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Response of Catalytic Combustion-type Sensor to Different Amounts of Diesel Particulate Matter

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The catalytic combustion-type PM (diesel particulate matter) sensors coated with Ag/TiO₂ and Pt/TiO₂ catalysts were fabricated for the selective detection of soot and SOF (soluble organic fraction), respectively, and their responses were evaluated against different amounts of soot and PM which were pre-loaded on the sensor elements. The possible dependence of the sensor signal on the amount of SOF and soot was proven. It was also suggested that the enhancement of the oxidation rate of the solid PM on the surface of the sensor elements was important in order to realize the catalytic combustion-type PM sensor.

1. Introduction

Diesel-engine vehicles are superior to gasoline-engine vehicles in combustion efficiency, fuel economy and emission of CO and CO₂ gases¹⁾. The diesel engine, however, exhausts harmful substances of nitrogen oxides (NOx) and diesel particulate matter (PM). Therefore, the removal technology of harmful substances should be developed for diesel vehicles to survive. As for PM removal, diesel particulate filter (DPF) loaded with a catalyst system is regarded as the most effective and promising technology to control PM emission²⁻⁴⁾. In order to guarantee the efficient and stable operation of the diesel engine system with the DPF after-treatment, onboard PM monitoring technology is indispensable. PM sensors so far proposed are physical sensors based on optical⁵⁻⁸⁾, electrical resistance⁹⁻¹²⁾ and radio-frequency¹³⁾ methods as well as an electrochemical device consisting of a proton-conductor and Pt electrodes^{14,15)}. Very recently, we have proposed a catalytic combustiontype PM sensor as a new type of a chemical sensor¹⁶. Catalytic combustion-type sensors detect combustible gases by converting the heat generated by the catalytic combustion of targeted gases into electric signal, and are widely used to detect combustible gases such as hydrogen, volatile organic compounds (VOCs), and various hydrocarbon gases¹⁷⁻²⁰⁾. We have demonstrated¹⁶⁾ that PM can be in principle detected by the catalytic combustion-type sensor because PM contains soot (C) and soluble organic fraction (SOF) as combustible substances and that the selective detection of SOF and soot is possible by using catalysts which can selectively oxidize each component. In addition to the simple sensor structure, the selective detection of SOF and soot is an advantage of the proposed combustion-type PM sensor over sensors so far reported.

The principle of the catalytic combustion-type PM sensor is shown schematically in Fig. 1. Solid PM comes flying on the exhaust gas stream and lands on the surface of the sensor element. When the surface of the element is

active enough to oxidize PM at the operating temperature, the temperature of the element increases by the heat of combustion and the temperature increase is detected by the resistivity change of a Pt wire incorporated in the body of the element. In addition, if we use catalysts and/or operation temperatures which can separately oxidize SOF and soot, selective detection of SOF and soot is possible.

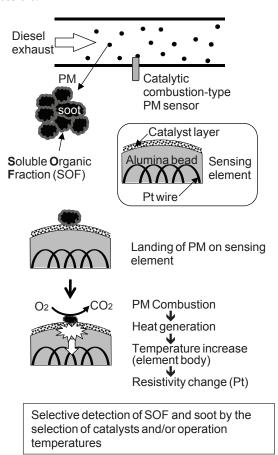


Fig. 1 Concept of catalytic combustion-type PM sensor.

Since PM is a solid substance, it is quite difficult to simulate diesel exhausts in laboratory tests and to evaluate the sensing performance under the simulated real condition. This is a reason why the programmed heating of the sensor pre-loaded with PM was used in our study¹⁶; PM was pre-loaded on the sensing element, and the sensing performance was measured during the programmed heating in air. Even with the preliminary study¹⁶, we have succeeded to show the possibility to construct the catalytic combustion-type PM sensor and to detect SOF and soot separately by the proper selection of the catalytic materials and operation temperatures.

In order to realize the catalytic combustion-type PM sensor, more detailed investigations are required with respect to relation between the sensor response and concentration of PM, how to trap or accumulate PM on the surface of sensor elements in the exhaust flow, sensing characteristics under isothermal operation, and so on. The purpose of the present study is to measure responses of the catalytic combustion-type PM sensor which we have just developed against different amounts of pre-loaded soot and SOF.

