Investigation of Transition Metal Oxide Catalysts for Diesel PM Removal Under Plasma Discharge Conditions

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Abstract: Seven different transition metal oxides (TiO₂, ZnO, V₂O₅, Fe₂O₃, Co₃O₄, MnO₂, and CuO) have been investigated for oxidation of diesel particulate matter (PM) under plasma discharge conditions. The experiments were carried out by measuring PM oxidation rates over each catalyst using a batch-type dielectric barrier discharge reactor. It was found that TiO₂, ZnO, V₂O₅, and Fe₂O₃ can promote PM oxidation, among which Fe₂O₃ is most desirable catalyst for PM oxidative removal as PM oxidation rate promoted by Fe₂O₃ is highest under plasma discharge conditions. The mechanism of PM catalytic oxidation over the metal oxides has been suggested to follow the redox catalytic cycles from the correlation of the catalytic oxidation rates with the formation enthalpies per oxygen atom of the catalysts. O atoms generated by plasma discharges may play an important role in promoting the re-oxidation of the catalysts. The highest catalytic activity for the PM oxidation with Fe₂O₃ has been suggested to be due to the balance between the reduction rate and the re-oxidation rate within the redox catalytic cycles.

Keywords: Transition metal oxide, catalytic oxidation, dielectric barrier discharge, diesel particulate matter, redox catalytic cycle.

INTRODUCTION

Diesel engines have higher combustion efficiency than gasoline engines. The spread of diesel engines has a beneficial effect on CO₂ emission reduction. However, diesel engines emit particulate matter (PM) and nitrogen oxide (NOx) that are harmful to human beings.

Emission regulations for PM and NOx emitted from diesel vehicles have become increasingly stringent globally [1-3]. After-treatment systems have been desired for current diesel vehicles to satisfy the new emission regulations. Related with the after-treatment system of PM, a diesel particulate filter (DPF) system is known as the most common one [2, 4-7]. However, the use of DPF results in an increase in fuel economy. It is also a problem that a lot of noble metal catalysts are used for removing the deposited PM, such noble metal catalysts provide enough activities for the PM removal at a higher temperature than that of the exhaust gases from the diesel engines.

Plasma technologies have a potentiality as an effective method for PM removal [8-10]. We have developed a dielectric barrier discharge (DBD) reactor driven by a pulse power supply as an alternative to the DPF method [11-15]. The mechanism of PM removal is suggested to include two steps; the first step is the PM deposition (precipitation) due to plasma discharges, and the second step is the PM oxidation by oxygen (O) atoms generated by plasma discharges. Our PM removal system using plasma discharges has been evaluated by Japan Automobile Research Institute. It has been found that the PM emission from a light-duty vehicle installed with a DBD reactor can satisfy the post new long-term emission regulation that will go into effect in 2009 in Japan [16]. The PM deposition in the DBD reactor is a key factor for enhancing PM removal by oxidation, but also the cause increasing pressure loss due to the excess PM deposition. In order to remove the excessively-deposited PM, catalysts are considerable to promote PM oxidation [17, 18]. Unfortunately, catalysts, such as Fe₂O₃, have activities at a temperature higher than 500 °C [19], far higher than the exhaust gas temperature (about 200 °C) [16]. The authors have demonstrated the catalysts of activities to promote PM oxidation in presence of NO₂ or O₃ which can be produced by plasma discharges. It has been found by thermo-gravimetric analysis that transition metal oxides have catalytic activities to PM oxidation and MnO₂, for example, has a PM oxidation efficiency higher than the noble metal catalysts even at the exhaust gas temperature [20]. The catalytic activities of these transition metal oxides are considered to change in plasma discharge spaces in which there are many active oxygen species such as O atoms, OH radicals, NO₂, and O₃ and energized electrons and ions, and UV lights generated by plasma discharges. A few studies have reported PM oxidation by NO₂, O₃, and OH [10, 11, 21, 22]. However, little knowledge can be found to understand the PM catalytic oxidation under plasma discharge conditions. In this study, we have compared the PM oxidative activities of seven different transition metal oxides under plasma discharge conditions using a batch-type DBD reactor. The mechanism of PM catalytic oxidation under plasma discharge conditions is proposed.
MATERIALS AND METHODOLOGY

