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Effects of a Platinum−Cerium Bimetallic Fuel Additive on the Chemical Composition of Diesel Engine Exhaust Particles

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The use of a platinum−cerium bimetallic fuel additive has been proposed as a cost-effective strategy for reducing particulate matter (PM) and NO_x emissions from diesel-powered engines. Although previous studies have demonstrated that the use of platinum−cerium bimetallic fuel additive reduced emissions from diesel engines, there have been no reported investigations of how the use of these fuel-borne catalysts (FBCs) impact the chemical and physical properties of diesel PM emissions. The present study demonstrates that the use of a platinum−cerium bimetallic fuel additive has a significant impact on the detailed chemical composition and size distribution of PM emitted from a diesel engine. Tests were conducted to explore the impact of different fuel concentrations of the fuel-borne catalyst at different engine-operating conditions. These tests were performed with a medium-duty diesel engine that was not equipped with exhaust gas recirculation or a diesel particulate filter (DPF). The results demonstrated that the use of the additive significantly reduced the emissions of $PM_{2.5}$ and carbonaceous species. The reduction was 34% for the $PM_{2.5}$ mass, 54% for the $PM_{2.5}$ elemental carbon, and 23% for the $PM_{2.5}$ organic carbon when 0.1 ppm Pt and 7.5 ppm Ce of the additive were used. Emissions of particle-phase metals originating from the additive had a significant contribution to particle matter emissions when 0.7 ppm Pt and 42 ppm Ce of the additive were used. The particle size distribution of platinum in the PM emissions was different from the size distribution of cerium. The cerium/platinum ratio in the $PM_{2.5}$ diesel particle emissions ranged from 119 to 656, which was much higher than the ratio in the fuel additive that was 58.5 ± 5.6, indicating a higher penetration of cerium through the engine.

1. Introduction

Diesel engine exhaust emissions contribute significantly to urban and global air pollution.[1,2] Regulatory agencies worldwide have been tightening emissions standards for diesel engines as the weight of evidence documenting the toxicity of diesel particulate matter (PM) accumulates.[3−5] Although the improvements in the modern diesel engine design and combustion conditions have led to significant reductions in both NO_x and PM emissions, these reductions have not been sufficient to meet new standards without additional control measures. Further reductions in emissions can be achieved more efficiently if engine development is coupled with diesel fuel reformulation and/or the use of fuel additives.[6,7] Metal-based additives have been reported to be effective in reducing diesel emissions in two ways: (1) the metals react with water vapor in the exhaust emissions to produce highly reactive hydroxyl radicals, and (2) the metals serve as an oxidation catalyst and thereby lower the oxidation temperature for diesel soot and lead to increased particle burn out.[8−10] Usually, the fuel-borne catalyst (FBC) is added as an organometallic compound and emitted in the exhaust as a particulate phase oxide, often present as nanometer-sized particles formed by the homogeneous nucleation of the oxidized additive.[11,12]

A variety of FBCs were studied in the past, including cerium (Ce), iron (Fe), cerium−iron (Ce−Fe), platinum (Pt), platinum−cerium (Pt−Ce), manganese (Mn), and copper (Cu).[12−14] The

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use of organo-platinum FBCs with and without efficient post-combustion filtration has been demonstrated to significantly reduce tailpipe emissions of regulated air pollutants and smog precursors,[15] whereas fuel-borne Pt catalysts are currently approved in the U.S. for use in many specialty diesel vehicles and applications are pending for broader use. The use of a platinum−cerium bimetallic fuel additive represents a potential promising strategy for controlling emissions from diesel engines because the temperature of which the Pt−Ce additives (in this case, 0.5 ppm Pt and 5 ppm Ce) efficiently catalyzed the oxidation of soot was the lowest (in this case, 275−300 °C) among the many combinations of fuel additives.[12,14]

The inorganic and organic composition of fine PM emitted from diesel-powered motor vehicles, with and without after-treatment devises, has been the subject of several studies,[16−19] which has been used in numerous source apportionment studies, air-quality models, climate-change models, and health-effect studies;[20−24] however, very few studies have addressed the chemical characteristics of diesel PM when FBCs were used.[8,25,26] Even less information is available on the emission characteristics of diesel engine exhaust particles where a platinum−cerium bimetallic fuel additive was applied. The characterization of diesel engine emissions using a novel fuel amendment technology allows us to proactively understand future air pollution problems and prevent potential problems before the widespread adoption of the technology increases the inertia of the market to a level where even small changes are difficult. This paper demonstrates the significant impact of the use of a platinum−cerium bimetallic fuel additive on the detailed chemical composition of PM emitted from a diesel engine.