2. Experimental

2.1 Preparation of catalysts

Two TiO₂ supported catalysts, 5 wt% Pt/TiO₂ and 5 wt% Ag/TiO₂, were used in this study, which were developed as SOF and soot oxidation catalysts, respectively²¹⁾ and used in the previous study on catalytic combustion-type PM sensor¹⁶⁾. They were prepared by an ordinary impregnation method and calcination in air at 700 °C for 5 h from TiO₂ (Reference Catalyst of Catalysis Society of Japan, JRC-TIO-4), diammine dinitro platinum (II) (Kojima Chemicals, HNO₃ solution) and silver nitrate (Kishida Chemical). XRD measurements (Rigaku, RINT2200) revealed the presence of Ag and Pt metals on rutile TiO₂. Specific surface areas measured by the BET method (BELSORP-mini, BEL JAPAN, Inc.) were 9.8 and 7.2 m² g⁻¹ for Pt/TiO₂ and Ag/TiO₂, respectively.

2.2 Catalytic performance for PM oxidation

Carbon black (CB, Sigma-Aldrich) was used as a substitute for soot. Hexadecane ($C_{16}H_{34}$, density; 0.771-

0.777 g ml⁻¹ (20 °C); Tokyo Chemical Industry, Co. Ltd.) was used as a substitute of SOF, because it is one of main components of diesel oil. Simulated PM was prepared by liquid-phase adsorption of hexadecane on CB in n-hexane²¹. Catalysts and simulated PM (ca.5 wt%) were mixed by spatula carefully for 10 min. PM oxidation reaction was measured by thermogravimetry (TG) and differential thermal analysis (DTA) (Shimadzu, DTG-60). The catalyst/PM mixture was heated at a rate of 10 °C min⁻¹ from 30 °C to 800 °C in a flow of synthetic air (21% O_2 and 79% N_2 , 100 mL min⁻¹).

2.3 Fabrication of sensing elements

Fig. 2(a) shows the schematic drawing of the sensing device. γ-Al₂O₃ bead with a diameter of about 1.5 mm, which was fabricated on a coiled Pt wire heater, was used as base structures of the sensing and compensating elements. The sensing element was fabricated by coating a catalyst layer on the alumina bead, as schematically shown in Fig. 2(b). A coating paste was prepared by mixing 0.2 g of a catalyst with 1.0 g of α-Terpineol as a binder (nacalai tesque, C₁₀H₁₈O) by a mixer (LMS, VTX-3000L) for 30 min. The coating paste was applied on the surface of the alumina bead by handwork with a paintbrush so as for the paste to uniformly cover the alumina bead, and then the element was heated at 600 °C for 2 h in air by the internal Pt heater in order to remove the binder and stabilize the sensing element. Although the exact amount of the loaded catalyst was not determined by the present coating method and the loading of the strictly equal amount in each coating procedure was not expected, SEM observation (HITACHI, Miniscope TM-1000) confirmed that the surface of the alumina beads was nearly completely covered with the catalyst layers.

Due to the difficulty in supply of solid PM with the gas stream, the method of pre-loading of PM on the sensor element was adopted (Fig. 2(b)). The paste with CB (0.05 g) and α -Terpineol (1.0 g) was prepared by the method same as the preparation of the catalyst paste. The CB layer was formed on the catalyst layer (CB-loaded sensing element) by the hand-application of the CB paste on the sensing element and the subsequent heat-treatment at 200 °C for 1 h in air by the internal Pt heater to remove the binder. In addition to the standard CB-loaded sensing

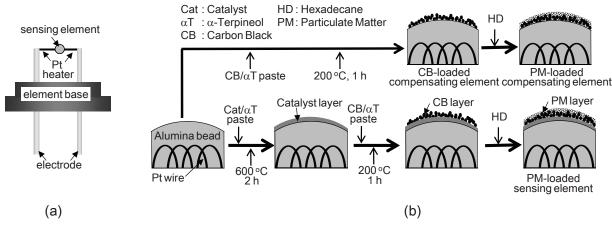


Fig. 2 Sensing device (a) and fabrication procedure of sensing elements (b).

elements mentioned above, three CB-loaded sensing elements were prepared to check the effect of the CB loadings (Table 1). Because of the loading method of CB, the exact amount of CB loaded on the sensor element was not determined, but the amount expected to be roughly proportional to the concentration of the paste (CB/ α -Terpineol).

