Development of catalytic combustion-type monitoring devices of diesel particulate matter

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: Development of catalytic combustion-type monitoring devices of diesel particulate matter

(接触燃焼式ディーゼルパティキュレート検知デバイスの設計指針に関する研究)

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論 Ý 内 旨 容 Thesis Summary

The development of catalytic combustion-type PM monitoring devices of diesel particulate matter was subjected in this thesis. In order to achieve effective PM sensing devices, it is essential to conduct a detailed research on catalytic materials, including their morphology, their active species and thermal conductivity. Therefore, we investigated the CB oxidation activity of catalyst materials, the in-situ chemical state of the Ag active species during CB oxidation, CB sensing performance, and the correlation between the thermal conductivity of catalytic materials and its sensing performance in each chapter.

The major conclusion of each chapter are as follows:

In chapter 1, the background of diesel engines, the diesel vehicles emission standards, the mechanism of the PM formation and its characterization were introduced in this chapter. Furthermore, several technologies of PM control which are popular for laboratory test or practical application in market were also reported. Additionally, the background of PM sensor in terms of its classification and the present research status were indicated.

In chapter 2, the properties of the several catalyst materials (Ag/HZSM-5, Ag/TiO₂, Ag/α-Al₂O₃, Ag/CeO₂ and Ag/SiO₂) and their CB oxidation performance were discussed. Ag/HZSM-5 (890) and Ag/TiO₂ exhibits a higher CB oxidation activity among them in TC mode, but not good in LC mode for Ag/HZSM-5 (890) catalyst. The Ag/SiO₂ catalyst shows the best in LC mode among them. Furthermore, the Ag/HZSM-5 (890) shows the best CB oxidation activity when the Ag content is fixed at 4.5 wt.%. In addition, we compared the CB oxidation activity of the Ag supported HZSM-5 with the high Si/Al ratio (1500, Ag/890) and the low Si/Al ratio (40, Ag/840), showing that Ag/890 catalyst exhibits a better oxidation activity than the Ag/840 catalyst. There are two oxidation stages in TC mode and a low catalytic performance in LC mode with Ag/840 catalyst. The reason is that a lot of Ag ions exchange with the Bronsted acid sites of HZSM-5 (840) and exist in the pores of HZSM-5 (840), resulting in a huge reduction of the contact points between the CB and the Ag active species.

In chapter 3, the in-situ chemical state of Ag species in Ag/HZSM-5 (Si/Al=1500) were investigated in detail. Well dispersed ultrasmall Ag nanoparticles (NPs) are prepared on HZSM-5 support by impregnation method and their properties as CB oxidation catalysts were systematically studied. The Ag catalyst are found to exhibit superior oxidation performance with low ignition temperature of as low as 298 °C in the TC mode. The low ignition temperature is ascribed to the well dispersed silver nanoparticles that increases the physical contact area with CB particles. Using in-situ XAS measurements, we were able to unambiguously correlate the CB oxidation activity to the metallic Ag, which are stable from 250 to 600 °C. However, when further increasing the temperature, e.g., at 800 °C, cationic Ag appears due to the ion exchange interaction with the OH groups on the surface of HZSM-5. Such interaction increases the high temperature sintering stability of ultrasmall Ag NPs, providing the fabricated Ag/HZSM-5 catalyst

reproducible CB oxidation performance after multiple cycles measurement. Another possibility for explaining the stability of metallic Ag NPs is the physical anchor effect of the pores on the surface of HZSM-5.

In chapter 4, the soot-sensing properties of the combustion-type sensor coated with Ag-supported catalysts (Ag/TiO₂, Ag/ α -Al₂O₃, and Ag/CeO₂) were investigated. The catalyst with an intrinsically high CB oxidation activity had a high response speed although the response speed had no relationship with the CB oxidation activity regardless of the contact state between the catalyst and the CB. Moreover, the difference in CB oxidation activity between the TC and LC modes was consistent with the difference in the response speed between V_{10} and V_{50} . We concluded that the catalyst with the high intrinsic CB combustion activity improves the response property at an initial combustion. On the other hand, the catalyst having the CB oxidation activity, which does not depend on the contact state between the CB and the catalyst, improves the response property at later oxidation. In this study, we demonstrated not only the preliminary result of the detection for the soot oxidation under operation temperature but also guided a catalyst design for the soot oxidation.

In chapter 5, the relationship among the CB oxidation activity, the CB sensing performance and thermal conductivity of the Ag /HZSM-5 and Ag/SiO₂ catalysts were discussed. For the Ag/SiO₂ catalyst, the CB sensing performances were consistent with the CB oxidation activity. However, this rule did not apply to the Ag/ HZSM-5 catalyst with porous structure, which showed a poor sensing performance even though it exhibited an excellent intrinsic CB oxidation activity. The Ag/HZSM-5 catalyst with porous structure inhibited the CB oxidation heat from transferring to the Pt detector inside of the sensor element, resulting in a poor sensing performance of the combustion-type soot sensor. In other words, the improvement of the soot sensing performance depends on not only excellent intrinsic soot catalytic activities of the catalysts but also the superior thermal conductivity of these materials.

The future research related to the catalyst will also be focused on the supported silver catalyst in various complex environments that matches the application situations, such as multiple catalysis which catalyze the soot and gaseous exhaust together. On the other hand, considering the soot sensing performance of this combustion-type sensor device depends on two aspects—the intrinsic soot catalytic activities of the catalysts and the superior thermal conductivity of these materials. So it cannot monitor the soot combustion state online accurately if ignoring the thermal conductivity of catalytic materials. Therefore, we try to improve the sensing device and make it more available in the real application. Such as improving the detecting way from electric signal which conversed from soot combustion heat to the change of O_2/CO_2 partial pressure in the combustion chamber. Additionally, we plan to use the real diesel PM instead of the carbon black used in our previous research, and measure the real catalytic performance and its real sensing performance.