Preparation of K Modified Three-Dimensionally Ordered Macroporous MnCeO$_x$/Ti$_{0.7}$Si$_{0.3}$O$_2$ Catalysts and Their Catalytic Performance for Soot Combustion

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Abstract: Soot particles in diesel engine exhaust is one of the main reasons for hazy weather and elimination of them is urgent for environmental protection. At present, it is still a challenge to develop new catalysts with high efficiency and low cost. In this paper, a kind of K modified three-dimensionally ordered macroporous (3DOM) MnCeO$_x$/Ti$_{0.7}$Si$_{0.3}$O$_2$ catalysts are designed and synthesized by a sample method. Due to the macroporous structure and synergistic effect of K, Mn, and Ce, the K$_n$MnCeO$_x$/Ti$_{0.7}$Si$_{0.3}$O$_2$ (K$_n$MnCeO$_x$/M-TSO) catalysts exhibit good catalytic performance for soot combustion. The catalytic activity of K$_0.5$MnCeO$_x$/M-TSO was the best, and the $T_{10}$, $T_{30}$, and $T_{90}$ are 287, 336, and 367 $^\circ$C, respectively. After the prepared catalyst was doped with K, the physicochemical properties and catalytic performance changed significantly. In addition, the K$_0.5$MnCeO$_x$/M-TSO catalyst also somewhat exhibits sulfur tolerance owing to it containing Ti. Because of its simple synthesis, high activity, and low cost, the prepared K$_n$MnCeO$_x$/M-TSO catalysts are regarded as a promising candidate for application.

Keywords: 3DOM structure; K$_n$MnCeO$_x$/M-TSO; soot combustion; catalysts

1. Introduction

Diesel engines have been widely used in automobile, ship, light truck, heavy machinery, and other fields because of its excellent thermal efficiency and durability [1,2]. However, diesel engines are also considered to be one of the major sources of soot particles emission and a cause of hazy weather [3,4]. With increasing awareness of environmental protection, the standards on exhaust emission of diesel engines have become increasingly stringent. Therefore, it is urgent to eliminate soot particles to meet emission standards. Nowadays, post-treatment technology is considered to be one of the effective ways to eliminate soot particles. However, since the spontaneous combustion temperature of soot particles (550–650 $^\circ$C) is higher than the exhaust temperature of the diesel engine (150–450 $^\circ$C), the development of new catalysts with low cost and excellent catalytic performance is one of the main challenges in the application of post-treatment technology [5,6].

At present, owing to three-phase gas(O$_2$)-solid(soot)-solid(catalyst) reaction for soot combustion, various catalysts were prepared to improve the contact efficiency between soot and catalyst [7,8]. Different morphologies of catalysts with nanotube array, nanobelt, nanofiber, nanowire, disordered macropore, and 3DOM structures are studied to enhance effective contact [9–14]. Among the above morphologies, due to the interconnected macroporous structure with large pore diameter ($>50$ nm) and low diffusion resistance, the 3DOM catalyst has enough migration space for soot particles in its internal pores, which are expected to show excellent catalytic ability [15–17]. Many previous studies have shown that the catalytic performance of 3DOM oxide-based catalysts for soot combustion is superior.
to that of corresponding nanoparticle catalysts due to their structural effects [18–20]. To improve the intrinsic activity, a series of 3DOM oxides-supported Au and Pt catalysts have also been prepared in our research group, and the prepared 3DOM oxides-supported noble metal catalysts exhibit excellent catalytic ability in soot combustion reaction [21–23]. However, it is unsatisfactory that the application of noble metals is restricted by their high cost.

In recent years, considering the economy of catalyst cost, a number of rare earth oxides and transition metals have been studied for soot combustion [20,24–26]. MnO_x-CeO_2 mixed oxides with Mn and Ce synergistic effects have become one of the low cost and high performance catalysts [27–30]. In addition, alkali metals, especially potassium (K), exhibit excellent catalytic ability in soot combustion reaction. However, because of the low melting point of K, K-contained catalysts have weak thermostability in repeated cycles. To improve the stability of K-based catalysts, the incorporation of K into other stable structures is considered to be a promising way to resolve the problem of thermostability, and many kinds of K-doped catalysts have been reported by previous literature [31–33]. However, how to effectively combine the good contact efficiency of 3DOM structure and high catalytic activities of K, Mn, and Ce in one system of catalysts is also a research hotspot in the design and preparation of catalysts [34,35].

