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Silver supported electrospun CeO_2 fibrous catalyst with macro-structure for diesel soot combustion

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Abstract

Catalytic combustion of diesel soot is a key technology in meeting tightening emission regulations. Since the soot is a solid reactant with diameters in sub-μm to μm ranges, efficient soot oxidation catalysts such as Ag/CeO_2 should have suitable porous structure to ensure good soot/catalyst contact. Inorganic nanofiber webs prepared by an electrospinning method have a characteristic three dimensional structure with high surface area and tunable inter-fiber pores close to the size of soot, so that electrospun CeO_2 nanofibers must be possible candidates for PM oxidation catalysts. Hence, in this study, electrospun CeO_2 nanofibers with and without the Ag active ingredient were prepared, and their soot oxidation performance was evaluated. Soot combustion performance of Ag/CO_2 and CeO_2 nanofibrous catalysts were close to those of most active catalysts hitherto reported.

1. Introduction

Diesel engine is one of the environmentally -friendly vehicle devices, because it emits less CO_2 and is more fuel efficient, compared with gasoline engine. However, there are still the great challenges about the emission control of particulate matter (PM). Currently, the various catalysts have been studied for effective soot combustion using platinum group metals (PGM)-free catalyst, including pure oxides, perovskites and spinel oxide catalysts, alkali and alkali earth metals catalysts and cerium oxide catalysts [1-5]. Among them, catalysts based on cerium have been widely suggested for effective accelerating soot oxidation, because cerium oxides with fluorite structure can be made for the redox transfer of Ce^{3+} and Ce^{4+} ion states [6].

2. Experimental

2.1. Preparation of nanofibrous CeO_2 and Ag/CeO_2 catalyst

Nanofibrous CeO_2 catalyst was prepared by electrospinning method. To synthesize precursor solution, $Ce(NO_3)_3{\cdot}6H_2O$ and PVP were mixed in DMF-EtOH solution. The precursor solution was then electrospun via about 18 kV of high voltage. A Schematic illustration of the electrospinning process is shown in Fig. 1. Finally, collected fiber webs were calcined at 500, 800 and 1000°C in air to completely remove the polymer and produce the CeO_2 nanofiber webs.

4.5 wt% Ag/CeO_2 nanofiber was synthesized by the loading and decomposition of $AgNO_3$. The prepared CeO_2 nanofiber webs were mixed in an aqueous solution of $AgNO_3$, and then they were heated at 250°C for evaporation to dryness. After drying, collected materials were thermally treated at 350°C for decomposition of metal complex salts and then calcined at 500°C.

2.2. Soot combustion performance

To evaluate the soot combustion performance, 5 wt% carbon black (Sigma-Aldrich) as a simulated model material of diesel soot and catalyst were mixed by using tight contact (TC) and loose contact (LC) modes. TGA of soot combustion was measured with Shimadzu DTG-60 under air

condition (100 mL min^{-1}) and heating rate of 10°C min^{-1}.

3. Reusults and discussion

The morphology of fibrous structure was characterized by using SEM, showing images and fiber diameter distribution of CeO_2/PVP and CeO_2 nanofibers. Average diameter of CeO_2 fiber presented narrow distribution, together with the reduced diameter. Each selected 100 samples showed the fibers with average diameter of 770 nm before calcination. The value decreased to 246 nm after calcination at 500°C, 253 nm at 800°C, and 241 nm at 1000°C (see Figure. 2). The reduced average diameter suggests that a distance between inter-particulates in the fiber decreased due to the PVP removal.

As shown in Figure 3b and c, Ag/CeO_2 fiber is irregularly composed of two elemental components of Ag (red spots) and Ce (white spots) atoms. Further evidence of Ag on the CeO_2 fiber was provided from the result of overall EDS spectrum, showing the Ag and cerium peaks in Figure 2a.

