

## Postprint: Enhancing the Purification Performance of POC Pollutants Using Perovskite Catalysts

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### Abstract

Through engine bench tests, the purification performance of a particulate oxidation catalyst (POC) coated with  $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.7}\text{Bi}_{0.3}\text{O}_3$  catalyst for particulate matter and other diesel emission pollutants under real diesel exhaust conditions was investigated. The results show that: the combined use of POC with a commercial diesel oxidation catalyst (DOC) achieves over 90% removal efficiency for HC and CO; the mass removal efficiency of PM increases with catalyst loading; under operating conditions of 2510 r/min, 100% load, the PM purification efficiency of POC 20 is 89.8%, of which 38.7% is attributed to oxidation. This demonstrates that the catalyst exhibits good diesel particulate matter purification performance and has the potential to replace noble metal catalysts in commercial POC.

### Full Text

### Preamble

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### Study on Enhancing POC Pollutant Purification Performance by Perovskite Catalysts

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### Abstract

The purification performance of a particulate oxidation catalyst (POC) coated with  $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.7}\text{Bi}_{0.3}\text{O}_3$  catalyst was investigated under real diesel engine

exhaust conditions through engine bench tests. The results demonstrate that the combined use of POC and a commercial diesel oxidation catalyst (DOC) achieves over 90% removal efficiency for hydrocarbons (HC) and carbon monoxide (CO). The mass removal rate of particulate matter (PM) increases with higher catalyst loading. Under engine operating conditions of 2510 r/min and 100% load, the PM purification efficiency of POC-20 reaches 89.8%, with 38.7% attributable to oxidation processes. These findings indicate that the  $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.7}\text{Bi}_{0.3}\text{O}_3$  catalyst exhibits excellent diesel particulate purification performance and holds potential as a substitute for noble metal catalysts in commercial POC applications.

**Keywords:** Particulate Oxidation Catalyst (POC); Perovskite; Catalytic Oxidation; Diesel Engine; Particulate Matter (PM)

Diesel engines are widely used in transportation and construction machinery due to their superior power performance, fuel economy, and durability. However, the inherent trade-off effect between particulate matter (PM) and nitrogen oxides (NOx) formation during in-cylinder combustion means that conventional in-cylinder purification measures alone cannot meet increasingly stringent emission regulations. Researchers worldwide have recognized that a combination of optimized combustion technologies and exhaust aftertreatment systems is essential for diesel engines to comply with China IV and China V emission standards. Particulate oxidation catalysts (POC) typically employ open-structured stainless steel or ceramic substrates coated with noble metal catalysts, purifying diesel exhaust particulates through both physical trapping and catalytic oxidation. Unlike diesel particulate filters (DPF), POC's open structure significantly reduces the impact of trapped particulates on engine exhaust back pressure. Studies have shown that POC combined with diesel oxidation catalysts (DOC) can achieve over 60% particulate removal efficiency. However, noble metal catalysts suffer from poor sulfur resistance, susceptibility to sintering deactivation, and high costs, limiting their practical application. Perovskite-type transition metal composite oxides offer an alternative with low cost, excellent oxidation catalytic activity within the soot combustion temperature range, good thermal stability, and high sulfur resistance, making them promising for diesel particulate purification applications.

Previous research has demonstrated that the A- and B-site partially substituted perovskite composite oxide catalyst  $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.7}\text{Bi}_{0.3}\text{O}_3$  exhibits effective catalytic oxidation performance for model soot (Degussa Printex-U carbon black). Building upon this work, the present study prepared POCs coated with  $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.7}\text{Bi}_{0.3}\text{O}_3$  catalyst using multiple impregnation coating methods and investigated the catalytic activity for diesel particulate oxidation under real exhaust conditions, as well as the influence of catalyst loading on POC pollutant purification effectiveness.

