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Complete List of Authors:	Itoh, Yoshihiko; Toyota Central R&D Labs., Inc., Sakabibara, Yuji; Toyota Central R&D Labs., Inc., Shinjoh, Hirofumi; Toyota Central R&D Labs., Inc.,

Low-Temperature Oxidation of Particulate Matter Using Ozone

Yoshihiko Itoh, Yuji Sakakibara and Hirofumi Shinjoh*

TOYOTA CENTRAL R&D LABS., INC.

41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan

Low-temperature oxidation of particulate matter (PM) was investigated using ozone, which has high oxidation ability. Granular carbon was first used as a model PM to investigate the influential factors for PM oxidation with ozone. The PM collected from diesel exhaust using a diesel particulate filter was then evaluated to determine the oxidation performance of ozone. Carbon was effectively oxidized by ozone at low temperatures less than 573 K and the oxidation rate was larger than ten times that for NO_2 at 423 K; however, the oxidation rates were decreased by the thermal decomposition of ozone and reaction with NO as an exhaust gas component. The oxidation rate when using ozone could be calculated with inclusion of these factors using the Arrhenius equation. The PM oxidation characteristics were similar to those for granular carbon. The results indicate that oxidation with ozone is a promising method for low-temperature PM oxidation and optimized performance with ozone could be achieved.

1. INTRODUCTION

Diesel particulate filters (DPFs) used for the reduction of particulate matter (PM) emissions from diesel engines require appropriate regeneration by the oxidation of PM accumulated in the DPF because accumulated PM causes clogging of the DPF, which decreases engine performance and efficiency by increasing exhaust backpressure. Although PM oxidation using high-temperature exhaust gas by the addition of extra fuel into the exhaust system is generally used for DPF regeneration, it is difficult to execute this method for low exhaust temperature, such as the conditions experienced under traffic congestion.

NO_2 generated from NO contained in diesel exhaust gas has been applied for the regeneration of DPFs used with commercial diesel engines.[1] However, high NO_2 concentrations are required to achieve sufficient PM oxidation rates at low temperatures. Moreover, the NO oxidation performance of the oxidation catalyst is decreased at low temperatures, which leads to an increase of NOx emissions.

Non-thermal plasma (NTP) has been proposed as a solution to this problem.[2,3] This method has potential for low-temperature PM oxidation with reasonable energy consumption to generate NTP, but it has not yet been applied practically, due to difficulties in the attachment of the reactor setup to conventional exhaust systems, such as DPFs, and lack of reliability for high-voltage electrode operation in the exhaust gas.

Ozone has higher activity as an oxidant than Cl_2 or H_2O_2, and harmful effects to the environment and human health are eliminated by the thermal decomposition of ozone to O_2. Ozone has low reactivity with carbon or PM under atmospheric conditions;[4] however, it has been reported that PM oxidation is promoted by ozone[5] and that ozone injection to diesel exhaust is effective for direct PM oxidation by ozone or by NO_2 generated through the ozone-NO reaction.[6] There have been various PM oxidation rates reported from different investigations and the essential PM oxidation properties of ozone under the conditions of diesel exhaust remain unclear

because the quantitative effects of temperature and the exhaust gas components have yet to be clarified.[5,6] Therefore, we have investigated the applicability of low-temperature PM oxidation using ozone with particular focus on the effect of temperature and the presence of other components contained in diesel exhaust gas.

2. EXPERIMENTAL

The experimental setup used in this study is presented in Fig. 1. The PM oxidation properties of ozone were investigated according to the following steps. Firstly, to investigate the fundamental oxidation properties of ozone, granular carbon (Kishida Chemical Co. Ltd., 1-1.7 mm pellets, reagent grade, 3 mL) was used as a model PM with crushed quartz (1-1.7 mm pellets, 7 mL). Secondly, PM collected from the DFP (30 mm diameter, length 50 mm, 0.155 cells/cm^2) of an automotive diesel engine (2 L displacement, 4-cylinder, direct injection) was evaluated. The engine operation conditions were a torque of 30 Nm at 2000 rpm and the amount of PM collected was 80 mg. After the PM was collected, the DPF was heat treated at 573 K for 1 h in air to remove the soluble organic fraction (SOF). A straight flow system was applied by modification of the DPF, as shown by the PM in the DPF section of Fig. 1, to eliminate the effect of the accumulated PM on the filter surfaces for constant PM oxidation.