In this paper, a series of K-modified 3DOM MnCeO_x/Ti_0.7Si_0.3O_2 catalysts were synthesized by a simple preparation method. The catalysts have 3DOM structure and three active components of K, Mn, and Ce. The physicochemical properties of the as-prepared catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), temperature-programmed reduction with H_2 (H_2-TPR), temperature-programmed desorption with O_2 (O_2-TPD), temperature-programmed oxidation with NO (NO-TPO), etc. The effect of macropore structure combined with the synergistic effect of K, Mn, and Ce is expected to improve the catalytic ability of the synthesized catalyst in soot combustion reaction.

2. Experimental Section
2.1. Catalysts Preparation
2.1.1. Synthesis of Highly Well-Defined PMMA Microspheres

Monodispersed polymethyl methacrylate (PMMA) microspheres were synthesized by the emulsifier-free emulsion polymerization method with potassium persulfate (KPS) as the initiator and methyl methacrylate (MMA) as the raw material. Ordered macroporous templates were prepared by centrifugal precipitation self-assembly method. The preparation method was reported in our previous work [36].

2.1.2. Synthesis of 3DOM Ti_0.7Si_0.3O_2

3DOM Ti_0.7Si_0.3O_2 was prepared by the colloidal template method. Tetrabutyl titanate, tetraethyl orthosilicate (TEOS), HCl, H_2O, and ethanol were weighed according to a certain stoichiometric ratio and magnetically stirred for 3 h to obtain a homogeneous and clarified solution. The PMMA crystal template was immersed in the precursor solution for 1 h. After suction filtration and drying, the PMMA colloidal template was removed by calcination with air in a tubular furnace. The heating rate was 1 °C/min, it was calcined at 310 °C for 3 h, and then heated to 600 °C and subsequently calcined for 4 h.

2.1.3. Synthesis of K Modified 3DOM MnCeO_x/Ti_0.7Si_0.3O_2

The 3DOM MnCeO_x/Ti_0.7Si_0.3O_2 catalysts were synthesized by the incipient wet impregnation method. The raw materials and amount of catalyst preparation are listed in Table 1. Ce(NO_3)_3·6H_2O, 50% Mn(NO_3)_2, and KN_3 solution were dissolved in water, and the total volume was about 2 mL. The impregnated 3DOM Ti_0.7Si_0.3O_2 was treated by ultrasonic for 15 min and dried at 80 °C for 12 h. The dried solid was calcined at 550 °C for 4 h to obtain 3DOM K_nMnCeO_x/Ti_0.7Si_0.3O_2. To easily express the prepared catalysts, the 3DOM Ti_0.7Si_0.3O_2 is abbreviated by M-TSO.
Table 1. Expression of catalyst and amount of raw materials.

| Catalysts                  | KNO$_3$/g | Mn(NO$_3$)$_2$/g | Ce(NO$_3$)$_3$/g | 3DOM TiSiO/g | 3DOM SiO$_2$/g |
|----------------------------|-----------|------------------|------------------|--------------|---------------|
| MnCeO$_x$/M-TSO            | 0         | 0.823            | 0.998            | 0.5          | —             |
| K$_{0.1}$MnCeO$_x$/M-TSO   | 0.023     | 0.823            | 0.998            | 0.5          | —             |
| K$_{0.3}$MnCeO$_x$/M-TSO   | 0.070     | 0.823            | 0.998            | 0.5          | —             |
| K$_{0.5}$MnCeO$_x$/M-TSO   | 0.116     | 0.823            | 0.998            | 0.5          | —             |
| K$_{0.7}$MnCeO$_x$/M-TSO   | 0.163     | 0.823            | 0.998            | 0.5          | —             |
| K$_{0.9}$MnCeO$_x$/M-TSO   | 0.209     | 0.823            | 0.998            | 0.5          | —             |
| K$_1$MnCeO$_x$/M-TSO       | 0.232     | 0.823            | 0.998            | 0.5          | —             |

2.2. Physical and Chemical Characterization

XRD spectrum was obtained using the Rigaku Ultima IV X-ray diffractometer with Cu K$_\alpha$ radiation. The scanning range was 10–90$^\circ$ and the scanning speed was 10$^\circ$/min. The phase identification of the catalyst was performed by comparing with the reference data of JCPDS.

The surface morphology and pore structure of the catalyst were observed by the Hitachi SU8010N scanning electron microscope under 1 V–5 kV accelerating voltage. To improve the quality of SEM photos, the samples were treated by spraying gold.