2. Experimental Section

2.1. Test Configurations. The engine used for the present study was a 1996 model year, 3116 Caterpillar, 6.6 L, medium-duty diesel engine without an exhaust gas recirculation system or diesel particulate filter after-treatment system. The engine speed and load were controlled using an engine dynamometer. The same engine was used throughout the experimental matrix, while the driving conditions and the concentrations of a platinum−cerium bimetallic fuel additive (Platinum Plus DFX, Clean Diesel Technologies, Inc., an EPA-registered diesel fuel additive) were changed. The original additive contains 183.1 ± 9.2 mg/L of platinum and 10 392 ± 748 mg/L of cerium. The ratio of cerium/platinum (Ce/Pt) is 58.5 ± 5.6. The additive was diluted 1500-fold by the fuel that we used as the manufacturer

Table 1. Experimental Matrix for Bimetallic Fuel Additive and Engine Operations

test code	D1	D2	D3	D4	D5	D6	D7	D8
additive concentration (ppm Pt)			0.13	0.13	0.13	0.13	0.70	0.70
additive concentration (ppm Ce)			7.5	7.5	7.5	7.5	42	42
start mode[a]	cold	hot	cold	hot	hot	hot	hot	hot
engine speed (rpm)	1600	1600	1600	1600	700	1600	1600	1600
torque (N m)	225	224	225	224	38	674	226	226
engine power (bkW)	36	36	36	36	2	107	37	36

[a] A cold-start sampling was started at the time when the engine was started. A hot-start sampling was started 2 h after the engine had been running.

Table 2. Properties of Fuel Used in This Study

analysis	value	ASTM method
density at 15 °C (g/cm³)	0.870 ± 0.001	D1217
gross heating value (BTU/lb.)	19400 ± 283	D5865/E711
carbon (wt %)	86.94 ± 0.04	D5373
hydrogen (wt %)	12.53 ± 0.08	D5373
nitrogen (wt %)	< 0.05	D5373
oxygen (wt %)	0.30 ± 0.08	D5373
sulfur (wt %)	< 0.05	D4239
ash (wt %)	< 0.01	D3174

recommended to obtain the best performance in terms of reducing the emission of regulated pollutants. We also had the additive diluted 300-fold to simulate an "overdose" use of the additive. Consequently, we tested three levels of the concentration of the additive: 0, 0.1, and 0.7 ppm Pt. Note that we are using a bimetallic additive but identifying the fuel used by the Pt level in this paper because the Ce/Pt ratio of the fuel was constant. Table 1 shows the experimental matrix of this study. Our goal was not to replicate a driving cycle or extremes of engine operation but to evaluate the impact of the fuel-borne catalyst at points representative of typical engine operation conditions. The experimental matrix covers the range of the engine map of interest. Commercially available ultra-low sulfur diesel was purchased from Landmark Services Cooperative, Cottage Grove, WI. Table 2 shows the properties of fuel used. The platinum additive was splash-mixed with the diesel fuel using a pump to stir the mixture from the bottom to the top of the fuel storage vessel. When fuel mixtures were changed, the fuel lines to the engine were purged and fuel filters were replaced with new filters. The engine was then run for over 2 h at high speed−medium torque to flush the engine of the previous fuel mixture concentration.

2.2. Testing Procedure. A dilution source sampler was used to dilute hot tailpipe emissions with clean dilution air. The sampler described by Hildemann et al.[27] and Schauer et al.[28,29] was used, which is comprised of a dilution tunnel followed by a residence time chamber. The sampler was designed to simulate dilution in the atmosphere and to allow for sufficient residence time for equilibrium to establish between the gas and particle phase for semi-volatile components of the emissions. At the downstream end of the sampler, samples of diluted exhaust were collected from the residence time chamber to allow for measurement of the fine PM concentration and chemical composition. The samples collected during the study are shown in Figure 1. All of the sampling lines were made from either stainless steel or polytetrafluoroethylene (PTFE)-coated aluminum to minimize particle losses and to avoid the adsorption of semi-volatile emissions to the sampling surfaces.

