Study on Nano Fibrous Catalysts Prepared by Electrospinning Method for Control of Diesel Exhaust Emissions

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（エレクトロスピニング法で調製したナノファイバー触媒のディーゼル排ガス処理特性に関する研究）

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主 論 文 の 要 旨

Thesis Summary

Diesel internal combustion 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, due to the high cost of platinum based catalysts, various catalysts have been studied for effective soot combustion using platinum group metals (PGM)-free catalyst, including pure oxides, perovskites and spinel oxides catalysts, alkali and alkali earth metals catalysts and cerium oxides 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]. Furthermore, alkaline and alkaline earth perovskite-type oxides have been reported to exhibit high catalytic activity for soot combustion owing to improved oxygen mobility because of the formation of ion vacancies [7, 8]. As the synthetic method, electrospinning is a very convenient method that uses an electrical charge to fabricate nanofiber mats [9]. In general, electrospun nanofiber mats exhibit high porosity [10]. Hence, the change of morphology from particles to fibers can significantly increase the surface area for catalytic reaction [11], especially, in the reaction of macro-pore sized feeds, such as soot oxidation. The increased pore sizes of catalyst are able to conduct an ingression of soot into their inner pores, which is attributed to the significant increase of contact area between catalyst and soot. In this thesis, CeO_2, $La_{1-x}Sr_xCo_2Fe_8O_{3-\delta}$ perovskite, ZrO_2 nanofibrous mats with uniform three dimensional structure and large pore size (> 50 nm, macroporous structure) were prepared by electrospinning method followed by thermal treatment. Ag or Mn nanoparticles

were loaded on the surface of the prepared nanofiber to accelerate the catalytic oxidation of diesel soot. For performance of the diesel soot oxidation, a simulated model diesel soot substance was prepared by mixing 5 wt% carbon black with the prepared catalyst and then applied to two types of contact mode (tight contact (TC) and loose contact (LC)) [12], and compared with commercial or particle type catalysts.

Firstly, as shown in Fig. 1, ceria oxide (CeO_2) nanofibers with diameters of about 250 nm were produced via the electrospinning method. They were then applied as new support materials for silver nanoparticles and their effectiveness as diesel soot oxidation catalysts was examined. The crystal structure of the Ag was confirmed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HR-TEM), and energy dispersive spectroscopy (EDS). The diesel soot oxidation experiment was performed using a mixture of carbon black and the fabricated catalyst. In the tight contact and loose contact modes, the highest temperatures of both the CeO_2-fiber-supported Ag catalysts (Ag/CeO_2) calcined at 500 ◦C and the CeO_2 fibers calcined at 500 ◦C were shifted to a lower temperature range, compared with JRC-CEO-3 (a commercial catalyst). In addition, the activation energy also showed similar catalytic properties.

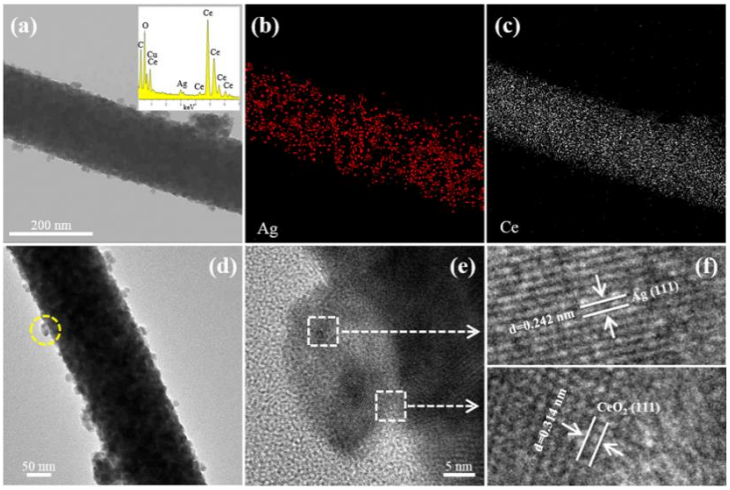

Figure 1. DES and HR-TEM images of Ag/CeO_2-500 nanofibers: (a - c) DES (inset: EDS spectrum) and (d - f) HR-TEM images.

Secondly, as observed in Fig. 2, we report $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-\delta}$ perovskite oxide catalysts

with a unique three-dimensional (3D) fiber web structure that increases the large contact area by trapping soot in the unique pore structure for effective catalytic activity. This feature was carefully analyzed using scanning transmission electron microscopy (STEM) tomography to investigate the location of the soot on the web. The structure of the web, with a thickness of approximately 55 µm, indicated that the soot particles were caught by the 3D pores between the fibers. The relationship between the Sr amount and activate oxygen was also characterized by means of XPS. The results show that the Sr amount of 0.4 produced the highest amount of active oxygen species (O^-) that are essential for soot oxidation reaction. The developed catalyst exhibited a good catalytic performances due to the optimized perovskite chemical structure and the greatly increased number of the contact points owing to the 3D inter-fiber spaces.