Catalyst Support on Alumina Plates

Transition metal oxides were adopted as the main candidates for the PM oxidation catalyst in this study, because these oxides have shown high catalytic activities to diesel PM oxidation owing to redox catalytic cycles [20]. Noble metals were not selected as the candidates because of resource depletion and rising prices. The transition metal oxides in powders were TiO$_2$, ZnO, V$_2$O$_5$, Fe$_2$O$_3$, Co$_3$O$_4$, MnO$_2$, and CuO. All of these catalyst powders were of commercial origins and used without any treatment. These catalyst powders were supported on surfaces of the alumina plates (50×50×1 mm$^3$) constituting a DBD reactor according to the following procedure (Fig. 1). 1) The alumina plates were degreased by ultrasonic immersion cleaning with acetone for more than one hour, and dried at room temperature. 2) One surface of the alumina plate was coated with approximately 0.4 mL perhydro-polysilazane 20 wt% of xylene solution (PHPS; EPN-X200, Exousia) uniformly by spraying; PHPS is marketed as a silica-coating agent, and a pure silica layer is provided on a substrate from PHPS reacting with H$_2$O and/or O$_2$ in the atmosphere at a temperature of above 450 °C. 3) Immediately after spraying PHPS, the powder of each catalyst was individually dispersed uniformly by sieve method (# 250 μm, w.d. 160 μm) on the PHPS coated surface of the alumina plate. 4) PHPS was hardened by evaporating the xylene solvent in PHPS at 30°C for more than 24 hours. 5) The PHPS-fixed catalyst powder on the alumina plate surface was sintered at 450 °C for one hour after brushing off unfixed catalyst powder. The specific surface areas of the fixed catalysts were geometrically calculated based on observations with an electronic microscope, because the reaction between PM and a catalyst was a solid-solid reaction and thus roughness of the catalyst should be ignored. The characteristics of fixed catalyst powders are listed in Table 1.

Batch-Type DBD Reactor

The basic structure of the batch-type DBD reactor was composed with one aluminum plate (30×30×0.3 mm$^3$) and two alumina plates (50×50×1 mm$^3$). The aluminum plate was sandwiched by the two alumina plates as one set. Three sets were arranged in parallel with two discharge gaps of 0.5 mm by inserting four alumina spacers (50×10×0.5 mm$^3$) as shown in Fig. (2). The two alumina plate surfaces at the middle of the three sets were supported with the catalyst powder. Approximately 2 mL of 0.1 wt% PM/acetone suspension liquid was applied on each alumina plate surface supported with the catalyst powder, where the PM was collected from the exhaust gas of a diesel engine (2C, Toyota). The applied suspension liquid was dried at 100 °C for 10 hours to remove acetone from the alumina plate surface. The amount of PM deposited on each alumina plate surface is approximately 1.6 mg. The aluminum plate at the middle of the three sets was connected to a high voltage (HV) output of

![Fig. (1). Procedure of catalyst supporting.](image)

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>TiO$_2$</th>
<th>ZnO</th>
<th>V$_2$O$_5$</th>
<th>Fe$_2$O$_3$</th>
<th>MnO$_2$</th>
<th>Co$_3$O$_4$</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity / %</td>
<td>99.9</td>
<td>99.0</td>
<td>99.0</td>
<td>99.0</td>
<td>99.5</td>
<td>99.7</td>
<td>99.7</td>
</tr>
<tr>
<td>Average Particle Size / μm</td>
<td>0.17</td>
<td>0.30</td>
<td>0.27</td>
<td>0.18</td>
<td>0.20</td>
<td>0.26</td>
<td>0.22</td>
</tr>
<tr>
<td>Specific Surface Area / m$^2$·g$^{-1}$</td>
<td>2.70</td>
<td>1.46</td>
<td>2.87</td>
<td>1.94</td>
<td>0.80</td>
<td>1.35</td>
<td>1.39</td>
</tr>
<tr>
<td>Actual Surface Area / 10$^{-3}$ m$^2$</td>
<td>5.4</td>
<td>6.6</td>
<td>10.0</td>
<td>6.8</td>
<td>6.9</td>
<td>11.4</td>
<td>27.3</td>
</tr>
<tr>
<td>Formation Enthalpy / kJ·g-Oatom$^{-1}$</td>
<td>−469.9</td>
<td>−348.3</td>
<td>−310.1</td>
<td>−274.7</td>
<td>−260.0</td>
<td>−222.8</td>
<td>−157.3</td>
</tr>
</tbody>
</table>
a pulse power supply and other two aluminum plates were connected to the earth.