The specific surface area, pore size, and pore volume of the catalyst were determined by BET technique using the Micromeritics TriStar II: 3020 specific surface analyzer. The samples were analyzed after degassing at 300 $^\circ$C for 3 h.

H$_2$-TPR measurements were performed by the Micromeritics AutoChem II 2920 Chemical Adsorption Instrument. The sample was first purged with argon at 300 $^\circ$C for 1 h, and then dropped to room temperature. After switching the gas flow to a hydrogen–argon mixture, the instrument rose to 850 $^\circ$C (heating rate was 10 $^\circ$/min) and the thermal conductivity detector (TCD) was used to monitor H$_2$ consumption signals.

O$_2$-TPD was determined by the TP-5076 adsorption instrument. The 100 mg sample was pretreated in O$_2$ atmosphere at 300 $^\circ$C for 1 h, and then dropped to room temperature. The flow rate was switched to He flow (60 mL/min), and the temperature was raised to 900 $^\circ$C at a heating rate of 10 $^\circ$/min. TCD was used to monitor desorption oxygen.

NO-TPO measurements were performed by the NO$_x$ Analyzer nCLD 62. After pretreatment of 0.1 g catalyst in argon atmosphere at 200 $^\circ$C for half an hour, the reaction gas was changed. The total flow rate was 50 mL/min, containing 1000 ppm NO, 10% O$_2$, and the rest was argon. The temperature program was set to rise from 50 $^\circ$C to 600 $^\circ$C at a heating rate of 2 $^\circ$/min. The instrument can monitor the content of nitrogen oxides in the outlet gas in real time.

2.3. Catalytic Activity Measurements

The catalytic activity of catalysts for soot combustion was evaluated by temperature programmed oxidation (TPO) in a fixed bed tubular quartz reactor ($\Phi = 8$ mm). The model soot was Printx-U particulates (25 nm diameter, purchased from Degussa, Frankfurt, Germany). The elemental composition of Printx-U particles was 94.2% C, 3.1% O, 0.8% H, 0.4% S, 0.2% N, and 4.7% others [37]. Measures of 0.01 g of soot and 0.1 g of catalyst were weighed and mixed uniformly at a mass ratio of 1:10 to simulate loose contact conditions, and then they were loaded into the quartz reactor. The reaction gas (50 mL/min) included 10% O$_2$, 2000 ppm NO, and the rest was argon. We set the heating program from 100 $^\circ$C to 650 $^\circ$C, with a heating rate of 2 $^\circ$/min. The main components of the outlet gas were N$_2$, NO, CO$_2$, and CO. The outlet gas compositions were analyzed by an online gas chromatograph (GC, Agilent 7890B) equipped with a flame ionization detector (FID). Complete conversion of CO and CO$_2$ to CH$_4$ over nickel catalyst was maintained at 380 $^\circ$C before entering FID. The temperature $T_{10}$, $T_{50}$, and $T_{90}$ of 10%, 50%, and 90% conversion of soot particles can be used to evaluate the catalytic activity. The selectivity of CO$_2$ is another
essential standard for evaluating the catalytic combustion of soot. Equation (1) was the calculation method applied.

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

\([\text{CO}_2]_{\text{out}}^{\text{max}}\) and \([\text{CO}]_{\text{out}}^{\text{max}}\) are, respectively, expressed as the concentration of \(\text{CO}_2\) and \(\text{CO}\) in the reaction product when the reaction temperature is the peak temperature, and \(S_{\text{CO}_2}^m\) is the selectivity of \(\text{CO}_2\) when the soot combustion rate is the fastest.

Other reaction conditions remain constant; the sulfur resistance of the catalyst to soot combustion was tested by changing the gas composition of the reaction gas. The total gas flow rate was 50 mL/min, containing 100 ppm or 300 ppm \(\text{SO}_2\), 10% \(\text{O}_2\), 2000 ppm \(\text{NO}\), and the rest was argon.

