$, $\text{Mn}_{0.9}\text{K}_{0.1}\text{Co}_2\text{O}_4\text{-P}$, $\text{Mn}_{0.8}\text{K}_{0.2}\text{Co}_2\text{O}_4\text{-P}$, $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4\text{-P}$, respectively. To more clearly express the loading amounts, the weights of blank honeycomb ceramics (HC) and $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4\text{-HC}$ are listed in Table 5. Compared with the blank honeycomb ceramics (HC), the $\text{Mn}_{1-n}\text{K}_n\text{Co}_2\text{O}_4$ active components are successfully loaded on the honeycomb ceramics and the loading weight ranges are about 2.5 g, which proves that the loading method is effective for the synthesis of monolith catalysts.

Table 5. The weights of monolith $Mn_{1-n}K_nCo_2O_4$ -HC catalysts and blank honeycomb ceramics (HC).

Catalyst	m_{HC}/g	m_{fre}/g	$\Delta m/g$
$MnCo_2O_4$ -HC	55.67	58.29	2.62
$Mn_{0.9}K_{0.1}Co_2O_4$ -HC	56.31	58.78	2.47
$Mn_{0.8}K_{0.2}Co_2O_4$ -HC	57.39	59.92	2.53
$Mn_{0.7}K_{0.3}Co_2O_4$ -HC	55.65	58.24	2.59

m_{HC} : the weight of blank ceramics; m_{fre} : the weight of fresh monolith catalyst; Δm : the weight of coat-layer after calcined. $\Delta m = m_{fre} - m_{HC}$.

4.2. Physical and Chemical Characterizations

The crystal phase structures of the catalysts were measured with an X-ray diffractometer (Shimadzu XRD 6000 with Cu $K\alpha$ radiation, $\lambda = 0.15406$ nm). The step size of X-ray diffraction is 0.02 degrees. The scan rate is 4 degrees per minute in the 2θ range of 5–90 degrees. The morphologies of catalysts were studied by scanning electron microscopy (ZEISS Gemini SEM 300, accelerating voltage 5 kV). The valence information and binding energy results of each element were characterized by X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI-1600 ESCA spectrometer).

H_2 -TPR measurements were performed using a Micromeritics AutoChem II 2920 (USA) dynamic adsorption analyzer. The mass of the catalyst for H_2 -TPR is 200 mg. To remove moisture and impurities on the surface, the catalyst was pretreated in helium at 400 °C for 120 min. The catalyst was conducted the reducing test in the temperature range of 50–750 °C, and the reducing gas contained 5% hydrogen and 95% helium. Heating rate was 10 °C/min. The signal was detected and recorded by the thermal conductivity detector (TCD). Soot-TPR were tested on gas chromatography GC-4320. Firstly, 0.1 g powder catalyst and 0.01 g soot with the mode of loose contact were treated at 300 °C for 30 min in Ar (50 mL/min) to remove other impurities. The temperature was raised from 150 to 800 °C with heating rate of 2 °C/min. The composition and concentration of exhaust gas were detected by gas chromatography GC-4320 with an FID detector.

The Raman and in-situ Raman spectra were conducted on inVia Reflex-Renishaw spectrometer. The wavelengths of the laser used were 325 and 532 nm. The atmosphere composition of in-situ Raman was the same as the activity measurements.

In-situ Raman spectra were also obtained on inVia Reflex-Renishaw spectrometer. The reaction gas compositions were NO (2000 ppm), O_2 (10 %) and He (equilibrium gas), and the total flow rate was 50 mL/min. For different atmospheres of in-situ Raman spectra, the gas compositions of NO (2000 ppm)/He (equilibrium gas), O_2 (10 %)/He (equilibrium gas) and NO (2000 ppm), O_2 (10 %)/He (equilibrium gas) were selected according to experimental conditions. The contact mode for monolith catalyst and soot was loose contact.

The characterization in this work was all obtained by research of the monolith catalysts, except for the results of the soot-TPR and partial XRD measurements.

4.3. Activity Measurements

Catalyst activity was tested by a temperature-programmed oxidation (TPO) reaction. Soot particles (Printex-U diameter ~25 nm) were used to simulate PM_{2.5} in diesel exhaust, which contained C (92.0%), H (0.7%), O (3.5%), N (0.1%), S (0.2%), and others (3.5%). The active components of the monolith catalysts were spinel catalyst coatings. Therefore, the mass ratio of soot to active components was 1:10 in the activity test. The heating rate of TPO was 2 °C/min. The reaction atmosphere contained NO (2000 ppm), O_2 (10 %), argon gas as equilibrium gas, and the total flow rate was 50 mL/min. The soot particles were mixed in an appropriate amount of deionized and thoroughly stirred to form a suspension. At this time, the honeycomb ceramics monolith was immersed in the suspension and the parallel channel would be filled by it. Then the honeycomb ceramics monolith catalyst was dried in the vacuum oven at 80 °C for 48 hours to achieve the purpose of removing moisture. In this way, the soot was in a state of loose contact with the catalyst coating of honeycomb ceramics.

The cycle test followed these steps. Firstly, an activity test was performed on the monolith catalyst. Then, the reacted monolith catalyst was immersed in the same soot suspension and the surface of monolith catalyst was filled by soot suspension. After that, the impregnated monolith catalyst was dried at 80 °C in a vacuum oven for 48 h until the solvent evaporated. Finally, the dried monolith catalyst can be tested for the second cycle under the same reaction conditions for the activity test. In the following cycles the above steps were repeated.