A gas generator was used to mix N_2, H_2O, NO, NO_2, C_3H_6 and CO as the model diesel exhaust gas, in addition to an ozonizer (Nippon Ozone Co. Ltd., IO-1A6). The oxidation rate was measured according to the CO and CO_2 concentrations, which were measured using a non-dispersive infrared analyzer (Shimadzu Corp., GCT-7000). Ozone and other gas components were measured using an ozone monitor (Ebara Jitsugyo, Co. Ltd., PG-620 PA) and an exhaust gas analyzer (Horiba, Ltd., MEXA-9100D), respectively. The experimental conditions employed

are shown in Tables 1 and 2 for PM carbon oxidation (PM and C ox.), the thermal decomposition of ozone (O_3 decomp.) and the reaction of ozone with other gas components (O_3 react.).

The accuracy for the ozone concentration measurements was 1%, and that for other gas components was within 2%. The temperature of the reaction vessel for the oxidation of carbon or PM in DPFs was controlled to within 1 K.

3. RESULTS AND DISCUSSION

3.1 FUNDAMENTAL STUDY ON THE OXIDATION OF CARBON USING OZONE

The temperature dependence of the carbon oxidation rate using ozone is shown in Fig. 2. Carbon was oxidized by ozone at low-temperature conditions under 573 K. The carbon oxidation rate increased with the amount of supplied ozone (inlet ozone concentration) and had a maximum at 523 K. For quantitative evaluation, the oxidation rates calculated using the Arrhenius equation represented in Eq. 1 are also shown in Fig. 2.

$$r = 79.883\, C_{O3,\,supp.} e^{-2088.5/T}, \quad (1)$$

where r is the rate of carbon oxidation (mmol/h), $C_{O3,\,supp.}$ is the amount of supplied ozone (mmol/h), and T is the temperature (K).

However, the oxidation rates calculated using Eq. 1 correspond well with the experimental values for supplied ozone from 5 to 25 mmol/h (190 to 930 ppm) at temperatures below 423 K. The difference between the calculated and experimental oxidation rates increased with the temperature at over 423 K. The calculated oxidation rates increased monotonically with the temperature, whereas the experimental values decreased at 573 K.

The thermal decomposition of ozone occurs increasingly at higher temperature. The deviation between the calculated and experimental oxidation rates may be attributed to a decrease in the amount of ozone reacting with carbon due to thermal decomposition. Thus, the thermal decomposition properties of ozone were measured by removing carbon from the apparatus and described using another Arrhenius equation:

$$C_{O3,\,T} = 1000 C_{O3,\,supp.}^{\,1.22}\, e^{-4440/T}, \quad (2)$$

where $C_{O3,\,T}$ is the amount of thermally decomposed ozone (mmol/h).

Figure 3 shows that the ozone residual ratio decreases over 400 K, which indicates significant decomposition of ozone at higher temperatures and almost complete decomposition at over 573 K. Figure 4 shows the experimental and calculated (Eq. 2) temperature dependence of the ozone thermal decomposition rate. The experimental results correspond well with that calculated from Eq. 2.

Figure 5 shows the temperature dependence of the carbon oxidation rate calculated using Eq. 3, which combines Eqs. 1 and 2, compared with the experimental carbon oxidation rates. Equation 3 describes the decrease in the oxidation rate of carbon at higher temperatures with good correspondence to the experimental results for temperatures up to 573 K. Therefore, the temperature dependence of the carbon oxidation rate using ozone could be successfully calculated with consideration of the thermal decomposition of ozone.

$$r_T = 79.883(C_{O3,\,supp.} - C_{O3,\,T}) e^{-2088.5/T}, \quad (3)$$

where r_T is the rate of carbon oxidation with the thermal decomposition of ozone (mmol/h).