3. Result and Discussion

3.1. Structural Features of the Synthesized Catalysts

3.1.1. XRD Patterns of the Prepared Catalysts

The XRD patterns of \(K_x\text{MnCeO}_x/\text{M-TSO}\) catalysts with different K doping amounts, M-TSO support, and \(K_0.5\text{MnCeO}_x/\text{M-SiO}_2\) are shown in Figure 1. For M-TSO support, the pattern peak for 20 of 25.4°(101) belongs to anatase \(\text{TiO}_2\) (marked by “◆” in Figure 1a; JCPDS Card No. 21-1272) [38–40]. As shown in Figure 1b, \(\text{MnCeO}_x/\text{M-TSO}\) catalyst exhibits four feature peaks, which are located at 2θ of 28.8°(111), 33.5°(200), 47.6°(220), and 56.8°(311) (marked by “▲” in Figure 1b), and these correspond to diffraction peaks of \(\text{CeO}_2\). However, the peak of anatase \(\text{TiO}_2\) disappeared, which is related to coverage of M-TSO surface by \(\text{MnCeO}_x\) oxides. It can be seen from Figure 1c–h that the XRD patterns of \(K_x\text{MnCeO}_x/\text{M-TSO}\) catalysts also belonged to the \(\text{CeO}_2\) crystal structure when the K was doped into \(\text{MnCeO}_x/\text{M-TSO}\). However, compared with reported crystal structure of pure \(\text{CeO}_2\) (JCPDS Card No. 43-1002), a slight shifting towards a higher diffraction angle of 2θ was observed on \(K_x\text{MnCeO}_x/\text{M-TSO}\) catalysts, in which the 2θ was shifted from 28.5 to 28.8° for the crystal face of (111) [41,42]. In addition, Figure 1c–h also exhibits that no feature peaks of \(\text{KNO}_3\), \(\text{KO}_x\), or \(\text{MnO}_x\) can be observed. The above phenomena indicate that due to the large lattice spacing of \(\text{CeO}_2\), K and Mn have been doped into the lattice of \(\text{CeO}_2\). It can be seen from Figure 11 that the XRD pattern of the \(K_{0.5}\text{MnCeO}_x/\text{M-SiO}_2\) catalyst also belongs to the \(\text{CeO}_2\) crystal structure.
3.1.2. SEM Images of the Catalysts

Figure 2 is the SEM images of prepared catalysts. Figure 2a indicates that macroporous structures can be well observed in the M-TSO support. The diameters of the macropores are about 290–330 nm and the wall thicknesses of macropores are about 30–50 nm. Meanwhile, three small pores with diameter of 80–120 nm, which formed in the contact area of two PMMA spheres, can be also obtained in a macropore, and they are interconnected with other adjacent macropores [43]. When the MnCeO\(_x\) and K\(_y\)MnCeO\(_x\) are loaded on the M-TSO support, the pore structure of MnCeO\(_x\)/M-TSO and K\(_y\)MnCeO\(_x\)/M-TSO are well maintained (Figure 2b–e). The SEM results indicate that the loading processes of MnCeO\(_x\) and K\(_y\)MnCeO\(_x\) do not destroy the pore structure of M-TSO support, and also demonstrate that the 3DOM structure of the M-TSO support is stable and strong. As shown in the SEM image of Figure 2, the prepared catalyst has uniform pore sizes, which are arranged highly periodically and connected through small windows [44]. The ordered pore structures are beneficial to improving catalyst-soot contact efficiency.

3.1.3. N\(_2\) Adsorption–Desorption Isotherms of the Prepared Catalysts

The N\(_2\) adsorption-desorption isotherm and the pore size distribution of the prepared catalyst can be seen in Figure 3. Based on the IUPAC, the prepared catalysts have typical type II adsorption-desorption isotherm [45]. However, the hysteresis loops of prepared catalysts are different with each other when MnCeO\(_x\) and K\(_y\)MnCeO\(_x\) are loaded on the M-TSO support. As shown in Figure 3A(a–c), the M-TSO support exhibits weak intensity of the hysteresis loop, while MnCeO\(_x\)/M-TSO and K\(_{0.1}\)MnCeO\(_x\)/M-TSO catalysts exhibit obvious hysteresis loops at high relative pressure. However, with increasing the doping dosage of K, the hysteresis loops of the K\(_y\)MnCeO\(_x\)/M-TSO catalysts are changed to indistinct (Figure 3A(d–h)). The pore size distributions in Figure 3B also indicate that MnCeO\(_x\)/M-TSO and K\(_{0.1}\)MnCeO\(_x\)/M-TSO catalysts have obvious mesoporous structures at the range of 2–40 nm, while the other samples do not exhibit mesopores. Textural properties of prepared catalysts are listed in Table 2. Compared with M-TSO support, MnCeO\(_x\)/M-TSO and K\(_{0.1}\)MnCeO\(_x\)/M-TSO catalysts exhibit higher surface area and total pore volume, which are well agreed with the results of N\(_2\) adsorption-desorption isotherms and pore size distributions. With the increase of K doping, the surface area decreases, and the value reduces to 30.1 m\(^2\)/g. The above phenomena are possibly related to the accumulation pores of MnCeO\(_x\) and K\(_{0.1}\)MnCeO\(_x\) active components on the surface of M-TSO, while the morphologies of K\(_y\)MnCeO\(_x\) may be changed at high doping dosage of K. With the increase of K doping, the total pore volume of K\(_y\)MnCeO\(_x\)/M-TSO decreased first, and then kept stable, while the pore size decreased first, and then increased. This
phenomenon may be related to the deposition of \( \text{K}_n\text{MnCeO}_x \) active components on the surface of M-TSO. When the doping of K is increased, a mass of K or KMnCeO\(_x\) species are filled into the surface gaps of M-TSO and reduce the amounts of small pores. Therefore, the pore size increases with the increasing of K doping. Figure 3A(i), Figure 3B(i), and Table 2 show that K\(_{0.5}\)MnCeO\(_x\)/M-TSO also has a lower specific area and a larger pore size than that of K\(_{0.5}\)MnCeO\(_x\)/M-TSO.