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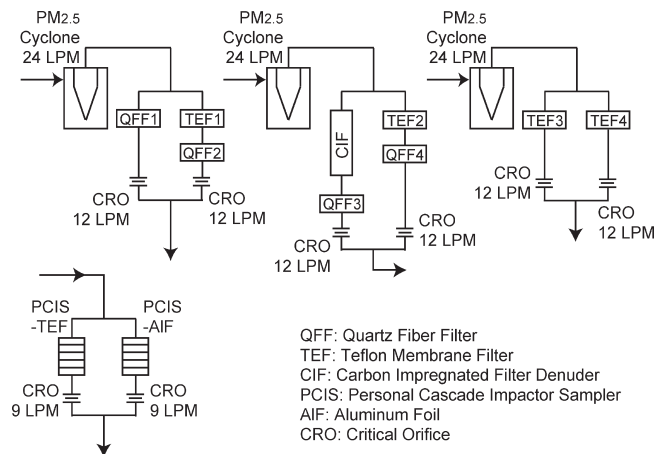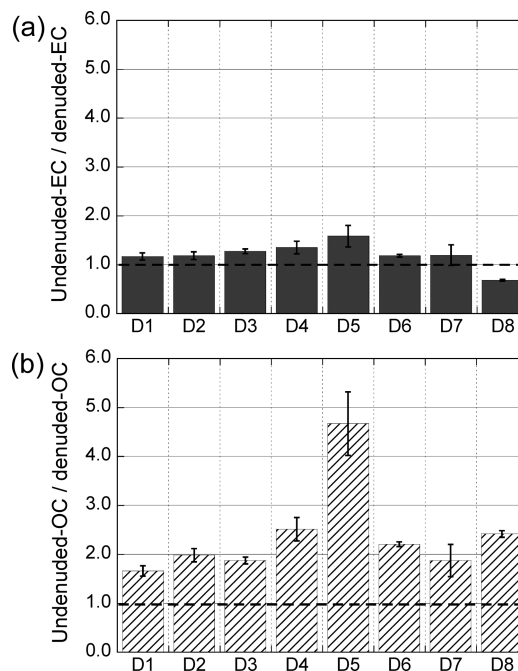
Figure 1. Schematic of sampling equipment connected to the dilution sampler.

The size distribution of the PM and size-segregated chemical composition were obtained using the Sioutas personal cascade impactor samplers (PCISs).[30] Particles were separated into the following aerodynamic particle diameter ranges: < 0.25, 0.25−0.5, 0.5−1.0, 1.0−2.5, and 2.5−10 μm. Mass concentrations and chemical composition were obtained from PM collected on PTFE membrane filters. Cleaned aluminum foils were used to collect PM for the analysis of carbonaceous materials. A flow rate of 9 L/min was maintained using calibrated critical orifices throughout the PCIS sampling.

PTFE-coated aluminum cyclones were used upstream of the sampling media (except for PCIS) to obtain $PM_{2.5}$ (PM that passes through a size-selective inlet with a 50% efficiency cutoff at an aerodynamic diameter of 2.5 μm) in the exhaust gases. A 24 L/min flow rate through each of the cyclones was maintained using calibrated critical orifices. $PM_{2.5}$ samples were collected on either quartz fiber or PTFE filters. A carbon-impregnated cellulose denuder (Sunset Laboratory, Inc.) was used in one of the sampling trains to remove semi-volatile organic gases upstream of a $PM_{2.5}$ sample to avoid adsorption artifacts for the analysis of organic and elemental carbon (OC and EC).[31]

2.3. Analytical Procedures. Four separate sets of 47 mm PTFE membrane filters for $PM_{2.5}$ mass determination were weighed before and after sampling in a temperature- and humidity-controlled room with a robotic filter weighing apparatus. Uncertainty (here, it means the relative standard deviation of the data obtained by weighing of the four sets of the filters) ranged from 2 to 18%. OC and EC were measured by the NIOSH ECOC method using the ACE-Asia protocol,[32] using a 1.5 cm^2 punch of the quartz fiber filters or a well-defined section of the aluminum foil impactor substrate. Because no pyrolysis carbon was observed in the samples and because the high EC loadings on the filter prevented the direct determination of the ECOC split time, the split time of ECOC analysis was set at the time when He/O_2 was introduced into the analyzer. To estimate the organic matter (OM) mass concentration, a multiplier of 1.2 was applied to the organic carbon data for diesel PM.[33] Inorganic ions were extracted by deionized water (Milli-Q) and analyzed