It appears that the carbon oxidation rate with ozone is dependent on the residual amount of ozone at the carbon. These results indicate that those gas components that have high reactivity with ozone would decrease the carbon oxidation rate. The rate constants for the reaction of various gas components with ozone were reported to be in the following order: NO > NO_2 > C_3H_6 > SO_2 > C_3H_8 > CH_4 > CO.[7-12] Figure 6 shows the residual ratio of ozone reacted with NO, NO_2, C_3H_6 and CO; the results indicate that ozone is entirely consumed by NO with the lowest concentration, whereas CO has no affect on the ozone residual ratio. The order of reactivity with ozone was NO > NO_2 > C_3H_6 > CO, which is consistent with previously reported results.[7-12]

Therefore, NO would significantly decrease the carbon oxidation rate by ozone consumption. The amount of the ozone consumption can be estimated by evaluating the ozone/NO reaction ratio both experimentally and by calculation using Eq. 4, and the results are shown in Fig. 7. The reaction ratio was larger than 1 and increased with temperature, which may be due to the formation of NO_3 and N_2O_5 in addition to NO_2.[13] The amount of ozone reaction with NO can be described by Eq. 5 using Eq. 4:

$$k_{O3,\,NO} = 0.65316\, e^{0.00286T}, \quad (4)$$

$$C_{O3,\,NO} = k_{O3,\,NO}\, C_{NO}, \quad (5)$$

where $k_{O3,\,NO}$ is the ozone/NO reaction ratio, $C_{O3,\,NO}$ is the amount of ozone reacted with NO (mmol/h), and C_{NO} is the amount of inlet NO (mmol/h).

Considering these results, the ozone-NO reaction would be faster than the thermal decomposition of ozone. Therefore, ozone at the inlet would be consumed by the ozone-NO reaction before thermal decomposition could occur. The amount of thermally decomposed ozone with NO could thus be explained by Eq. 6. Consequently, the carbon oxidation rate with NO

could be explained by Eq. 7 from a combination of Eqs. 1 to 6. Figure 8 shows the calculated results for the carbon oxidation rate using ozone containing NO from Eq. 7, in addition to the experimental results. The calculated results correspond well with the experimental results for ozone supplied at 15 to 25 mmol/h (560 to 930 ppm) at 423 K. Consequently, the oxidation rate of carbon using ozone with consideration of the effect of NO reaction and thermal decomposition is well described by Eq. 7:

$$C_{O3,\,T,\,NO} = 1000\,(C_{O3,\,supp.} - C_{O3,\,NO})^{1.22}\,e^{-4440/T}, \quad (6)$$

$$r_{T,\,NO} = 79.883(C_{O3,\,supp.} - C_{O3,\,NO} - C_{O3,\,T,\,NO})e^{-2088.5/T}, \quad (7)$$

where $C_{O3,\,T,\,NO}$ is the amount of thermally decomposed ozone and that reacted with NO (mmol/h), and $r_{T,\,NO}$ is the oxidation rate with thermal decomposition and reaction of ozone with NO (mmol/h).

To simulate the exhaust gas, ion exchanged water was added to the inlet N_2 gas; however, water vapor contained in the exhaust gas had no effect on the rate of carbon oxidation using ozone.

3.2 APPLICATION OF OZONE FOR PM OXIDATION

PM oxidation was conducted using ozone and compared with the results for carbon oxidation, and the results are shown in Fig. 9. The PM oxidation rate using ozone was similar to that for carbon at 373 and 423 K, which confirms that the carbon material used in this study was suitable as a model material for PM oxidation.

The PM oxidation rates with various gas components at 423 K are shown in Fig. 10. The PM oxidation rate with ozone decreased significantly in the presence of NO. For gas containing

ozone and NO_2, the effect on the PM oxidation rate was less than that for ozone and NO. Without ozone, NO and NO_2 showed extremely low efficiency for PM oxidation at 423 K. Thus, PM oxidation by NO_2 [1] is ineffective under low-temperature conditions. At the same temperature, NO is completely oxidized to NO_2 by reaction with ozone and the supplied ozone is entirely consumed, so that the PM oxidation rate using ozone containing NO was similar to that for NO_2 without ozone.