![Figure 3](image_url)

**Figure 3.** Nitrogen adsorption-desorption isotherms (A) and pore size distributions (B) of prepared catalysts (a: M-TSO; b: MnCeO\(_x\)/M-TSO; c: K\(_{0.1}\)MnCeO\(_x\)/M-TSO; d: K\(_{0.3}\)MnCeO\(_x\)/M-TSO; e: K\(_{0.5}\)MnCeO\(_x\)/M-TSO; f: K\(_{0.7}\)MnCeO\(_x\)/M-TSO; g: K\(_{0.9}\)MnCeO\(_x\)/M-TSO; h: K\(_1\)MnCeO\(_x\)/M-TSO; i: K\(_{0.5}\)MnCeO\(_x\)/M-SiO\(_2\)).

Table 2. Textural properties of prepared catalysts.

| Catalysts       | Surface Area (m\(^2\)/g) \(^a\) | Total Pore Volume (m\(^3\)/g) \(^b\) | Pore Size (nm) \(^c\) |
|-----------------|----------------------------------|-------------------------------------|------------------------|
| M-TSO           | 51.3                             | 0.123                               | 9.9                    |
| MnCeO\(_x\)/M-TSO | 81.1                             | 0.218                               | 9.4                    |
| K\(_{0.1}\)MnCeO\(_x\)/M-TSO | 69.7                             | 0.218                               | 11.2                   |
| K\(_{0.3}\)MnCeO\(_x\)/M-TSO | 45.0                             | 0.121                               | 10.1                   |
| K\(_{0.5}\)MnCeO\(_x\)/M-TSO | 44.2                             | 0.105                               | 8.9                    |
| K\(_{0.7}\)MnCeO\(_x\)/M-TSO | 36.7                             | 0.101                               | 10.5                   |
| K\(_{0.9}\)MnCeO\(_x\)/M-TSO | 31.8                             | 0.109                               | 13.8                   |
| K\(_1\)MnCeO\(_x\)/M-TSO     | 30.1                             | 0.101                               | 14.1                   |
| K\(_{0.5}\)MnCeO\(_x\)/M-SiO\(_2\) | 31.2                             | 0.100                               | 13.1                   |

\(^a\) Calculated by BET method; \(^b\) Calculated by BJH desorption cumulative volume of pores between 1.7 nm and 300 nm diameter; \(^c\) Calculated by BJH desorption average pore diameter.