The method for SO₂ resistance test was carried out in the atmosphere containing 200 ppm SO₂ with the equilibrium gas Ar and poisoning treatment at 300 °C for 6 h. Gas flow was 50 mL/min. The water resistance test was similar with the reaction conditions for activity test except for 2% water vapor in the reaction gases. The water vapor was obtained by continuous bubbling method under 25 °C in gas washing bottle.

To achieve the loose contact mode for soot-TPR, the powdered catalyst and soot particles were mixed in a burette with a length of 10 cm and a diameter of 2 cm, and then the burette was vibrated up and down for a total of 10 min. In the process of vibration, the mixture was stirred every 2 min.

The activities of catalysts were reflected by the combustion temperatures of soot particles. The gas chromatography GC-4320 was used to detect the concentration of CO and CO₂ produced in the soot combustion. Total amount of CO₂ produced by soot was obtained by integration of concentration-temperature curve, and then the proportion of CO₂ at every temperature point was calculated to draw soot conversion-temperature relationship curve. Soot conversion rate reached 10% and the corresponding temperature was considered, as T₁₀. T₅₀ and T₉₀ were achieved by the same principle. In addition, T_m, the temperature at which the CO₂ concentration in the reaction reached its maximum, was also one of the indicators for reflecting catalyst activity. During the catalytic combustion of soot, the generation of CO should be minimized. Therefore, the selectivity of CO₂ was also an important indicator for catalysts. The selectivity and maximum selectivity of CO₂ in the product were calculated according to formulas (1) and (2), respectively

$$S_{\text{CO}_2} = \frac{[\text{CO}_2]_{\text{out}}}{[\text{CO}_2]_{\text{out}} + [\text{CO}]_{\text{out}}} \times 100\% \quad (1)$$

$$S_{\text{CO}_2}^{\text{m}} = \frac{[\text{CO}_2]_{\text{out}}^{\text{max}}}{[\text{CO}_2]_{\text{out}}^{\text{max}} + [\text{CO}]_{\text{out}}^{\text{max}}} \times 100\%. \quad (2)$$

The Mn_{0.7}K_{0.3}Co₂O₄-HC catalyst was put in the water and treated in ultrasonic for 5~30 min. The frequency of the ultrasonic instrument (KQ-250E) is 40 KHz with the power of 250 W. The peeling rate for the coat-layer was calculated as follows formula.

$$\text{Peeling rate}(\%) = \frac{m_{\text{f}} - m_{\text{t}}}{m_{\text{f}} - m_{\text{HC}}}.$$

m_{f} and m_{t} are the weights of fresh and treated monolith catalysts, respectively. m_{HC} is the weight of blank honeycomb ceramics.

5. Conclusions

In this work, a series of monolith Mn_{1-n}K_nCo₂O₄ catalysts with different contents of K substitution were prepared by the simple citric acid method and they exhibit good catalytic performance for soot combustion. Among the as-prepared catalysts, the Mn_{0.7}K_{0.3}Co₂O₄-HC catalyst exhibited the best catalytic performance, and the values of T₁₀ and T_m for soot combustion are 310 and 439 °C, respectively. The results of XRD and Raman confirm that the K ions entered the spinel lattice. The XPS results indicate that the amounts of Co³⁺ and the oxygen vacancy increased with the increasing of K content. More importantly, H₂-TPR and soot-TPR also demonstrate that the mobility of active oxygen is enhanced and many more active oxygen species can participate in soot combustion than that of the MnCo₂O₄-HC catalyst due to the K substitution for Mn. Meanwhile, the catalyst coating is

more closely attached to the honeycomb ceramics surface and the coat-layer peeling rate is less than 5%. However, the as-prepared catalysts can be taken as one kind of candidate catalyst for in-depth research because of their facile synthesis, low cost and high catalytic activity. The results of this work highlight inexpensive metals and facile coating methods for the efficient preparation of monolith catalysts. Despite the systematic investigation of monolith catalysts for soot catalytic oxidation based on the MnCo_2O_4 spinel developed in the laboratory, the main challenge remains to improve the redox properties and contact efficiency of the coatings. The as-prepared catalysts can be taken as one kind of candidate catalyst for in-depth research for practical application because of facile synthesis, low cost and high catalytic activity.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12030295/s1>, Figure S1: The soot conversion curves of cycle test (a) and resistance of sulfur and water (b) over $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC monolith catalyst; Figure S2: Raman spectra of cobalt oxide and manganese oxide under different laser wavelength of 532 nm (a,c) and 325 nm (b,d); Figure S3: Raman spectrum of soot under laser wavelength of 532 nm; Figure S4: In-situ Raman spectra of MnCo_2O_4 -HC (a,d and g), $\text{Mn}_{0.9}\text{K}_{0.1}\text{Co}_2\text{O}_4$ -HC (b,e and h) and $\text{Mn}_{0.7}\text{K}_{0.3}\text{Co}_2\text{O}_4$ -HC (c,f and i) monolith catalysts under laser wavelength of 532 nm for different atmosphere. Reaction conditions: heating rate was 2 °C/min. The reaction atmosphere contained NO (2000 ppm), O_2 (10%) and He as equilibrium gas, and the total flow rate was 50 mL/min Table S1: The summary of catalytic performance, TPR temperature, cationic valences and active oxygen content.

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