From these results, the optimum amount of supplied ozone for effective PM oxidation could be elucidated. Although these results show that ozone is effective for the oxidation of PM, countermeasures to inhibit ozone consumption by the ozone-NO reaction are required for the effective utilization of ozone for PM oxidation. NOx reduction, NO oxidation to NO_2 or an intermittent supply of high-concentration ozone relative to NO would be effective for this purpose.

In contrast, the PM oxidation rate using ozone was much higher than that reported previously from thermogravimetric analysis (TGA).[5] This would be presumed to enhance the thermal decomposition of ozone and lower the contact probability of ozone and PM relative to this experiment, due to the long residence time of ozone in the vessel and the small contact area of PM on the TGA sample pan.

The specific ozone yields for an industrial ozone generator are reported to be around 100 g/kWh.[14,15] The oxidation rate of PM at 473 K in this study was estimated to be 7–10 g/kWh when including countermeasures for NO, which is similar to PM oxidation by NTP.[2] Consequently, ozone is suitable for the regeneration of a DPF with consideration of the fuel efficiency penalty (1%) with ozone generation.

High-temperature exhaust gas for high load during engine operation would cause a decrease in the PM oxidation rate. This could be avoided by lowering the exhaust gas temperature by setting

the DPF near the tailpipe and/or by injecting cooling air into the exhaust in front of the DPF. The harmful effects of residual ozone to the environment and on human health could be removed by setting an ozone decomposition catalyst after the DPF. Although this method has some problems in practical application, we consider that these could be addressed with such solutions.

4. CONCLUSIONS

A high oxidation rate of carbon used as a model PM was achieved using ozone at low temperature below 523 K. However, the thermal decomposition of ozone at temperatures exceeding 523 K and the reaction of ozone with NO decreased the oxidation rate. The carbon oxidation rate could be described with inclusion of these effects using an Arrhenius equation, and this could be applied for the oxidation of PM. These results indicate that the oxidation of PM with ozone is a promising low-temperature PM oxidation method and that the optimum PM oxidation performance applied for the actual exhaust systems of diesel engines could be estimated.

ACKNOWLEDGMENT

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227 **18(5)**, 1752-1758.

228 Table 1. Inlet gas concentration

	Concentration							
	O_3 (ppm)	NO (ppm)	NO_2 (ppm)	C_3H_6 (ppm C)	CO (ppm)	O_2 (%)	H_2O (%)	N_2
PM and C ox.	0-930	0-550	0-550	-	-	10	3	balance
O_3 decomp.	0-930	-	-	-	-	10	3	balance
O_3 react	400-930	0-550	0-550	0-1000	0-1000	10	3	balance

229

230 Table 2. Inlet gas temperature and total gas flow rate

	Inlet gas temperature (K)	Total gas flow rate (L/min)
PM and C ox.	298-573 (steady-state)	10
O_3 decomp.	298-573 (heating 10 K/min)	10
O_3 react.	298-573 (steady-state)	10