3.1.4. H\(_2\)-TPR Profiles of the Prepared Catalysts

The inherent redox property of the catalyst is the key to enhance the catalytic activity and deep oxidation of soot. In this work, to clearly investigate the influence of different K doping amounts and different active components, five representative catalysts, i.e., M-TSO, MnCeO\(_x\)/M-TSO, K\(_{0.1}\)MnCeO\(_x\)/M-TSO, K\(_{0.5}\)MnCeO\(_x\)/M-TSO, and K\(_1\)MnCeO\(_x\)/M-TSO, were determined by H\(_2\)-TPR. Since no obvious reduction peak is observed in Figure 4a at a low temperature (<500 °C), it indicates that the redox ability of M-TSO was very weak. The weak reduction peak observed at 650 °C is related to the reduction reaction of Ti\(^{3+}\) in M-TSO [46]. When MnCeO\(_x\) and K\(_x\)MnCeO\(_x\) are loaded on the M-TSO support, the reduction peak positions and types of prepared catalysts have distinct differences with that of M-TSO support. As shown in the Figure 4b–e, the reduction peaks can be divided into four ranges of 178–250 °C, 280–350 °C, 350–450 °C, and >650 °C. Due to the large negative reduction potential, MnO was not reduced to Mn\(^0\), even above 950 °C. Therefore, MnO was considered to be the final state for the preparation of catalyst reduction [47,48]. According to the reduction process of Mn-based oxides, the first peak at 178–250 °C may be attributed to MnO\(_2\) reduction to Mn\(_2\)O\(_3\), the second peak at 280–350 °C could be related to Mn\(_2\)O\(_3\)
reduction to Mn$_3$O$_4$, and the third peak at 350–450 °C could belong to the Mn$_3$O$_4$ reduction to MnO [16,49]. The fourth peak at >650 °C is assigned to the reduction of CeO$_2$ to Ce$_2$O$_3$. Compared with MnCeO$_x$/M-TSO catalyst, the doping of K into MnCeO$_x$ will lead to the lower reduction temperature (Figure 4c). However, with increasing the K doping amounts, the reduction temperature is increased. The H$_2$-TPR results indicate that the doping of K in MnCeO$_x$/M-TSO catalyst can modify the reduction properties of K$_x$MnCeO$_x$/M-TSO catalysts and is beneficial for regulating catalyst activities.

Figure 4. H$_2$-TPR curves of prepared catalysts (a: M-TSO; b: MnCeO$_x$/M-TSO; c: K$_{0.1}$MnCeO$_x$/M-TSO; d: K$_{0.5}$MnCeO$_x$/M-TSO; e: K$_1$MnCeO$_x$/M-TSO).

3.1.5. O$_2$-TPD Results of the Prepared Catalysts

The active oxygen species are essential for improving catalytic activity for deep oxidation of soot combustion. To conformably compare with the H$_2$-TPR results, the same samples as those of H$_2$-TPR that were determined were studied by O$_2$-TPD, and the results are shown in Figure 5. The oxygen desorption peaks of prepared catalysts can be divided into three peaks, and the temperature regions are located at T ≤ 250 °C, 250 °C ≤ T ≤ 500 °C, and T ≥ 500 °C, respectively. However, the M-TSO support exhibits only two obvious oxygen desorption peaks, which are located at 100 and 380 °C. The first oxygen desorption peak (named as α in the Figure 5) at T ≤ 250 °C belongs to the surface-active oxygen species (O$_{surf}$) or physically adsorbed oxygen [50]. The second peak, which is located at 250 °C ≤ T ≤ 500 °C and named as β, can be assigned to chemically adsorbed oxygen on the oxygen vacancies (O$_2^–$/O$^–$) [51]. The third peak, named γ, belongs to the desorption of lattice oxygen (O$^2–$) in the MnCeO$_x$ and K$_x$MnCeO$_x$ [52]. Compared with M-TSO support, it can be discovered that the third peaks are newly appeared. In addition, the shapes of the third peaks are also different with various K doping amounts. The reasons for the above phenomena are possibly related to the interaction of K and MnCeO$_x$.

3.1.6. NO-TPO Results of the Prepared Catalysts

Because of the relationship of “trade off” between soot and NO$_x$, NO$_x$ is an inevitable gas in the emission of diesel engines [53]. In addition, NO$_x$, especially NO$_2$, is an important factor to improve the catalytic performance. Based on the above reasons, the NO-TPO of the M-TSO support, MnCeO$_x$/M-TSO, and K$_{0.5}$MnCeO$_x$/M-TSO catalysts were studied, and the results of the test are shown in Figure 6. Owing to strong oxidation ability, soot particles can be directly oxidized by NO$_2$. Therefore, NO$_2$ participates in the reaction and changes the reaction path of soot combustion. The soot combustion reaction will change from gas(O$_2$)-solid(catalyst)-solid(soot) to gas(O$_2$)-gas(NO$_2$)-solid(soot), which is beneficial
to enhance the catalytic activity. As shown in the Figure 6A, M-TSO support exhibits low NO\textsubscript{2} concentration at the temperature range of 100–400 °C. When the temperature is higher than 400 °C, there is a little enhancement of NO\textsubscript{2} concentration, and the NO concentration decreases correspondingly. This result indicates that M-TSO support may exhibit low catalytic activity during soot combustion. The low NO\textsubscript{2} concentration also agrees well with the H\textsubscript{2}-TPR result of M-TSO support. Figure 6B,C exhibit the NO\textsubscript{x}, NO, and NO\textsubscript{2} concentration of the MnCeO\textsubscript{x}/M-TSO and K\textsubscript{0.5}MnCeO\textsubscript{x}/M-TSO catalyst. Compared with Figure 6A, the NO\textsubscript{2} concentration for the MnCeO\textsubscript{x}/M-TSO and K\textsubscript{0.5}MnCeO\textsubscript{x}/M-TSO catalyst has obvious enhancement at the temperatures of 200–500 °C. The generated NO\textsubscript{2} is expected to improve the catalytic activity of the MnCeO\textsubscript{x}/M-TSO and K\textsubscript{0.5}MnCeO\textsubscript{x}/M-TSO catalyst for soot combustion. As shown in Figure 6B, the temperature for the most concentration of NO\textsubscript{2} is about 300 °C, while it can be seen from Table 3 that the T\textsubscript{50} of K\textsubscript{0.5}MnCeO\textsubscript{x}/M-TSO catalyst for soot combustion is 354 °C. At a high temperature, part of NO\textsubscript{2} has been decomposed and cannot react with soot particles. From Figure 6C, the temperature for the most concentration of NO\textsubscript{2} for the K\textsubscript{0.5}MnCeO\textsubscript{x}/M-TSO catalyst is about 330 °C. This temperature is concordant with the T\textsubscript{50} of the K\textsubscript{0.5}MnCeO\textsubscript{x}/M-TSO catalyst. Therefore, most of the NO\textsubscript{2} can directly react with soot particles, which is beneficial to improve the catalytic activity.