Table 1 shows the TG and DTG data of diesel soot combustion with CeO_2, Ag/CeO_2 fibrous catalyst and reference CeO_2 (JRC-CEO-3) without Ag under LC and TC mode. The maximum temperatures for soot combustion (T_{max}) increased from 429 to 513°C with increasing the calcination temperatures (500, 800, 1000°C) and decreased with the increasing surface area. Additionally, the values of T_{ig} (soot ignition starting temperature) of CeO_2-500, CeO_2-800 and CeO_2-1000 were observed at 294, 379 and 381°C, and also completion temperatures (T_f) of soot combustion were observed at 497, 571 and 578°C, respectively. Similarly, the observed values of T_{ig}, $T_{max,L}$, $T_{max,H}$ and T_f in LC mode increased in conformity with increasing the calcination temperature. Under the LC mode, two maximum temperatures ($T_{max,L}$ and $T_{max,H}$) were shown. The lower temperature ($T_{max,L}$) was associated with oxidation of soot contacted with catalyst (catalytic combustion), while higher temperature ($T_{max,H}$) was related to oxidation of non-contacted soot.

The TG and DTG data of Ag/CeO_2 fibers were shown in Table 1. The T_{max} values of Ag/CeO_2-500, Ag/CeO_2-800 and Ag/CeO_2-1000 were observed at 429, 481 and 496°C in TC mode, while the T_{max} values in LC mode were obtained at 487, 485 and 614°C, respectively. Although only Ag/CeO_2-500 in LC mode was equal to CeO_2-500 in TC mode due to compact mixing of catalyst and carbon black in TC mode, the overall performance of Ag/CeO_2 fibers was generally higher than CeO_2 fibers under both LC and TC mode (see Table 1). This result distinctly demonstrated that the catalytic property of Ag is more efficient than impact of surface area.

4. Conclusion

Nanofibrous Ag/CeO_2 catalysts have been successfully prepared by electrospinning and Ag loading. The nanofibrous Ag/CeO_2 with the appropriate calcination temperature exhibited good catalytic performance in soot oxidation.

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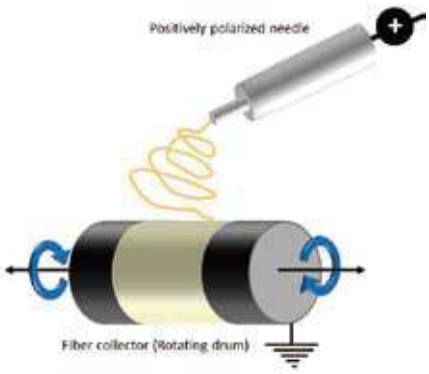

Figure 1. Schematic illustration of the electrospinning process.

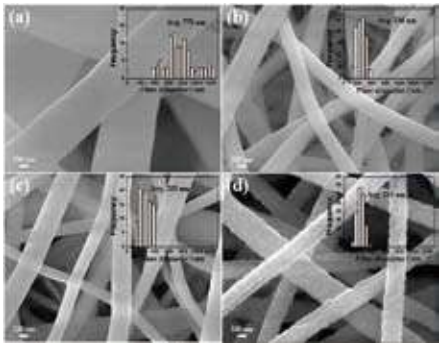

Figure 2. SEM images of electrospun nanofibers: (a) CeO_2/PVP nanofibers, (b) CeO_2 nanofibers calcinated at 500°C, (c) CeO_2 nanofibers calcinated at 800°C and (d) CeO_2 nanofibers calcinated at 1000°C

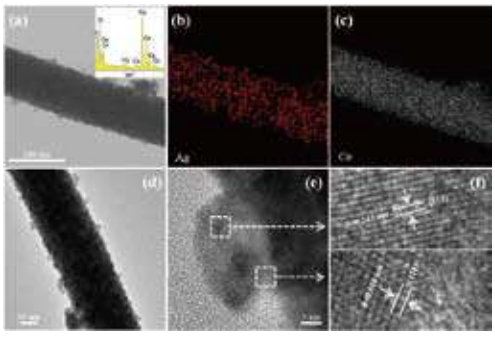

Figure 3. DES and HR-TEM images of Ag/CeO_2 nanofiber: (a - c) DES (insert: EDS spectrum) and (d - f) HR-TEM images

Table 1. The information of surface are and catalytic performance of the prepared samples under the TC and LC mode.

Catalyst	S_{BET} (m^2 g^{-1})	T_{max} (°C)[a]	
		TC mode	LC mode
CeO_2-500	20.4	429	465 596
CeO_2-800	3.45	504	530 633
CeO_2-1000	3.40	513	536 639
Ag/CeO_2-500	5.07	429	- 481
Ag/CeO_2-800	3.07	484	- 485
Ag/CeO_2-1000	2.74	496	- 514
JRC-CEO-3	81.94	448	- 606

[a] Temperature for the highest oxidation rate