Experimental Study of SOF Oxidation Catalysts under Plasma Discharge Conditions

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Oxidative activities of eight different transition-metal oxides and two different noble metals toward the soluble organic fraction (SOF) in diesel particulate matter (PM) have been investigated under plasma discharge conditions. The oxidation rate with ZnO has shown the highest value 99% higher than that without a catalyst and has exceeded that with noble metals. A mechanism of catalytic SOF oxidation under plasma discharge conditions has been proposed.

Diesel engines have a higher combustion efficiency and 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 potential 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 produced significant PM removal.[2] Deposition of PM on dielectric surfaces is an important factor for enhancing PM removal by plasma discharges, but it also causes an increase in pressure loss and a decrease in PM removal efficiency. Therefore, we have investigated catalysts that demonstrate high performance specifically under plasma discharge conditions, namely, plasma catalysts for the oxidation of deposited PM.[3,4]

It is known that a soluble organic fraction (SOF) occurs in diesel PM and that its content is approximately 20–60% of the total PM composition, although the content ratio varies according to engine scales and operating conditions. To promote SOF oxidation by plasma discharges, the plasma catalysts toward SOF are desired. In this paper, we have compared the oxidative activities of ten different catalysts toward a model substance of SOF under plasma discharge conditions. As the SOF model substance for this study, *n*-dodecane (C12) was adopted among *n*-alkane that are major components of SOF.[5] Many earlier studies have reported the comparison of catalytic activities for hydrocarbon oxidation.[6] To the best of our knowledge, however, little study has been reported on hydrocarbon catalytic oxidation under plasma discharge conditions.

Transition-metal oxides were adopted as the main candidates for the SOF oxidation plasma catalysts in this study; these materials are known to have oxidative activities due to redox catalytic cycles.[6] Noble metals were also examined on the SOF oxidative activities for comparison. The catalyst powders evaluated in this study were CeO_2, TiO_2, ZnO, V_2O_5, Fe_2O_3, Co_3O_4, MnO_2, CuO, Pd, and Pt. All of these catalyst powders were of commercial origins and used without any further treatment. The catalyst powders were supported on dielectric surfaces within a DBD reactor; the details of this original supporting method have been in a previous paper.[4] The properties of supported catalysts are listed in Table 1. The basic structure of the DBD reactor was constructed from one aluminum plate ($30 \times 30 \times 0.3\,mm^3$) and two alumina plates ($50 \times 50 \times 1\,mm^3$). The aluminum plate was sandwiched between the two alumina plates as one set. Three sets were arranged in parallel with two discharge gaps of 0.5 mm by inserting alumina spacers ($50 \times 10 \times 0.5\,mm^3$). The surfaces of two alumina plates at the middle of the three sets were supporting the catalyst powder. The vapor of *n*-dodecane was fed into discharge gaps in the DBD reactor by a bubbling (50 °C, $450\,mL{\cdot}min^{-1}$ with N_2) with O_2 ($50\,mL{\cdot}min^{-1}$) at a total flow rate of $500\,mL{\cdot}min^{-1}$. The DBD reactor and the gas lines were kept at a reaction temperature of 200 °C. The DBD reactor was connected to a pulse power supply (DP-12K03, Pulse Electric Engineering Co.) and earth. A pulsed voltage of 10 kV as a peak value was applied by the pulse power supply at a fixed pulse repetition frequency of 100 Hz, resulting in an energy injection of 0.82 W into the DBD reactor. To measure concentrations of reaction products, a part of the outlet gas of the DBD reactor was sampled for the analyses with gas chromatograph–flame ionization detectors (GC-FIDs; GC-14B, SHIMADZU; GC390B, GL Sciences), and the rest was sent into a Fourier transform infrared spectrometer (FT-IR; MIRAN SapphIRe SL, Thermo Fisher Scientific). The oxidation rate of *n*-dodecane (SOF) [$\mu g\text{-}C12{\cdot}min^{-1}$] was calculated from the concentrations of generated CO and CO_2 [$mg\text{-}C{\cdot}mL^{-1}$] multiplied by the outlet gas flow rate [$mL{\cdot}min^{-1}$]. The catalytic reaction rate [$mg\text{-}C12{\cdot}min^{-1}{\cdot}m^{-2}$] was calculated from the difference between the SOF oxidation rate with a catalyst and that without a catalyst [$\mu g\text{-}C12{\cdot}min^{-1}$], divided by the surface area of the supported catalyst [m^2].