![Figure 5](image-url)  
**Figure 5.** O\textsubscript{2}-TPD of prepared catalysts (a: M-TSO; b: MnCeO\textsubscript{x}/M-TSO; c: K\textsubscript{0.1}MnCeO\textsubscript{x}/M-TSO; d: K\textsubscript{0.5}MnCeO\textsubscript{x}/M-TSO; e: K\textsubscript{1}MnCeO\textsubscript{x}/M-TSO).

![Figure 6](image-url)  
**Figure 6.** NO\textsubscript{x}, NO, and NO\textsubscript{2} concentration over M-TSO support (A), MnCeO\textsubscript{x}/M-TSO catalyst (B), and K\textsubscript{0.5}MnCeO\textsubscript{x}/M-TSO catalyst (C).
Table 3. Catalytic performance of prepared catalysts for soot combustion.

| Catalysts       | T_{10}/°C | T_{50}/°C | T_{90}/°C | Sco_{2m}/% |
|-----------------|-----------|-----------|-----------|------------|
| Soot            | 457       | 552       | 594       | 41%        |
| M-TSO           | 376       | 517       | 565       | 50.5%      |
| MnCeO_{x}/M-TSO | 284       | 354       | 393       | 99.3%      |
| K_{0.1}MnCeO_{x}/M-TSO | 286   | 346       | 380       | 99.4%      |
| K_{0.3}MnCeO_{x}/M-TSO | 285   | 338       | 379       | 98.3%      |
| K_{0.5}MnCeO_{x}/M-TSO | 287   | 336       | 367       | 98.9%      |
| K_{0.7}MnCeO_{x}/M-TSO | 293   | 341       | 379       | 97.7%      |
| K_{0.9}MnCeO_{x}/M-TSO | 295   | 345       | 379       | 97.3%      |
| K_{1}MnCeO_{x}/M-TSO | 300   | 349       | 384       | 96.7%      |

3.2. Catalytic Performance in Soot Combustion

3.2.1. Catalytic Activities of the Prepared Catalysts

The catalytic activity of the prepared catalyst in soot combustion was evaluated by TPO test, and to better evaluate the catalytic activity of active components, the combustion performance of soot on M-TSO under the same conditions was compared. As shown in Table 3, the combustion temperatures T_{10}, T_{50}, and T_{90} of pure soot are 457, 552, and 594 °C, respectively. The combustion temperature of soot on M-TSO was slightly lower than that of pure soot. The catalytic activity of M-TSO was very weak, and the T_{10}, T_{50}, and T_{90} were 376, 517, and 565 °C, respectively. However, when MnCeO_{x} is loaded on the M-TSO support, the catalytic ability of the MnCeO_{x}/M-TSO catalyst in soot combustion reaction is obviously improved. When the K are doped into the MnCeO_{x}/M-TSO, the catalytic activities of K_{n}MnCeO_{x}/M-TSO catalysts are further improved. With the increase of K doping amounts, the catalytic activity of the catalyst increased continuously until the molar ratio of K to Mn reached 0.5; after that, with the further increase of the K doping amount, the catalytic activity decreased continuously. Among the prepared catalysts, the catalytic activity of the K_{0.5}MnCeO_{x}/M-TSO catalyst was the best, and the T_{10}, T_{50}, and T_{90} were 287, 336, and 367 °C, respectively. In addition, the CO_{2} selectivity of the MnCeO_{x}/M-TSO and K_{0.5}MnCeO_{x}/M-TSO catalysts are more than 96%, which is much higher than that of the M-TSO support.