**Plasma PM Removal System**

A plasma PM removal system including the batch-type DBD reactor is shown in Fig. (3). The batch-type DBD reactor was connected to a pulse power supply (DP-30K10, Pulse Electric Engineering Co.) and the earth. The discharge voltage and currents were measured with a voltage probe (P6015A, Tektronix) and two current probes (TCP202, Tektronix), respectively. The analogue signals from the voltage and current probes were recorded with a digital phosphor oscilloscope (TDS754D, Tektronix). The pulse power supply supplied pulsed voltage of a peak value of 12 kV at a fixed pulse repetition frequency of 200 Hz, resulting in approximately 1.0 W energy injection into the DBD reactor. A gas mixture of O₂ (10%) and N₂ (balance) was fed into discharge gaps of the DBD reactor at a flow rate of 500 mL/min and swept the gas products within the DBD reactor during the PM oxidation by plasma discharges. The DBD reactor and gas lines around it were kept at the reaction temperature of 200 °C within a thermostatic oven. The gas from the outlet of the DBD reactor was diluted N₂ gas (5.0 L/min) and then sent into a Fourier-transform infrared spectrometer (FT-IR;
Definitions

PM can be oxidized into CO and CO₂ by plasma discharges [12]. The generation rates \( r_i \) [mL min⁻¹] of CO and CO₂ were calculated using equation (1).

\[ r_i = F \cdot C_i \]  

(1)

where \( F \) is total gas flow rate into the FT-IR analysis cell (5500 [mL min⁻¹]), \( C_i \) is the gas concentration of \( i \). \( i \) denotes CO, CO₂ or CO+CO₂.

PM oxidation rate \( r \) [mg-C min⁻¹] was defined as oxidized PM weight per minute which was calculated from the generation rate \( r_{CO+CO2} \) using equation (2).

\[ r = \frac{M(C)}{RT} r_{CO+CO2} \]  

(2)

where \( M(C) \) is molecular weight of carbon [g mol⁻¹], \( R \) is the gas constant [L atm K⁻¹ mol⁻¹], \( T \) is the temperature in FT-IR analysis cell [K].

The catalytic oxidation rates \( r_c \) [mg-C min⁻¹ mm⁻²] was defined as the differences between the maximum PM oxidation rates with the catalysts \( r \) and that without the catalysts \( r_{Non} \) divided by surface areas \( S \) [m²] of each catalyst (Table 1) using equation (3).

\[ r_c = \frac{r - r_{Non}}{S} \]  

(3)

RESULTS AND DISCUSSION

Fig. (4) shows the generation rates of CO, CO₂, and the sum of them (CO+CO₂) at various elapsed times during the PM oxidation by plasma discharges using the DBD reactor without catalyst support. The plasma discharges began at the elapsed time zero. During the first two minutes, the generation rates of the products increase rapidly, because a respond time of approximately two minutes is required for the FT-IR analysis. The generation rate of CO is at a level of 0.02 ml min⁻¹ [20 to 30% of the generation rate of (CO+CO₂)] at an elapsed time longer than 3 minutes. The generation rate \( r_{CO+CO2} \) peaks at the elapsed time between 15 to 20 minutes, and then decreases gradually. CO and CO₂ are not observable after 180 minutes elapsed time. Actually, at 180 minutes of the elapsed time, 96% of the carbon balance has been obtained only from integrated products of CO and CO₂, though that at 30 minutes the carbon balance is only 34%.