231

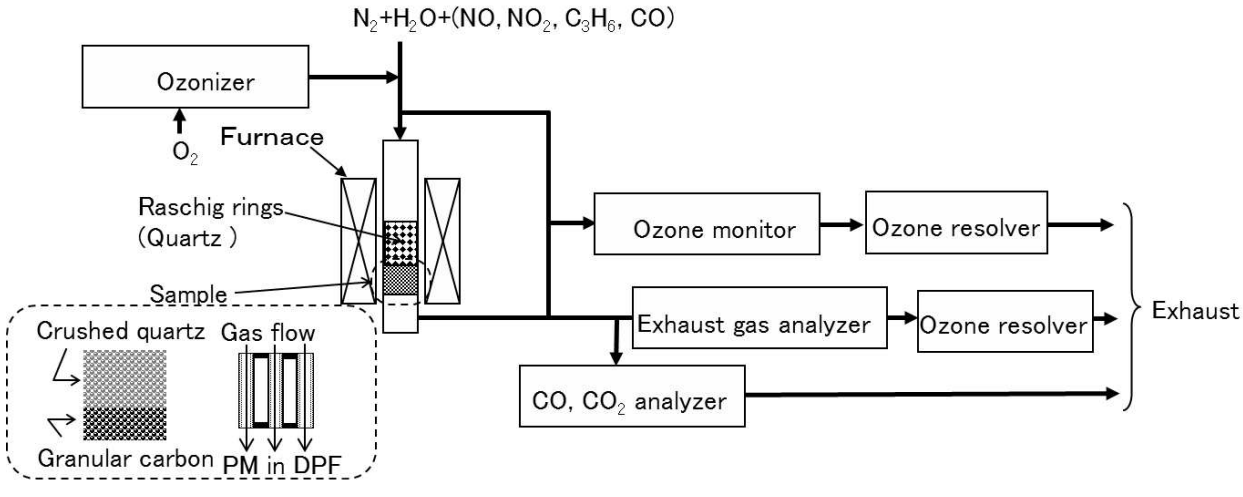

Figure 1. Experimental set-up

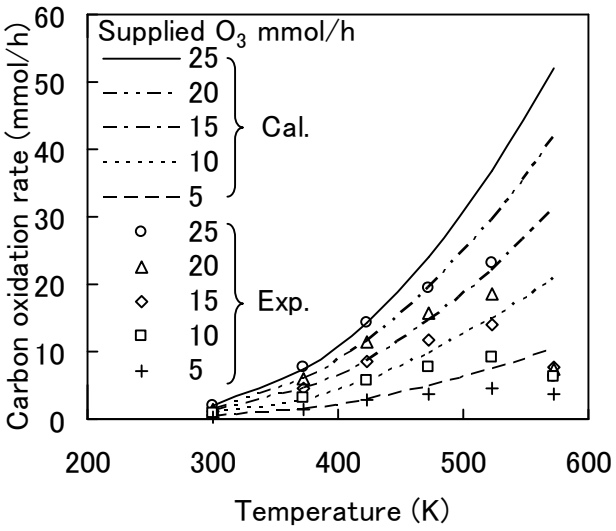

Figure 2. Experimental and calculated (without thermal decomposition of ozone) temperature dependence of carbon oxidation rate; 190-930 ppm ozone, 300-573 K.

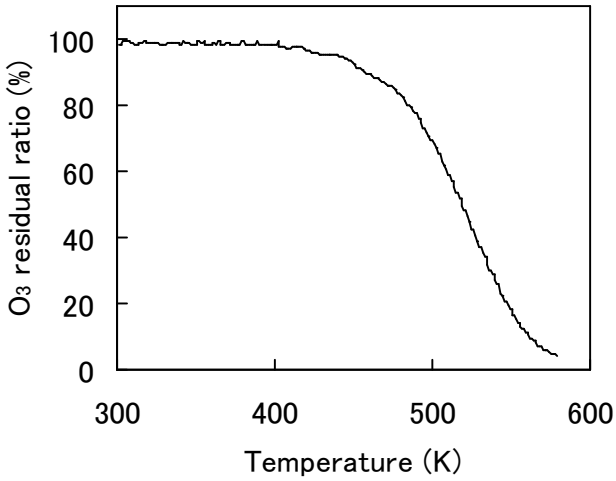

Figure 3. Temperature dependence of ozone residual ratio; 550 ppm ozone, 300-573 K.

