Effects of O_3 and NO_2 on Catalytic Oxidation of Diesel PM

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Oxidative activities of ten different catalysts to particulate matter (PM) emitted from a diesel engine have been compared by thermogravimetric analysis under an atmosphere containing O_3 and NO_2. MnO_2 has been found to exceed noble metal catalysts in the PM oxidation efficiency even at 300 °C. The PM oxidative activities of transition-metal oxides possessing high formation enthalpies are enhanced by the active oxygen species owing to acceleration of redox catalytic cycles.

Diesel engines have a higher combustion efficiency and a lower CO_2 emission than gasoline engines. Thus, the spread of diesel engines has a beneficial effect on prevention of global warming. However, diesel engines emit particulate matter (PM) and nitrogen oxide (NO_x) that are harmful to human beings and should be removed.

Plasma technologies have a potentiality as an effective method for PM removal.[1] We have developed a dielectric barrier discharge (DBD) reactor driven by a pulse power supply. The DBD reactor has achieved a high effect on PM removal.[2] For the practical use of the DBD reactor on an actual vehicle for a prolonged time, however, more effective removal of PM deposited in the DBD reactor and lowering electric power consumption for the plasma discharges are necessary to inhibit deterioration in fuel economy. Therefore, we have searched catalysts that demonstrate high performance PM removal under plasma discharge conditions.

When the exhaust gas from a diesel engine is treated within the DBD reactor, O_3 and NO_2 are present in the reaction gas with PM; these elements are generated from O_2 and NO contained in the exhaust gas by plasma discharges. These active oxygen species, O_3 and NO_2, are known to oxidize PM by their oxidative power.[3] We have supposed that the active oxygen species affect also catalytic activities for PM oxidation. In this paper, we have compared PM oxidative activities of ten different catalysts by thermogravimetric analysis under an atmosphere containing O_3 and NO_2. Some earlier studies have reported the comparison of catalytic activity for PM oxidation.[4] To the best of our knowledge, however, little study has been reported on the effects of O_3 and NO_2 on the PM oxidation catalytic activity, considering diesel engine emissions and plasma discharges.

Transition-metal oxides were adopted as the main candidates for the PM oxidation catalyst in this study; these materials are known to have oxidative activities due to redox catalytic cycles. Noble metals and alumina were also examined on the PM oxidative activities for comparison, although noble metals should not be used more for after-treatment of the vehicle emissions owing to resource depletion and rising production cost. The catalyst powders evaluated in this study were TiO_2, ZnO, V_2O_5, Fe_2O_3, Co_3O_4, MnO_2, CuO, Pd, Pt, and Al_2O_3. All of these catalyst powders were of commercial origins and used without any treatment. The characteristics of evaluated catalysts are listed in Table 1.

A thermogravimetric differential thermal analyzer (TG/DTA, Thermo Plus 8120, Rigaku Co.) was used to examine the PM oxidation catalytic activity in the following manner. The respective catalysts were mixed with PM homogeneously in definite proportion (oxygen bound to metal atom [mol]/PM identified as carbon [mol] 1; Pt and Pd were identified as PtO_2 and PdO, respectively) as analysis specimens of TG/DTA. A definite quantity of the analysis specimen (PM 0.036 mol) was sampled and put into TG/DTA. The weight decrease in the sample was measured while the temperature increased from 30 to 500 °C at a constant rise rate of 5 °C/min. The gases fed into the TG/DTA were; 1) O_2 10%, O_3 100 ppm, and NO_2 100 ppm with He balance and 2) O_2 10% with He balance. The total gas flow rate was 100 mL/min for both these conditions. PM weight decrease ratios were calculated as the decrease in analyzed sample weight [mg] divided by the initial weight of PM [mg].

Figure 1 shows the PM weight decrease ratios at the temperatures 500 (a) and 300 °C (b) with each catalyst. In both of the Figures 1a and 1b, the filled bar graphs show the results under the condition of containing the active oxygen species, O_3 and NO_2, and the shaded bar graphs show the results under the condition without these oxygen species. The PM weight decrease ratios with MnO_2 and that with Co_3O_4 are relatively higher than those with the other transition-metal oxides. At 500 °C, these two catalysts have been found to exceed the noble metal catalysts in the PM oxidation efficiency with or without the active oxygen species. Additionally, the performance of MnO_2 is higher than those of the noble metals even at a relatively low temperature, 300 °C; this temperature is a value that the exhaust gas temperature of diesel engines should reach.[5] These

Table 1. Catalysts properties

	TiO_2	ZnO	V_2O_5	Fe_2O_3	MnO_2	Co_3O_4	CuO	Pd	Pt	Al_2O_3
Manufacturer	Wako	Wako	Wako	Kishida	Wako	Wako	Wako	Kishida	Kishida	Rigaku
Purity/%	99.9	99.0	99.0	99.0	99.5	99.7	99.7	99.9	99.9	99.9
Average particle size/μm	0.17	0.30	0.27	0.18	0.20	0.26	0.22	0.47	0.64	1.17
Specific surface area/$m^2 \cdot g^{-1}$	2.70	1.46	2.87	1.94	0.80	1.35	1.39	0.34	0.18	0.59
Formation enthalpy/$kJ \cdot g\text{-}O_{atom}^{-1}$	−469.9	−348.3	−310.1	−274.7	−260.0	−222.8	−157.3	−85.4	−40.0	—