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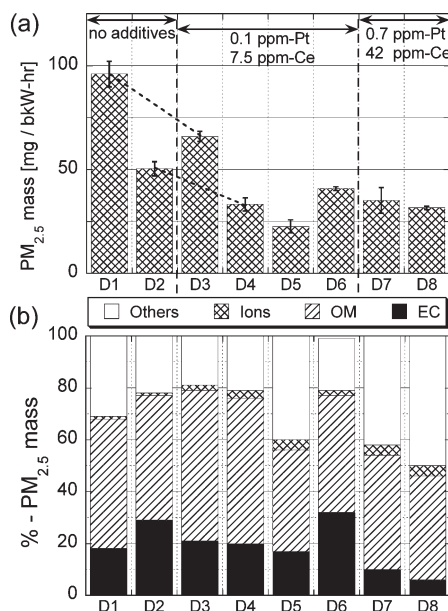
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Figure 2. (a) Ratio of the concentration of undenuded EC (QFF1) to that of denuded EC (QFF3). (b) Ratio of the concentration of undenuded OC (QFF1) to that of denuded OC (QFF3).

by ion chromatography for sulfate, nitrate, and ammonium. Elemental analysis was performed by acid digestion followed by inductively coupled plasma mass spectrometry (ICP−MS). The detailed procedure of the elemental analysis was described previously.[34]

2.4. Emission Rate Calculation. We denote emission data in mass per brake engine power in this paper. We calculated the emission data under the conditions of 25 °C and 1 atm using (1) fuel consumption rate (197 g of fuel bkW^{-1} h^{-1} at 1600 rpm and 150 g of fuel bkW^{-1} h^{-1} at 700 rpm) by referring to the engine specification data for the model CAT3116, (2) atomic composition of #2 diesel fuel (86.8 wt % C and 13.2 wt % H), (3) CO_2 concentration measured at the end of the residence time chamber, and (4) the dilution ratio (the volumetric ratio of dilution air/sampled engine exhaust).

3. Results and Discussion

3.1. Emission Characteristics of EC and OC. As part of the emissions characterization, we investigated the impact of the organics denuder on the measured emissions of OC and EC. Figure 2a shows the ratio of undenuded EC (QFF1) to denuded EC (QFF3) determined for the emissions tests with and without the FBC. The concentrations of undenuded $PM_{2.5}$ EC were similar to the concentration of denuded $PM_{2.5}$ EC (typically less than ±20%), a finding quite similar to that reported by Mader et al.[31] in an evaluation of the denuder technique. This result is not unexpected, because gaseous EC is minimal in the exhaust gas. Figure 2b shows the ratio of undenuded $PM_{2.5}$ OC (QFF1) to denuded $PM_{2.5}$ OC (QFF3) in the exhaust emissions. Here, we observe that the concentration of undenuded OC was 1.7−4.7 times greater than that of denuded OC, as a result of the absorption of semi-volatile organic gases present in the exhaust gas by the QFF.[31,32] The results show that the denuder successfully

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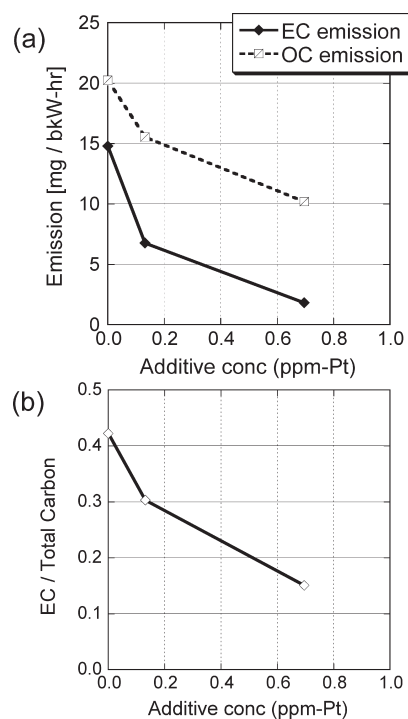
Figure 3. (a) Specific PM$_{2.5}$ emissions for each testing condition. (b) Chemical compositions of diesel exhaust based on the mass concentration of PM$_{2.5}$. OM concentrations were calculated using a correction factor of 1.2 for denuded OC. The ions contained ammonium, nitrate, and sulfate.

removed gaseous OC. Therefore, we were able to collect just the particulate OC fraction on the filters. As a result, we considered the denuded OC as the particulate OC fraction for further discussion in this study.