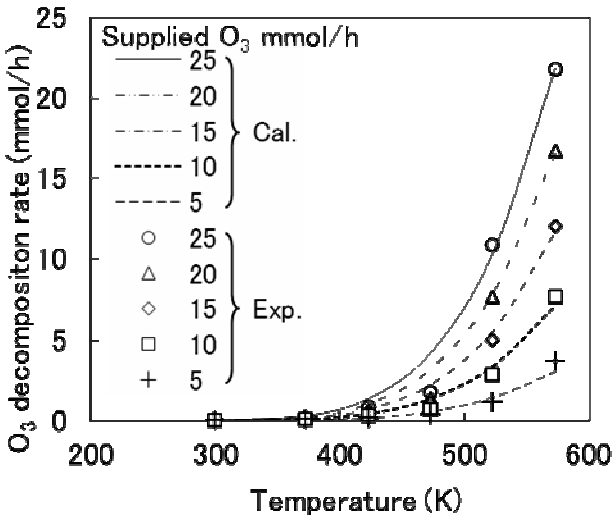

Figure 4. Experimental and calculated temperature dependence of the ozone decomposition rate; 190-930 ppm ozone, 300-573 K.

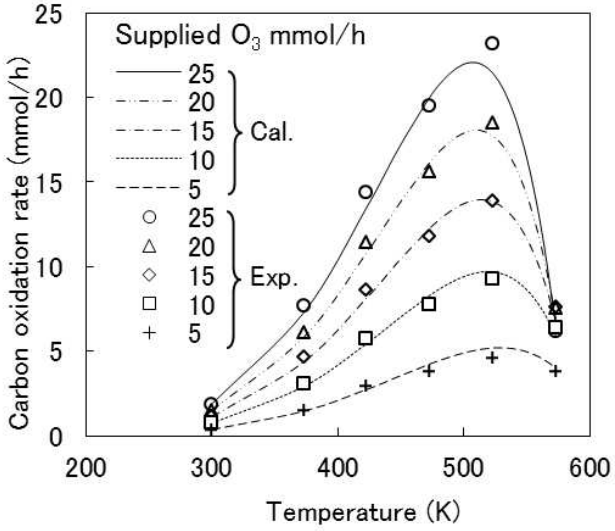

Figure. 5. Experimental and calculated (with thermal decomposition of ozone) temperature dependence of the carbon oxidation rate using ozone; 190-930 ppm ozone, 300-573 K.

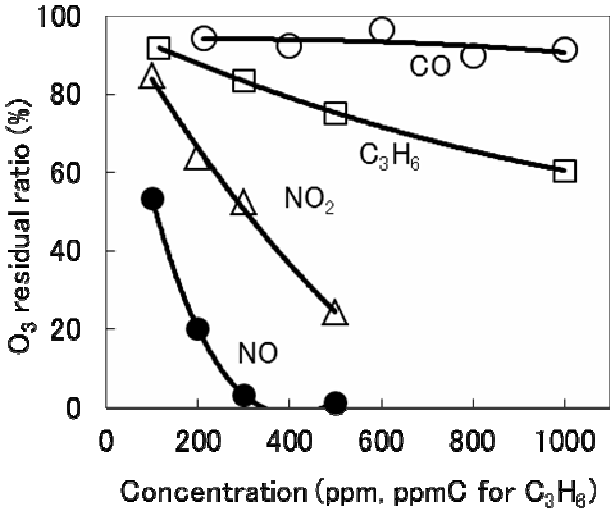

Figure 6. Ozone residual ratio containing other gas components; 400 ppm ozone, 423 K

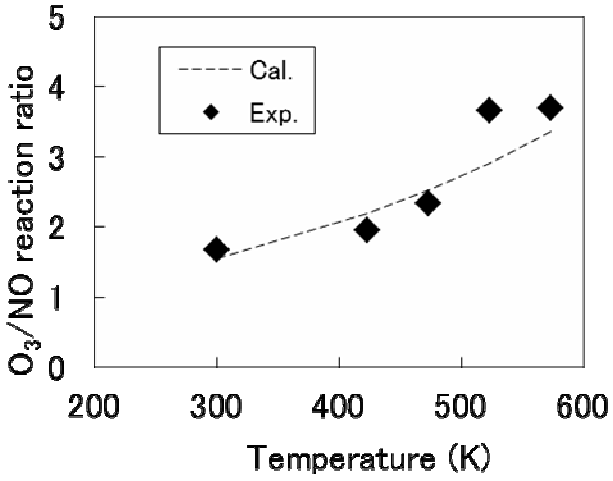

Figure 7. Calculated and experimental temperature dependence of ozone/NO reaction ratio; 550-930 ppm ozone, 100-500 ppm NO.