Table 1 CB-loaded sensing elements prepared

Element	Composition of coating past	
	CB (g)	α-Terpineol (g)
CB-loaded sensing element S	0.05	1.0
CB-loaded sensing element L	0.005	1.2
CB-loaded sensing element M	0.015	1.2
CB-loaded sensing element H	0.030	1.2

To prepare the PM-loaded sensing element, hexadecane was dropped on the surface of the standard CB-loaded sensing element S as uniform as possible. The amounts of hexadecane loaded were 5 μl (PM-loaded sensing element H), 3 μl (PM-loaded sensing element M) and 1 μl (PM-loaded sensing element L). Liquid hexadecane was expected to permeate through the porous CB layer, resulting in the formation of simulated PM by the adsorption of hexadecane on CB as well as the contact between hexadecane and the catalyst.

CB-loaded and PM-loaded compensating elements without the catalyst coating were prepared directly on the alumina bead by the procedures same as that for the corresponding sensing elements (Fig. 2(b)).

2.4 Measuring system of sensing performance

As sown in Fig. 3(a), sensing and compensating elements were placed in a sensor chamber, and the potential difference between two elements was used as a sensor signal which was derived from a bridge circuit (Fig. 3(b)). Gas flow rate was 100 ml min⁻¹. In the programmed heating method under flowing synthetic air, the elements were heated from 150 to 600 °C with an interval of 50 °C; the temperature of the elements was kept constant for 5 min at each measuring temperature. Isothermal evaluation was performed by the following two methods. For the purpose of the SOF detection, the temperature of the elements was increased as a stepwise manner from 30 to 200 °C under flowing air. For soot detection, on the other hand, the temperature of the elements was kept at 550 or 600 °C, and the gas flow was switched from N₂ to air.

3. Results and Discussion

3.1 Comparison between PM combustion and detection under programmed heating conditions

Fig. 4 shows the oxidation of simulated PM with Pt/ TiO₂ and Ag/TiO₂ catalysts measured by TG/DTA. In the present PM/catalyst mixture, weight losses originated in SOF and soot (CB) should be 2 wt% and 3 wt% within a weighting error, respectively. Weight loss was clearly

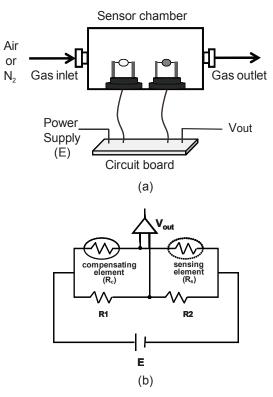


Fig. 3a Arrangement of sensing and compensating elements (a) and electrical circuit (b).

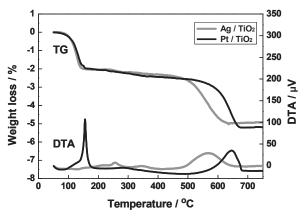


Fig. 4 TG and DTA curves of simulated PM with Pt/TiO₂ and Ag/TiO₂ catalysts.

divided into two steps; the first step with ca. 2 wt% loss was observed below 200 °C and the second one with ca. 3 wt% loss was observed above 450 °C. It can be ascribable that the first and second steps are originated from SOF and soot, respectively. The temperature range of the first weight loss was almost the same for the two catalysts, but an exothermic peak appeared with Pt/TiO₂ but not with Ag/TiO₂, indicating that the SOF in simulated PM was oxidized on Pt/TiO₂ but it desorbed (evaporated) from the Ag/TiO₂ catalyst before undergoing oxidation. These results indicate that Pt is more active for SOF oxidation than Ag. It is noted that the absence of the exothermic peak does not necessarily mean the inertness of Ag against SOF oxidation, because

in the present experimental method, desorption of SOF might occur below the temperature at which Ag becomes active for SOF oxidation.

Weight losses in the second step were accompanied with exothermic peaks, which is a sign of the occurrence of soot oxidation. The weight loss with Ag/TiO_2 occurred at lower temperature region than that with Pt/TiO_2 , indicating that the former is more active for soot oxidation than the latter. There results indicate that Pt is more active than Ag for the SOF oxidation and that the reverse is true for the soot oxidation.