3.2. Overall Chemical Characteristics of PM$_{2.5}$ in Diesel Exhaust for Different Additive Concentrations. Figure 3 shows the PM$_{2.5}$ mass emission rates under the different engine operating conditions, along with the relative contribution of OM, EC, and ions to the PM emissions. The PM$_{2.5}$ emissions ranged from 23 to 96 mg bkW^{-1} h^{-1}. The use of the Pt FBC significantly reduced the PM$_{2.5}$ emissions as compared to the case in which the FBC was not used. As expected from previous studies,[35,36] the cold-start operating conditions had emissions that were 91−98% greater than the parallel conditions that used a hot-start operating cycle. Carbonaceous matter (EC + OM) accounted for 68−77% of the PM$_{2.5}$ in the tests in which no platinum additive was used. The contribution of carbonaceous matter to PM mass, when using the 0.1 ppm Pt additive concentrations (D3−D6) was 76−79%, except for the idle condition where the carbonaceous fraction of the PM accounted for about 56%. Carbonaceous emissions tend to be lower while the engine is idling.[37,38] Carbonaceous fractions in the 0.7 ppm Pt additive tests (D7 and D8) accounted for 45−54% of PM$_{2.5}$ mass, which is consistent with the expectation that the inorganic component originating from the additives contributed substantially to the total PM mass, whereas the higher concentration of the additives effectively reduced carbonaceous species. It is important to note, however, that the use of 0.7 ppm Pt is not recommended by the additive

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Figure 4. EC and denuded OC emissions and their mass fraction for different additive concentrations with a hot-start condition. Total carbon means EC + denuded OC. A bimetallic fuel additive was used where the ratio of cerium/platinum (Ce/Pt) of the fuel was 58.5 ± 5.6.

manufacturer and such high contributions from metals would only result when a user of the additive intentionally or accidentally uses more additive than recommended. Figure 4 shows EC and denuded OC emission rates and the ratio of EC/total carbon (TC = OC + EC), for the different additive concentrations in the fuel. The additive significantly reduced these carbonaceous emissions. Table 3 shows the specific emission and percent reduction of PM$_{2.5}$, EC, and denuded OC based on the D2 result. Emissions were reduced by 34% for the PM$_{2.5}$ mass, 54% for the EC, and 23% for the denuded OC at the 0.1 ppm Pt additive concentration. As a comparison, cold-start emissions were reduced by 31% for the PM$_{2.5}$ mass, 20% for the EC, and 20% for the denuded OC at the 0.1 ppm Pt additive concentration. Although the additive effectively reduced the pollutants emission, a cold start preferentially emitted EC. Importantly, the mass fraction of EC was also reduced with additive use and continued to drop at higher additive concentrations. The additive reduces EC effectively when compared to OC. One possible theory about how the platinum additive works to reduce EC is that soot or soot-like compounds can be oxidized by NO$_x$, which is generated from NO by the platinum catalytic effect.[14] The carbon aromatic bond and double bond may be preferentially involved in this oxidation by NO$_x$ in comparison to aliphatic compounds, such as alkanes and alcohols. Because the OC emitted from diesel engines contains a significant amount of non-aromatic/nonsoot-like compounds,[34] the platinum additive can interact with EC and soot-like compounds or more effectively as compared to OC. Figure 5 shows the detailed emission profiles of diesel exhaust based on the mass concentrations in PM$_{2.5}$. The concentrations of Ce and Pt in PM$_{2.5}$ were less than 1 ppm when operating without the additive (D2). On the other

Table 3. Specific Emission and Percent Reduction of PM$_{2.5}$, EC, and Denuded OC Based on the D2 Result