3.2.2. Sulfur Resistances of Prepared Catalysts

Due to the methods of the formation of fossil fuels, sulfur compounds are unavoidable in the diesel engine exhausts. Many previous studies have proved that Ti has high sulfur resistance in the catalytic reaction. To demonstrate the sulfur resistance of prepared catalysts, the catalytic performances of the K_{0.5}MnCeO_{x}/M-TSO and K_{0.5}MnCeO_{x}/M-SiO_{2} catalysts under 100 ppm SO_{2} were estimated. It can be seen from Figure 7 that there are significant differences between the two catalysts at T_{10} temperature, which indicates that K_{0.5}MnCeO_{x}/M-TSO has somewhat sulfur resistance. However, the temperatures of T_{50} and T_{90} for the tested catalysts are similar. In addition, compared with the results of Table 3 and Figure 7, the catalytic activity of K_{0.5}MnCeO_{x}/M-TSO has certainly declined with increasing of SO_{2} concentration. The reason for the above phenomena may be related to the sulfuration of K_{0.5}MnCeO_{x} at high temperatures. In order to better explore the sulfur resistance, the reacted K_{0.5}MnCeO_{x}/M-TSO catalyst under 300 ppm SO_{2} was calcined at 550 °C for 4 h again to regenerate. After regeneration, the activity test was carried out again under 300 ppm SO_{2}. The result indicates that the activity of the regenerated K_{0.5}MnCeO_{x}/M-TSO catalyst is also certainly decreased (Figure 7).
The activity test was carried out again.

Figure 7. Catalytic performance of catalysts under 100 ppm or 300 ppm SO₂.

4. Conclusions

In summary, a K-modified 3DOM MnCeOₓ/Ti₀.₇Si₀.₃O₂ catalyst was prepared by a simple method, in which the catalyst had 3DOM structure and three active components of K, Mn, and Ce. The KₓMnCeOₓ/ M-TSO catalysts exhibit excellent catalytic performance for soot combustion because of the macroporous structure and synergistic effect of K, Mn, and Ce. The K₀.₅MnCeOₓ/ M-TSO catalyst has the best catalytic performance among the prepared catalysts, and the T₁₀, T₅₀, and T₉₀ are 287, 336, and 367 °C, respectively. The characterization results indicate that the physicochemical properties of catalysts are changed when the K is doped into the MnCeOₓ/ M-TSO catalyst, and different doping amounts of K have obvious influence on the catalytic performance. In addition, compared with the K₀.₅MnCeOₓ/ M-SiO₂ catalyst, the K₀.₅MnCeOₓ/ M-TSO catalyst also exhibits somewhat sulfur tolerance owing to it containing Ti. Meantime, the research results show that the prepared KₓMnCeOₓ/ M-TSO catalyst has the advantages of simple synthesis method, low cost, and high activity, and this has a certain application prospect.

Author Contributions: Conceptualization, C.Z. and X.Y.; methodology, C.Z.; software, C.P.; validation, D.Y., L.W. and C.P.; formal analysis, X.F.; investigation, C.Z. and D.Y.; resources, X.Y.; data curation, C.Z.; writing—original draft preparation, C.Z.; writing—review and editing, X.Y.; visualization, Z.Z.; supervision, X.Y.; project administration, Z.Z.; funding acquisition, X.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of China (22072095, U1908204, 21761162016); Key Research and Development Program of MOST (2017YFE0131200) for collaboration between China and Poland; General Projects of Liaoning Province Natural Fund (2019-MS-284); National Engineering Laboratory for Mobile Source Emission Control Technology (NELMS2018A04); University level innovation team of Shenyang Normal University; Major Incubation Program of Shenyang Normal University (ZD201901).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All the data during the study appeared in the submitted article.

Acknowledgments: The instruments and equipment used in this work are supported by Major Platform for Science and Technology of the Universities in Liaoning Province: The Engineering Technology Research Center of Catalysis for Energy and Environment and The Belt and Road International Joint Research Center of Catalysis for Energy and Environment.

Conflicts of Interest: The authors declare no conflict of interest.
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