Figure 1 shows a comparison of the SOF oxidation rates in the presence and absence of catalyst. The highest value was obtained using ZnO as the catalyst. The oxidation rate with ZnO

Table 1. Supported catalysts properties

	CeO_2	TiO_2	ZnO	V_2O_5	Fe_2O_3	MnO_2	Co_3O_4	CuO	Pd	Pt
Manufacturer	Mitsuwa	Wako	Wako	Wako	Kishida	Wako	Wako	Wako	Kishida	Kishida
Purity/%	99.9	99.9	99.0	99.0	99.0	99.5	99.7	99.7	99.9	99.9
Average particle size/μm	0.24	0.17	0.30	0.27	0.18	0.20	0.26	0.22	0.47	0.64
Supported surface area/$10^{-3}\,m^2$	14.7	27.3	11.4	6.9	6.8	17.7	10.0	12.3	33.4	11.7
Formation enthalpy/$kJ{\cdot}g\text{-}O_{atom}^{-1}$	−544.4	−469.9	−348.3	−310.1	−274.7	−260.0	−222.8	−157.3	—	—

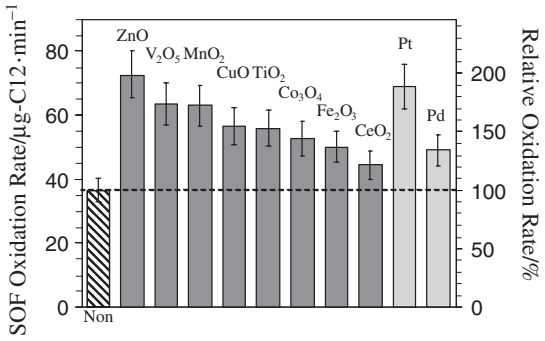

Figure 1. Comparison of the *n*-dodecane (SOF) oxidation rates between presence and absence of a catalyst.

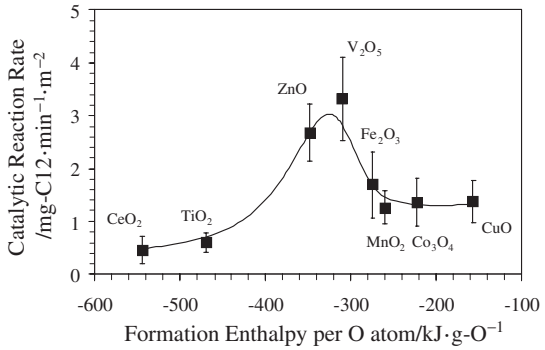

Figure 2. Catalytic reaction rates with respect to the formation enthalpies per oxygen atom of the catalysts.

was 99% higher than that without a catalyst and exceeded that with noble metals. The SOF oxidation efficiency of 5.3 g-C12·kW^{-1}·h^{-1} using ZnO is approximated from the oxidation rate (73 μg-C12·min^{-1}) divided by the energy injection (0.82 W); this value corresponds to the oxidation efficiency to remove 88% of SOF 0.6 g·h^{-1} (average emission from a light-duty vehicle in JC08 test mode) by an energy injection of 100 W. Relatively high oxidation rates have been obtained also with Pt, V_2O_5, and MnO_2. However, the utilization of a noble metal, such as Pt, as the plasma catalyst should be avoided because of resource-depletion and an increase in the production cost of a plasma reactor. The materials of V_2O_5 and MnO_2 also should not be used as the plasma catalysts because of high toxicities and high environmental burdens. Thus, ZnO is considered to be one of the best materials as plasma catalysts, which is relatively inexpensive and harmless.

Formation enthalpies per oxygen atom of metal oxides are recognized as a measure of the oxidative activities possessed by the metal oxides. Figure 2 shows the catalytic reaction rates with respect to the formation enthalpies per oxygen atom of the catalysts, listed in Table 1. The catalytic reaction rates have showed volcano-type correlation with the formation enthalpy in the same way as the PM oxidation;[3,4] such a correlation is a known characteristic of redox catalysts.[6] 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 too high a formation enthalpy, however, the metal atom is poorly reoxidized, and, therefore, such a metal oxide has low activity as oxidation catalyst because the redox catalytic cycle is difficult to perform. Therefore, the redox catalytic cycles are thought to act as an activation mechanism of the plasma catalysts toward the SOF oxidation, as well as the PM oxidation.[4]

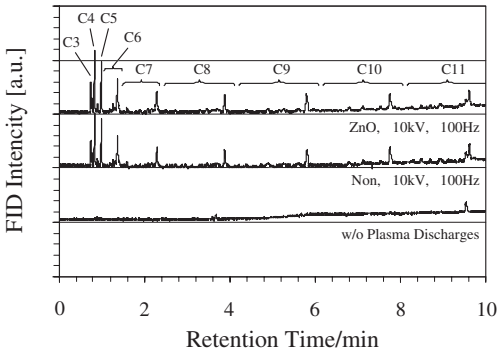

Figure 3. Analysis results of hydrocarbon products (C3–C11) in the outlet gas of the DBD reactor.

Figure 3 shows the analysis results of hydrocarbon products (C3–C11) in the outlet gas of the DBD reactor. Trace amounts of hydrocarbons have been contained in the outlet gas under the plasma discharge conditions, although the hydrocarbons have been scarcely obtained without plasma discharges. Additionally, the variety and amount of the generated hydrocarbons have been little affected by the presence of a catalyst. Hence, we propose a mechanism of SOF oxidation under plasma discharge conditions as the following two steps. 1) C–C bonds in SOF are dissociated by O atoms, radicals, and electrons generated by plasma discharges, and thus SOF is decomposed to hydrocarbons as intermediates. These elements due to plasma discharges are considered to affect also the activation of plasma catalysts. 2) SOF and the intermediates are oxidized to CO and CO_2 by O_3, NO_2, and O_2, which are present in diesel exhaust gas under plasma discharge conditions. The plasma catalysts are considered to perform at the second step to promote the oxidation to CO and CO_2.

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