Fig. 5 shows temperature dependences of the output voltage of sensors with Ag/TiO2 and Pt/TiO2 catalysts. PM-loaded sensing element H and the corresponding compensating element were heated stepwise from 150 °C to 600 °C under flowing air; the temperature of the elements was kept constant for 5 min at each measuring temperature. Although heating program used in Fig. 5 is different from that with the constant heating rate in TG/DTA measurements (Fig. 4), both results reflect the temperature dependence of PM oxidation. The obvious signal from the Pt/TiO₂-coated sensor was observed only when the temperature was kept at 150 °C. By referencing the TG/DTA result, the signal can be ascribable to the oxidation of SOF. SOF is oxidized on the sensing element while it desorbed from the inert referencing element (alumina bead) without generating heat. It is noted that the absence of the signal by SOF oxidation above 200 °C is due to the fact that pre-loaded SOF was completely exhausted by combustion during the operation at 150 °C. With the Ag/TiO₂-coated sensor, on the other hand, obvious signal appeared above 500 °C which is consistent with soot oxidation performance observed by TG/DTA. Drifts of the base lines with an increase in temperature seem to originate from differences in the heat capacity of sensing and compensating elements.

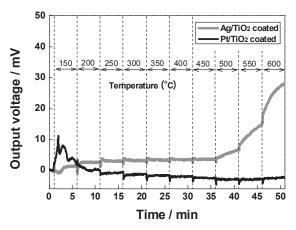


Fig. 5 PM sensing characteristics of PM-loaded sensing element H coated with Pt/TiO₂ and Ag/ TiO₂ catalysts.

3.2 Consideration to the relation between combustion and detection of PM

The above-mentioned results clearly indicate the possibility of detection of soot and SOF by the combustion-type sensor. For the conventional combustion-type sensor to detect gaseous molecules, the combustion of the target molecule proceeds on the surface of the sensor element, so that the heat generated by the combustion would be effectively conducted to the element body to give the sensor signal. Provided that the combustion reaction is the first order with respect to the concentration of the target molecule, the rate of combustion reaction, that is the generated heat per a fixed period of time, is proportional to the concentration of the target molecules, thus making the quantitative detection possible.

In contrast to the catalytic oxidation of gaseous molecules, the oxidation of solid PM by a solid catalyst is complicated (Fig. 6). Catalytic oxidation of PM is a three-phase reaction between a gaseous reactant (O_2) , a solid reactant (PM) and a solid catalyst. Since PM lands on the catalyst surface from the exhaust flow by the multi-layer deposition, only tiny parts of the first-layer PM can contact with the catalyst surface. This means that the fraction of the three-phase boundary at which the catalytic reaction occurs is a little as compared with the total volume of the trapped PM, and the propagation of the reaction to the PM remote from the boundary is necessary to combust a majority of deposited PM. It is probable that the catalytic oxidation of PM, which proceeds in the vicinity of the catalyst surface, contributes instantaneously to the heating of the sensing element. With progress of the oxidation toward remote PM, the efficiency of the transfer of the combustion heat to the element might decrease. In addition, the rate of combustion seems to be high for the PM near the threephase boundary by the action of the catalyst and low for the PM remote from the catalyst. The un-uniformity of the PM combustion in the deposited layer should make the PM sensing complicated. As can be seen from Fig. 5, the sensor signals of Ag/TiO2-coated element by the oxidation of solid soot did not reach steady values within 5 min at 500, 550 and 600 °C. The slope of the sensor signal which is the rate of heating of the element increased with increasing temperature. It is natural that the magnitude of the slope is closely related with the rate of PM combustion and/or the amount of combusted PM.

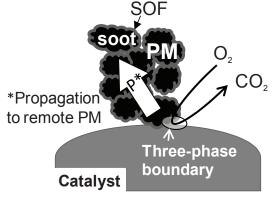


Fig. 6 Catalytic removal of PM at the three-phase boundary.

With taking such a complicated situation of PM combustion into consideration, the effects of pre-loading amount of CB and SOF were investigated in the following sections.

3.3 Effect of pre-loading amount of CB on sensing performance of Ag/TiO₂-coated element

Fig. 7 shows the PM sensing characteristics of the CB-loaded sensing elements L, M and H coated with the Ag/ TiO_2 catalyst: the programmed heating condition was the same as that used in Fig. 5. Sensor signals were observed above 500 °C, and the magnitude of the signal at each temperature increased with increasing the pre-loading amount of CB as L < M < H.

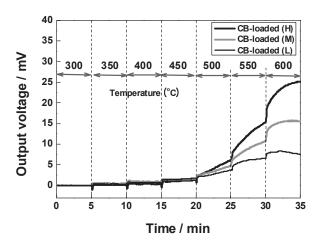


Fig. 7 PM sensing characteristics of CB-loaded sensing element L, M and H coated with Ag/TiO₂ catalyst.