In order to evaluate the catalytic effect of each catalyst on PM oxidation, we used the PM oxidation rates calculated using equation (2). Fig. (5) shows a comparison of the PM oxidation rates \( r \) with and without catalysts. CuO, MnO₂ and Co₃O₄ could not promote PM oxidation. Fe₂O₃, V₂O₅, ZnO, and TiO₂ have catalytic effects on PM oxidation, among which PM oxidation rate with Fe₂O₃ is highest. The PM oxidation rate with Fe₂O₃ has been improved approximately 34% in comparison with that without catalyst.

The comparison of catalytic oxidation rates with each catalyst is shown in Fig. (6). The four metal oxides, Fe₂O₃, V₂O₅, ZnO, and TiO₂, have positive catalytic oxidative rates under plasma discharge conditions, though the three metal oxides, CuO, MnO₂, and Co₃O₄, show negative catalytic oxidation rates. Those findings suggested that Fe₂O₃, V₂O₅, ZnO, and TiO₂ are useful to promote PM oxidation and Fe₂O₃ is the best catalyst for PM catalytic oxidation removal under plasma discharge conditions.
Related with catalytic oxidation of PM, the redox catalytic cycle is conceivable. Generally, a catalyst composed of a transition metal oxide is reduced to oxidize reactants, and then the reduced metal atom (M) is re-oxidized by oxidants present in the reaction atmosphere; this mechanism is known as a redox catalytic cycle described in the following equations (4) and (5). In plasma discharge space, additional re-oxidation reaction is considerable (equation (6)), where O atoms are generated by plasma discharges.

\[
\begin{align*}
M^{2n+}O_n & \rightarrow C + M^{2(n-1)+}O_{(n-1)} + CO \quad \text{(Reduction)} \quad (4) \\
M^{2(n-1)+}O_{(n-1)} + \frac{1}{2}O_2 & \rightarrow M^{2n+}O_n \quad \text{(Re-oxidation)} \quad (5) \\
M^{2(n-1)+}O_{(n-1)} + O & \rightarrow M^{2n+}O_n \quad \text{(Re-oxidation)} \quad (6)
\end{align*}
\]

A transition metal oxide of a relatively high formation enthalpy is liable to release the oxygen atoms bound to the metal atom and thus has a higher oxidative activity. If the formation enthalpy of a transition metal oxide is too high, however, the metal atom is poor to be re-oxidized, and therefore such a transition metal oxide has a low activity as an oxidation catalyst because the redox catalytic cycle is difficult to perform. In Fig. (7), the correlation of the catalytic oxidation rates with the formation enthalpies of the catalysts showing a peak (corresponding to Fe$_2$O$_3$) supports the concept that the redox catalytic cycles act practically as the catalytic mechanisms of the transition metal oxides. O atoms generated by plasma discharges may play an important role in promoting the re-oxidation of metal under plasma discharge conditions. The highest catalytic activity for the PM oxidation with Fe$_2$O$_3$ has been suggested to be due to the balance between the reduction rate and the re-oxidation rate within the redox catalytic cycles.

**CONCLUSION**

The catalytic activities of the seven transition metal oxides (TiO$_2$, ZnO, V$_2$O$_5$, Fe$_2$O$_3$, Co$_3$O$_4$, MnO$_2$, and CuO) for diesel PM oxidation under plasma discharge conditions have been investigated using a batch-type DBD reactor. TiO$_2$, ZnO, V$_2$O$_5$, and Fe$_2$O$_3$ can promote PM oxidation, but CuO, MnO$_2$, and Co$_3$O$_4$ have negative effects on PM oxidation. The PM oxidation rate with Fe$_2$O$_3$ is highest in comparison with other metal oxides. From the correlation of the catalytic oxidation rates with the formation enthalpies per oxygen atom of the catalysts, the redox catalytic cycles have been found to act practically as the catalytic mechanisms of the transition metal oxides. O atoms generated by plasma discharges may play an important role in promoting the re-oxidation of metal under plasma discharge conditions. The highest catalytic activity for the PM oxidation with Fe$_2$O$_3$ has been suggested to be due to the balance between the reduction rate and the re-oxidation rate within the redox catalytic cycles.

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