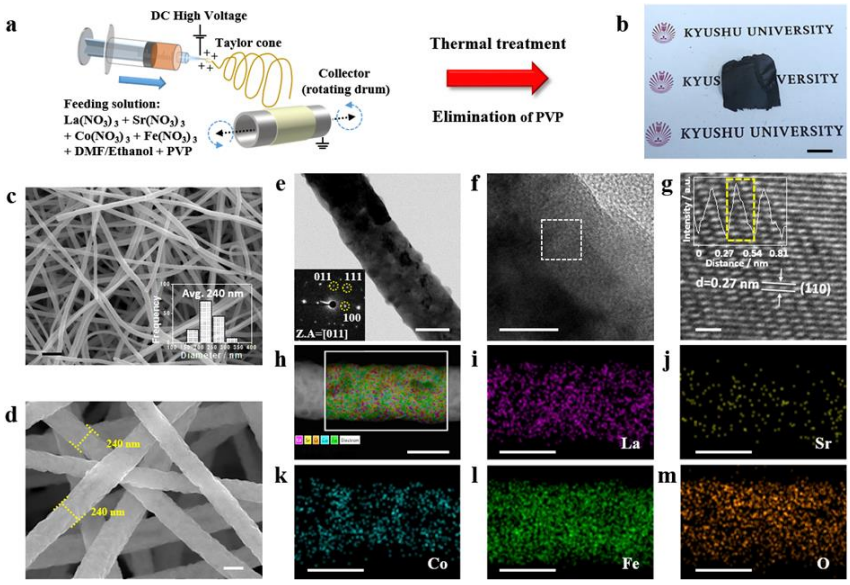

Figure 2. Schematic illustration and morphological characterization of the electrospun LSCF6428-web. (a) The synthesis process of fabricating LSCF nano-fibers via the electrospinning method and subsequent calcination. (b) Digital photograph of the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ fiber web calcined at 800 ℃. Scale bar, 1 cm. (c and d) SEM image of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF6428) nano-fibers (insert: fiber diameter distribution). Scale bars, 1 µm (c) and 200 nm (d). (e) Bright-field STEM image of LSCF6428 (inert: SAED pattern). Scale bar, 100 nm. (f and g) HRTEM images of LSCF6428 (insert: line profile). Scale bar, 20 nm (f) and 1 nm (g). (h-m) dark-field STEM image and EDX elemental mapping results for the LSCF-6428 fiber. Scale bar, 100 nm.

Finally, Ag and/or Mn particles loaded mesoporous zirconia oxide (ZrO_2) nanofibers were prepared by the electrospinning method followed by calcination at 600 ◦C for catalytic oxidation of diesel soot particles and benzene, as shown in Fig. 3. The presence and crystal structure of loaded Ag and Mn particles were confirmed by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The prepared catalysts were evaluated for their soot and benzene oxidation performance. Although ZrO_2 nanofibers with loaded Ag species exhibited better soot oxidation catalytic activity than the Mn loaded ZrO_2 fiber and pristine ZrO_2 nanofiber, Mn loaded ZrO_2 fibers also showed the high catalytic activity of benzene oxidation.

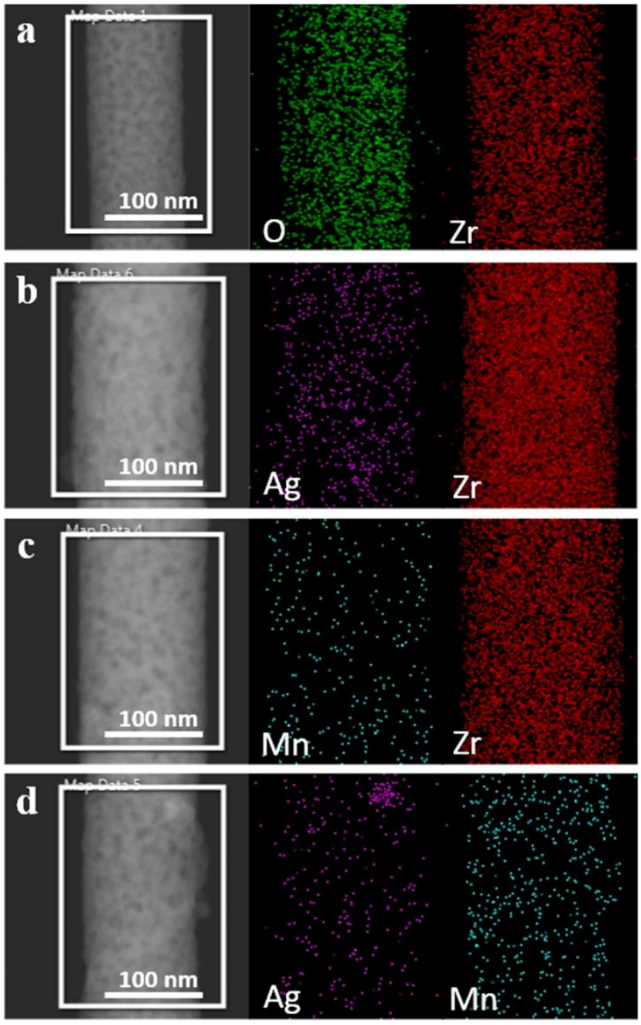

Figure 3. EDS mapping images of (a) ZrO_2, (b) Ag/ZrO_2, (c) Mn/ZrO_2 and (d) Ag-Mn/ZrO_2.

In conclusion, we suggested the Ag/CeO_2, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, Ag/ZrO_2 (or Mn/ZrO_2) fibrous catalysts with the large contact points between the soot particles and catalyst surfaces for diesel soot combustion. They showed higher catalytic activity than particle type catalyst, which is attributed to increase the number of triple phase boundary (TPB) sites. Therefore, it is confidently expected that developed fibrous materials can be a new approach and solution for control of pollutant from the diesel system.

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