The slope and shape of the output voltage during the operation at a constant temperature are different from sensing elements and operation temperatures. At 500 °C, for example, output voltages increased almost linearly with time for all the elements, indicating that the oxidation of CB did not reach the stead-state within 5 min. At 600 °C, on the other hand, the output voltage still increased with time for the element H, reached a steady value for the element M, and started to decrease for the element L. The decrease of the signal with the element L seems to be due to the fact that the amount of CB present on the element became insufficient to keep the temperature constant.

The ratio of the amounts of pre-loaded CB in sensing elements L, M and H are expected to be close to 1:3:6, though the exact values are not known under the present loading condition. If we assume that the oxidation of CB does not proceed below 450 °C, the amount of CB on sensing elements is in the ratio of 1:3:6 only when the temperature of the elements reaches 500 °C. The ratio of the output voltage at 23 min (3 min after reaching 500 °C) was 1(L):1.3(M):1.6(H). The slope of the voltage increase, which is considered to be relevant to the CB oxidation, was 1(L):1.4(M):2.3(H). Those ratios are far

from the ratio of the pre-loaded amount of CB probably due to the above-discussed non-uniformity of the oxidation of solid CB on the sensor element. Increases in sensor signals with the pre-loading amount of CB might originate from the increasing amount of oxidized CB both in contact with and remote from the catalyst, but the signal would not be proportional to the amount of pre-loaded CB because of the complicated situation of the CB combustion on the sensing element and transfer of the combustion heat to the element. If the deposited amount of PM (or CB) is enough low in order for the PM oxidation to proceed uniformly in the deposited layer and the deposited amount is proportional to the PM concentration in the exhaust, the quantitative detection of PM might be possible by the combustion-type sensor.

Under the assumed working condition of the combustion-type PM sensor, PM in an exhaust stream contacts with the sensor surface keeping at the constant temperature and undergoes the oxidation to generate heat. Therefore, evaluation of the sensing performance under the isothermal condition is indispensable. Used in the present isothermal evaluation of CB detection was the gas switching method from nitrogen to air at 550 and 600 °C (Fig. 8). When the atmosphere changed from N_2 to air, the sensor signals increased and reached the different steady values for the different CB-loaded

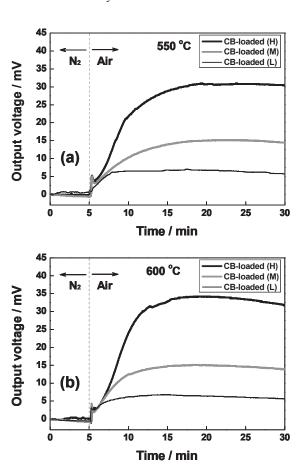


Fig. 8 PM sensing characteristics of CB-loaded sensing element L, M and H coated with Ag/TiO₂ catalyst under isothermal operation at (a) 550 °C and (b) 600 °C.

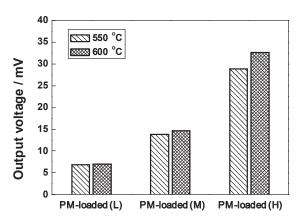


Fig. 9 Steady values of the output voltage observed with CB-loaded sensing element L, M and H coated with Ag/TiO₂ catalyst under isothermal operation at 550 and 600 °C. Data were taken at 15 min after the gas switching from N₂ to air.

elements. Fig. 9 shows steady values of the output voltage of the CB-loaded sensing elements L, M and H which were measured at 15 min after gas switching. For sensing element H, the output voltage at 600 °C was slightly larger than that at 550 °C. On the whole, however, the output voltages were hardly dependent on the operation temperature. As stated above, CB oxidation starts around 500 °C, and therefore the reaction proceeds at reasonably high rate at 550 and 600 °C. Even though the intrinsic rate of CB oxidation at 600 °C is higher than that at 550 °C, the fraction of oxidized CB, which is effectively used for the heating of the element body, might not be so much different because of the non-uniformity of CB oxidation. The ratios of the steady output voltages were 1(L):2.0(M):4.3(H) and 1(L):2.1(M):4.7(H) at 550 and 600 °C, respectively. Those ratios are still different from the expected value of 1:3:6, but the deviation under the isothermal condition is smaller than those discussed in the programmed heating experiments at 500 °C.