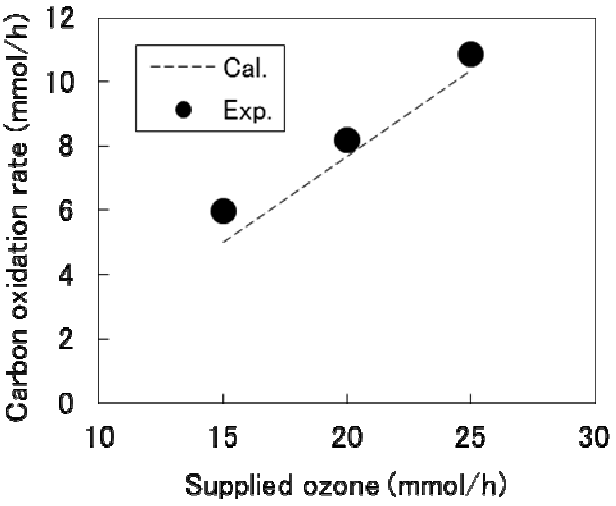

Figure 8. Experimental and calculated carbon oxidation rate using ozone containing NO and allowing for the thermal decomposition of ozone; 560-930 ppm ozone, 100 ppm NO, at 423 K.

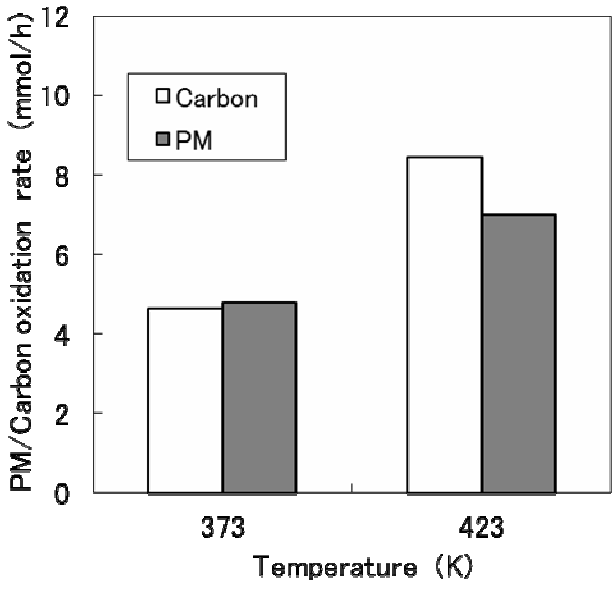

Figure 9. Comparison of oxidation rate for carbon and PM using ozone; 550 ppm ozone, at 373 and 423 K.

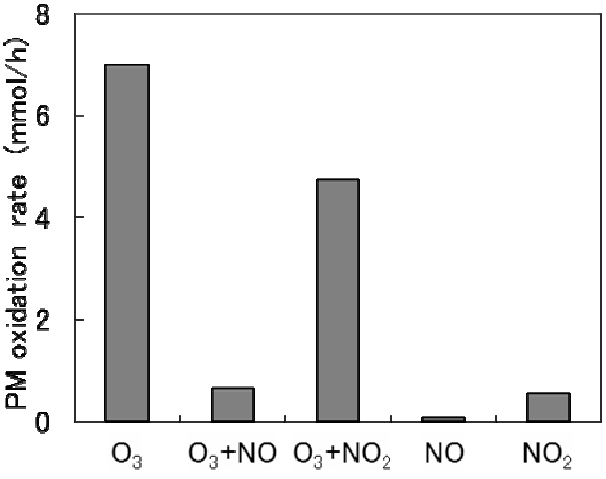

Figure 10. Comparison of PM oxidation rates using ozone, NO, and NO2, and mixtures thereof; 550 ppm ozone, NO and NO2, 423 K.