## 1.1 Experimental Equipment

The test engine was a CY4102-C3B diesel engine manufactured by Dongfeng Chaoyang Diesel Engine Co., Ltd., with main technical parameters shown in . The engine test bench was equipped with additional testing instruments and equipment listed in . Exhaust HC, CO, and NO<sub>x</sub> concentrations were measured using a HORIBA MEXA-9100D engine exhaust analyzer.

## 1.2 Catalyst Loading Method

The coating slurry was prepared by dissolving nano-sized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and pseudo-boehmite in tenfold-diluted nitric acid solution at a 1:4 mass ratio under continuous stirring to ensure uniformity. After adding 5% (wt/wt) PEG20000, the mixture was left to stand for one week to obtain a stable  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> coating slurry with pH 3 and viscosity of 1120 mPa · s. The La<sub>0.8</sub>Ce<sub>0.2</sub>Mn<sub>0.7</sub>Bi<sub>0.3</sub>O<sub>3</sub> catalyst was synthesized according to the method described in literature [6]. The synthesized catalyst powder was ground finely using a ball mill and mixed with the prepared coating slurry, with the catalyst accounting for 20% mass fraction of the entire slurry system. A commercial POC metal substrate was immersed in this slurry for 2 hours, after which residual liquid in the substrate channels was blown out with an air blower. The coated substrate was dried at 100°C for 24 hours and then calcined in a muffle furnace at 800°C for 3 hours. The mass of the calcined substrate was measured to calculate catalyst loading, and this process was repeated until the actual loading reached the predetermined target. For comparison, a blank catalytic converter was prepared by coating only the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> slurry without catalyst on a set of metal substrates, designated as POC-0. Two POCs with catalyst loadings of 10 g/L and 20 g/L were designated as POC-10 and POC-20, respectively. Additionally, a DOC was prepared using the same method on a honeycomb ceramic substrate with 20 g/L catalyst loading, designated as DOC-20.

## 1.3 Experimental Protocol

The study focused on comparing pollutant emissions from the raw engine and after POC installation across different loads at A, B, and C speeds in the thirteen-mode test cycle, with engine speeds of 1610, 2060, and 2510 r/min, respectively. Particulate number and size distribution before and after the POC were measured using a TSI Engine Exhaust Particle Sizer (EEPS-3090) covering 5.6–560 nm, with a two-stage dilution system at a total dilution ratio of 300:1 and sampling flow rate of 10 L/min. Particulate mass was collected on Pallflex polytetrafluoroethylene filters (EMFAB TX40HI20-WW, 70 mm diameter). The sampling procedure involved drying and weighing the filter, installing it in the sampler, and collecting particulates at 5 L/min for 30 minutes per operating condition. The post-sampling filter was dried until mass stabilized and reweighed, with the mass difference representing total collected particulate mass. Soluble organic fraction (SOF) was extracted from collected particulates using Soxhlet extraction with dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, Dima Company, USA) as the solvent

based on the principle of similar polarity. After extraction, the filter retained only soot and non-soluble metal inorganic salts. Filter mass was measured before and after extraction, with the difference representing SOF mass in the collected PM.

The conversion efficiency ( ) of various aftertreatment devices for diesel exhaust pollutants was calculated using equation (1), where  $\Phi_0$  represents pollutant emissions before the aftertreatment device and  $\Phi_1$  represents emissions after. Since POC-0 contained no catalyst, its PM purification efficiency represents the trapping efficiency of POC, while the difference between POC-10/POC-20 and POC-0 efficiencies represents the oxidation contribution.

## 2 Results and Discussion

### 2.1 Effect of Perovskite-Loaded POC and DOC on Engine Exhaust Back Pressure

[Figure 1: see original paper] shows the pressure drop across the four prepared aftertreatment devices during full-load engine tests. For the three metal-substrate POCs, pressure drop increased with catalyst loading but remained limited, whereas the cordierite-substrate DOC-20 exhibited significantly higher pressure drop than the POCs. As engine speed increased, the pressure drop across all three POCs gradually increased but remained below 10 kPa, while DOC-20 showed a sharp pressure drop increase, reaching 23.2 kPa at rated speed.