The rate of gas-phase oxidation is usually high enough to utilize it for combustion-type sensor and to guarantee the reasonable response time, if the conditions such as operating temperature and catalyst are properly selected. In the present case, Ag/TiO₂ is one of the most active catalysts for CB oxidation and temperatures of 550 and 600 °C are enough high for the efficient progress of the CB oxidation. Even under the suitable combination of the catalyst and the operation temperature, however, a few minutes (element L) and 10 min or more (element H) are required to reach the steady sensor signals. Time necessary to reach the steady value was shorter at high temperature due to the higher rate of the combustion reaction. The sensing element loaded with smaller amount of CB reached the steady values in shorter time, probably because the steady state of the oxidation throughout the CB layer might be realized easily with the small loading amount.

3.4 Effect of pre-loading amount of SOF on sensing performance of Pt/TiO₂-coated element

The sensing of SOF under the isothermal operation at 200 °C was investigated with PM-loaded sensing elements L, M and H with Pt/TiO₂ catalyst. As shown in Fig. 4, the Pt/TiO₂ catalyst becomes active for the SOF oxidation above 100 °C. Because the evaporation of SOF starts also above 100 °C in the case of Ag/TiO₂, the gas switching method couldn't be used for the isothermal detection of SOF. Instead, quick heating method was employed for the isothermal detection of SOF; PM-loaded sensing elements were quickly heated from 30 °C to 200 °C under flowing air.

Fig. 10 shows the time courses of the output voltage against the SOF detection. The output voltage increased suddenly when the temperature of the elements reached 200 °C and it exhibited complicated time courses. Judging from the shape of time course curves, SOF was removed from the sensor surface within 1 min (L) and 3 min (M, H) after reaching 200 °C. The ratio under the output voltage curves were in the ratio of 1(L):2.6(M):4.7(H) which must be proportional to the SOF molecules oxidized on the surface of the sensor element. The ratio expected from the pre-loaded SOF amounts is 1(L):3(M):5(H). Considering the possibility of evaporation of SOF during the heating process to and operating process at 200 °C, the observed ratio seems to be reasonably close to the expected value. It is probable that most of SOF molecules, which have desorbed (evaporated) from the remote PM, reach the surface of Pt/TiO₂ catalyst to be oxidized. It is recognized from Fig. 10, however, that the signal ratio at a designated time, for example, 20 sec after reaching at 200 °C is quite different from the ratio of the pre-loading amounts.

Under the assumed working condition of the combustion-type PM sensor, SOF molecules would reach the sensor surface by two states; gaseous molecules and adsorbed molecules on soot (CB). If the temperature of the exhaust is high enough for SOF molecules to behave as gaseous molecules, the detection of SOF might be

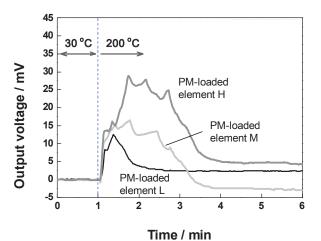


Fig. 10 SOF sensing characteristics of PM-loaded sensing element L, M and H coated with Pt/TiO₂ catalyst under the quick heating mode of the isothermal operation at 200 °C.

easy because the situation is close to the usual detection of gaseous molecules by the combustion-type sensor. When SOF molecules are adsorbed on soot (in the state of PM), the contact between PM and the catalyst as well as the propagation of the SOF oxidation in the adsorbed SOF layer might affect the sensing performance.

4. Conclusion

The responses of the catalytic combustion-type PM sensor against different amounts of soot and SOF were investigated. Ag/TiO₂ and Pt/TiO₂ catalysts were active for the oxidation of soot and SOF, respectively, and the sensor elements coated with Ag/TiO₂ and Pt/TiO₂ were used respectively for the selective detection of soot and SOF. Because of the difficulty in preparing the simulated diesel exhaust containing solid PM, model experiments were designed: PM was pre-loaded on the sensing element, and sensing performances were measured under the programmed heating condition in air or isothermal conditions which were realized by rapid switching of atmosphere from N₂ to air or by rapid heating. While the present results showed the possible dependence of the sensor signal on the amount of SOF and soot, issues to be investigated for the development of the catalytic combustion-type PM sensor have been clarified. The evaluation of the sensing performance in simulated or real diesel exhaust is of course necessary. In the basic aspect, the enhancement of the oxidation rate of the solid PM on the surface of the sensor elements is a key issue to be overcome. It might be necessary to investigate in more details from the aspects of the increasing contact between the catalyst and the PM landed on the sensing element as well as the operation modes of temperature.

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