test code	D2		D4		D8	
additive concentration (ppm Pt)			0.13		0.70	
additive concentration (ppm Ce)			7.5		42	
	emission (mg bkW^{-1} h^{-1})	reduction (%)	emission (mg bkW^{-1} h^{-1})	reduction (%)	emission (mg bkW^{-1} h^{-1})	reduction (%)
PM$_{2.5}$	50.3	0	33.2	34	31.6	37
EC	14.8	0	6.8	54	1.8	88
denuded OC	20.2	0	15.5	23	10.2	50
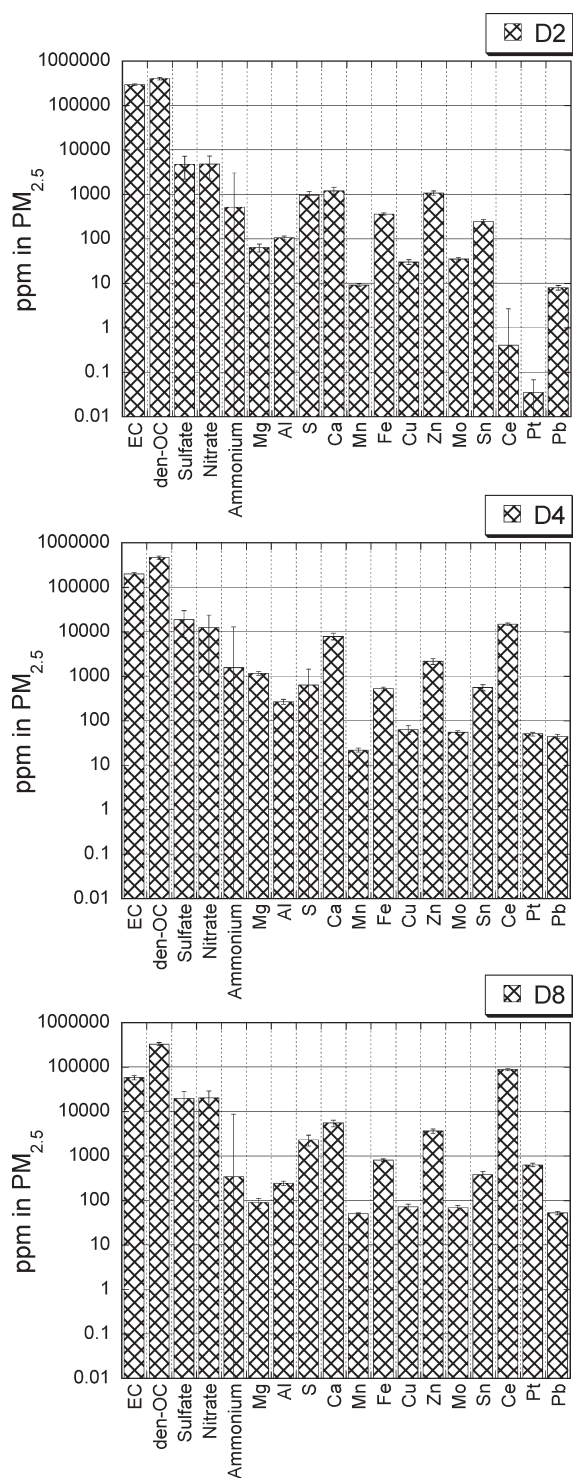
Figure 5. Detailed emission profiles of diesel exhaust based on the mass concentrations of PM$_{2.5}$ for the D2 (no additives), D4 (0.1 ppm Pt and 7.5 ppm Ce), and D8 (0.7 ppm Pt and 42 ppm Ce).

hand, Ce accounted for approximately 10% of the PM$_{2.5}$ mass with 0.7 ppm Pt additive (D8). Pt levels (630 ppm) in the PM$_{2.5}$ at the higher Pt loading were significant. Note that emissions of Ba and La were associated with those of Ce and Pt.

We calculated what fraction of added Pt in the fuel was present in the PM. As mentioned above, the fuel rate was 197 g of fuel bkW^{-1} h^{-1} in this study. When 0.1 ppm Pt was used, the Pt consumption rate was 25.6 μg of Pt in fuel bkW^{-1} h^{-1}. Actual emission data for Pt in PM$_{2.5}$ was 1.7 μg bkW^{-1} h^{-1}. Therefore, only 6.6% of the added Pt was coming out from the engine when 0.1 ppm Pt was used. Similarly, 14.3% of the added Pt was coming out from the engine when 0.7 ppm Pt was used. It means that more than 85% of the added Pt remains in the engine, at the beginning of the use of the additives, at least. A similar result was obtained by Shafer et al.,[26] who reported that the engine emission rates for platinum ranged from 10 to 22% of input platinum. On the contrary, 33% of the added Ce was emitted out from the engine for both cases (0.1 and 0.7 ppm Pt). Consequently, the cerium/platinum ratios (Ce/Pt) in the diesel particle samples were 298 for the D4 and 138 for the D8, which was 58.5 in the original platinum−cerium bimetallic fuel additive. These findings are consistent with previous studies[26] that documented an uncoupling of Ce and Pt emissions in engines operating without a DPF. The reduction of the native organo-Pt additive (Pt^{II} organic) in the fuel to elemental platinum in the engine is nearly quantitative, with a large fraction of the Pt reduction occurring on or near the surface of cerium oxide particles forming from the oxidation of the native organo-Ce in the fuel additive,[14,39,40] However, it appears that a significant fraction of the added Pt may be processed in the engine via chemical pathways that do not involve cerium/cerium oxide. Elemental platinum (and any higher valent platinum) is considerably more surface-reactive than cerium oxide and will "stick" to any number of surfaces in the engine/engine-exhaust train, thus the observed selective retention of Pt in the engine and resulting enrichment of Ce in the exhaust PM.