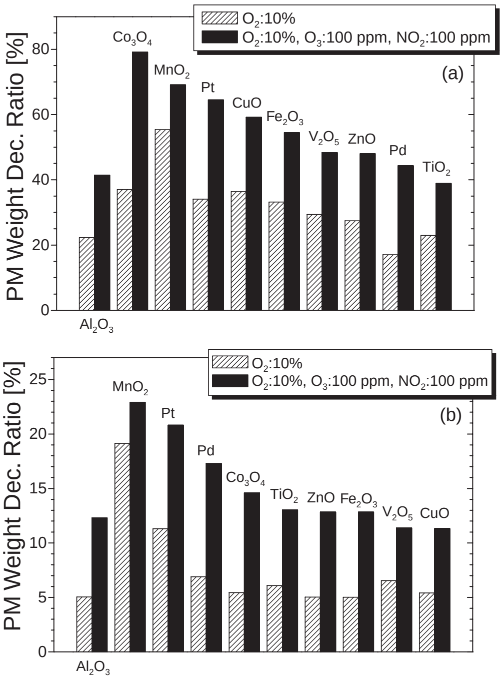

Figure 1. PM weight decrease ratios at the temperatures of 500 (a) and 300 °C (b) with catalysts.

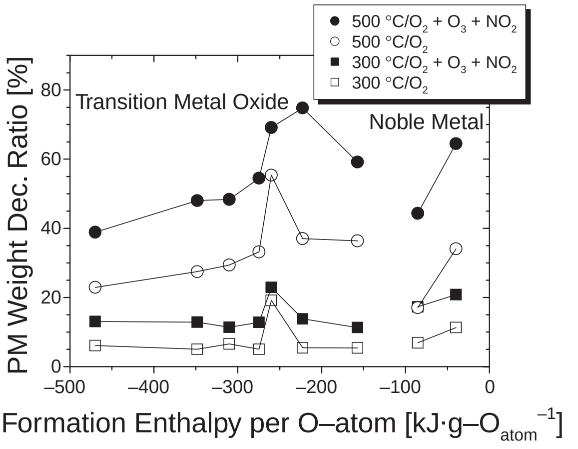

Figure 2. PM weight decrease ratios with respect to the formation enthalpies per oxygen atom of the catalysts.

results suggest that the transition-metal oxides, especially MnO_2, are effective to improve the performance of PM removal within the DBD reactor. These results, therefore, have significance in terms of reduction in noble metal usage.

The PM weight decrease ratios obtained under the presence condition of O_3 and NO_2 are higher than those obtained under the absence condition of O_3 and NO_2; this result means that the active oxygen species have the effect of accelerating the PM oxidation. Additionally, the effect of the active oxygen species on the PM oxidation is relatively higher at the lower temperature. We consider that this reason is because O_3 has been decomposed to O_2 at the higher temperature and the oxidative activity has lowered,[3] although the absolute values of PM weight decrease ratio is not sufficiently exact because the elevated temperature analysis with TG/DTA can not exactly treat as a differential reaction.

Catalysts composed of transition-metal oxides are reduced to oxidize reactants, and then the reduced metal atoms are reoxidized by oxidants present in a reaction atmosphere; these mechanisms are known as redox catalytic cycles. Formation enthalpies per oxygen atom are recognized as a measure of the oxidative activities possessed by metal oxide catalysts. Figure 2 shows a comparison of the PM weight decrease ratios with respect to the formation enthalpies per oxygen atom of the catalysts, listed in Table 1. Pt and Pd have been evaluated as PtO_2 and PdO, respectively. The PM weight decrease ratios tend to increase with the formation enthalpies of the transition-metal oxides through to approximately $-250\,\text{kJ·g-O}_{\text{atom}}{}^{-1}$, and then these values decrease with further formation enthalpies. A metal oxide of relatively high formation enthalpy is liable to release the oxygen atoms bound to the metal atom and thus has a higher oxidative activity. If a metal oxide has a too high formation enthalpy, however, the metal atom is poorly reoxidized, and, therefore, such metal oxide has a low activity as oxidation catalyst because the redox catalytic cycle is difficult to perform. In Figure 2, the correlations of PM weight decrease ratios with the formation enthalpies of the catalysts showing certain peaks prove that the redox catalytic cycles act practically as the catalytic mechanisms of the transition-metal oxides. As to the noble metals, Pt and Pd, the correlations of PM weight decrease ratios with the formation enthalpies of these catalysts are different from those of the transition-metal oxides. This result suggests that the noble metal catalysts have other reaction mechanisms different from the redox catalytic cycle.

The peaks of PM weight decrease ratios have been found to shift toward higher formation enthalpy owing to the presence of O_3 and NO_2; these shifts are more apparent at 500 °C. This finding means that the reoxidation of the transition-metal oxides is accelerated and that the reduction of these is inhibited by the active oxygen species. Therefore, the PM oxidative activities of the transition-metal oxides possessing the higher formation enthalpies are enhanced by the active oxygen species owing to acceleration of the redox catalytic cycles.

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