[Figure 2: see original paper] presents hourly PM emissions measured before four different aftertreatment devices at 2510 r/min and 100% load. All four devices increased engine PM emissions to varying degrees, with higher catalyst loadings resulting in greater PM emission increases, particularly for the cordierite-substrate DOC-20. This occurs because aftertreatment installation increases exhaust back pressure, effectively raising the engine's EGR rate and consequently increasing PM emissions.

### 2.2 Effect of $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.7}\text{Bi}_{0.3}\text{O}_3$ -Loaded Aftertreatment Devices on Gaseous Emissions

[Figure 3: see original paper] shows the HC and CO purification performance of the four aftertreatment devices combined with a commercial DOC during load characteristic tests at 2510 r/min. All four devices achieved high purification efficiencies for HC and CO when combined with the commercial DOC, with effectiveness increasing alongside catalyst loading. POC-20 and DOC-20 both achieved over 90% CO and HC purification efficiency across the entire load range.

The conversion efficiencies for SOF and dry soot were 85.5%, 91.3%, 98.0%, and 74.3% for SOF, and 17.3%, 62.6%, 92.9%, and 89.9% for dry soot across the four aftertreatment devices.

### 2.3 Effect of $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.7}\text{Bi}_{0.3}\text{O}_3$ -Loaded Aftertreatment Devices on Diesel Particulate Emissions

Figure 4: see original paper shows PM purification efficiencies of different POCs and DOC at 2510 r/min and 100% load. The catalyst-free metal substrate POC-0 achieved 52.7% trapping efficiency. Catalyst loading improved PM purification efficiency, which further increased with higher loading, reaching 65.5% for POC-10 and 89.8% for POC-20. Assuming identical physical trapping efficiencies for all POCs, the oxidation efficiencies for POC-10 and POC-20 were calculated as 12.3% and 38.7%, respectively. The cordierite-substrate DOC-20 exhibited minimal physical trapping, with its 81.6% PM purification efficiency attributed primarily to catalytic conversion.

Figure 4: see original paper and (c) show SOF and dry soot purification efficiencies for different aftertreatment devices at 2510 r/min and 100% load. [Figure 5: see original paper] illustrates POC-20 conversion efficiencies for PM, SOF, and dry soot at 2510 r/min under various loads. Purification efficiencies for all three components increased with engine load. At low loads, lower exhaust temperatures result in primarily physical trapping, while higher loads and temperatures enable combined physical and chemical oxidation. During the 2510 r/min load characteristic test, POC-20 achieved purification efficiencies of 57.6–94.2% for PM, 47.6–100% for SOF, and 51.2–92.9% for dry soot. Compared to DOC catalysts that show high SOF oxidation efficiency but minimal dry soot oxidation, perovskite-loaded POC demonstrates strong oxidation effects on both SOF components and dry soot.

## Conclusions

This study prepared  $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.7}\text{Bi}_{0.3}\text{O}_3$  catalyst on both metal POC substrates and cordierite ceramic honeycomb substrates using multiple impregnation coating methods, and investigated the purification performance of these perovskite-loaded POCs and DOC for PM and other pollutants under real diesel exhaust conditions through engine bench tests. The main conclusions are:

1. Installation of  $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.7}\text{Bi}_{0.3}\text{O}_3$ -loaded POC and DOC increased diesel engine exhaust back pressure and PM specific emissions before the aftertreatment devices.
2. When combined with a commercial DOC, all four prepared aftertreatment devices achieved over 90% removal efficiency for engine exhaust HC and CO. The PM removal efficiency of perovskite-loaded POC increased with catalyst loading, reaching 94.2% maximum PM removal at 75% load under 2510 r/min conditions.
3. At high speed and full load, POC-20 achieved conversion efficiencies of 98.0% for SOF and 92.9% for dry soot, with overall PM removal efficiency reaching 89.8%, of which 38.7% was attributed to oxidation processes.

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