3.3. Size Distribution of Particle Mass and Chemical Species. Figure 6 shows particle mass size distributions of diesel exhaust under the same start mode and engine load but with different platinum additive concentrations in the fuel. A total of 80% of the total mass was present in the less than a 0.25 μm fraction under no additive conditions (D2), whereas 60% of total mass was also distributed for the D4 (0.1 ppm Pt) experiment. The EC/OC data show that more than 99% of the detected carbonaceous species were distributed into the less than 0.25 μm fraction in each test condition. These facts suggest that the portion of the particles less than 0.25 μm were reduced under D4 conditions because the platinum

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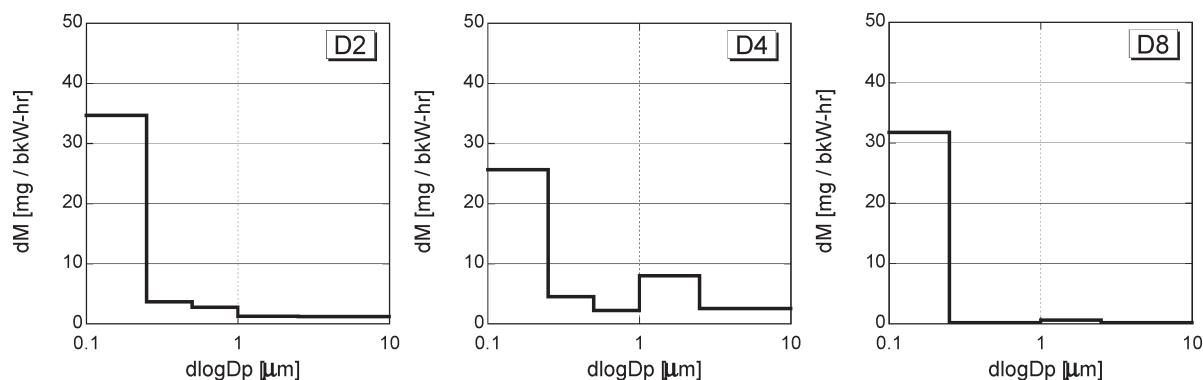
Figure 6. Particle mass size distributions (in mg bkW^{-1} h^{-1}) of the diesel exhaust under the conditions of a hot start and medium load. The bimetallic fuel additive concentrations were 0 ppm Pt for the D2, 0.1 ppm Pt for the D4, and 0.7 ppm Pt for the D8. The ratio of cerium/platinum (Ce/Pt) of the fuel was 58.5 ± 5.6.
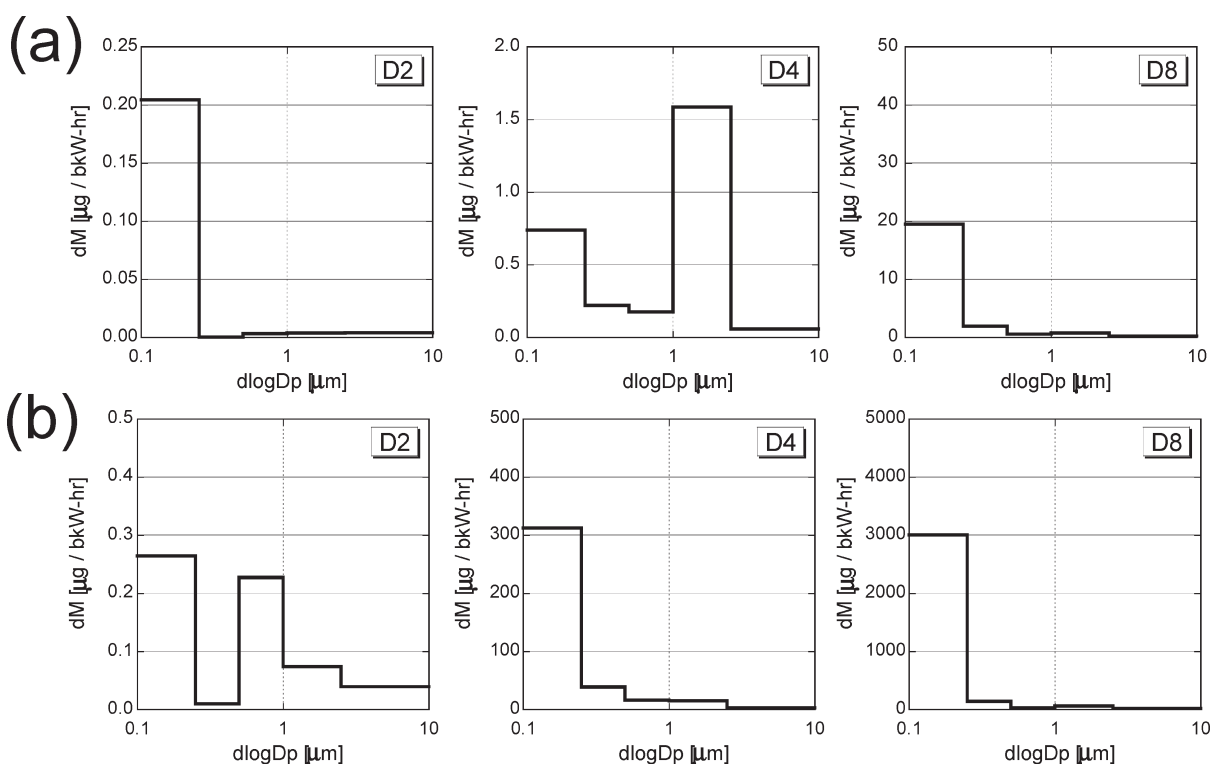
Figure 7. Size distributions (in μg bkW^{-1} h^{-1}) of (a) platinum and (b) cerium in diesel exhaust particles under the conditions of a hot start and medium load. The bimetallic fuel additive concentrations were 0 ppm Pt for the D2, 0.1 ppm Pt for the D4, and 0.7 ppm Pt for the D8. The ratio of cerium/platinum (Ce/Pt) of the fuel was 58.5 ± 5.6.

additive reduces carbonaceous species that form the smaller particles. Figure 7 shows the size distributions of platinum and cerium in diesel exhaust particles in the same manner as Figure 6. The size distribution patterns of platinum were different from those of cerium. A unique peak was found for platinum in the size range of 1.0−2.5 μm in the D4 experiment. Platinum in this size range accounted for 57% of the total platinum emissions for this sample. The peak in the 1.0−2.5 μm size fraction in D4 was also observed in the particle mass size distribution (Figure 5). This suggests that platinum particles promote particle aggregation. A total of 85% of the total platinum emission was distributed into the less than 0.25 μm fraction in the D8 experiment. A total of 81 and 92% of the total cerium emissions were distributed into the less than 0.25 μm fraction for the D4 and D8 experiments, respectively.

4. Conclusion

This paper details the physical and chemical emission characteristics of diesel engine exhaust particles where a platinum−cerium bimetallic fuel additive is applied and compares these characteristics to emissions from the engine without added FBC. Low concentrations of additive (0.1 ppm Pt and 7.5 ppm Ce in this study) significantly reduced the emission of PM$_{2.5}$ and carbonaceous species. The additive preferentially reduces emissions of EC in comparison to OC. Emission profiles of diesel exhaust based on the mass concentration of PM$_{2.5}$ were detailed in this paper. Cerium and platinum as well as barium and lanthanum accounted for a significant portion of the PM$_{2.5}$ mass when higher concentrations of the additives (0.7 ppm Pt and 42 ppm Ce in this study) were used. The fact that the size distribution patterns of platinum

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were different from those of cerium indicates the engine emissions for platinum could be different from that for cerium. Pt is considerably more surface-reactive than Ce and will stick to any number of surfaces in the engine/engine-exhaust train.