

Catalytic Formulation for NO₂ Suppression and Control

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ABSTRACT

To counter the adverse impact on the formation of harmful unregulated emissions such as nitro-polycyclic aromatic hydrocarbons (NPAH), catalyst companies and researchers have been developing catalytic coatings that have the capability of suppressing the formation of NO₂. NO₂ is formed at low exhaust temperatures with potentially greater concentrations at part load engine operation. Haldor Topsoe, a catalyst company from Denmark, developed such a catalytic coating for DPFs. A sample was provided to Southwest Research Institute (SwRI) to conduct this research with a view of potentially improving NO₂-suppressing formulations in the future.

The Haldor Topsoe diesel particulate filter (DPF) with its novel coating was tested together with three other DPFs and the results confirmed the capability of this DPF to suppress the formation of NO₂. This characteristic was apparent in all five engine test modes selected to cover the full engine operating range. On average, the NO₂ reduction when the exhaust flowed through the DPF was 55 percent from the engine-out levels for all five engine operating modes. This result contrasts with 39, 15, & -66 percent for the bare DPF, 0.88g/l, and 1.77g/l Pt coated DPFs, respectively.

BACKGROUND

There is mounting evidence from epidemiological and toxicological studies of transport-related air pollution showing adverse effects on health. Experimental research conducted indicates that these effects are related to the increased formation of oxygen reactive species and changes in antioxidant defense capacities at both systemic and organ levels. Studies conducted at INSERM U644 on Diesel engine emission toxicity using both in-vitro and in-vivo biological models exposed to

continuously sampled and diluted engine emitted aerosols, have identified that the major increase in oxidative stress induction was associated with the use of platinum based oxidation catalysts in Diesel engine exhaust. The studies also indicated that diluted emission filtration of the sampling line had no effect on modulating the observed emission impact [1]. Measurement of emission oxidant potential using electron spin resonance (ESR) techniques with 1-Hydroxy-3-carboxy-2,2,5,5-tetramethylpyrrolidine (CPH) as a spin probe revealed that the reactivity correlated well with NO₂ emission concentration as shown on Figure 1. This work was conducted on non-treated (NT) raw Diesel emission, as well as on Diesel exhaust treated with a platinum-based diesel oxidation catalyst (DOC). NO₂ concentrations were 15 and 140 ppm for NT and DOC-treated emissions, respectively.

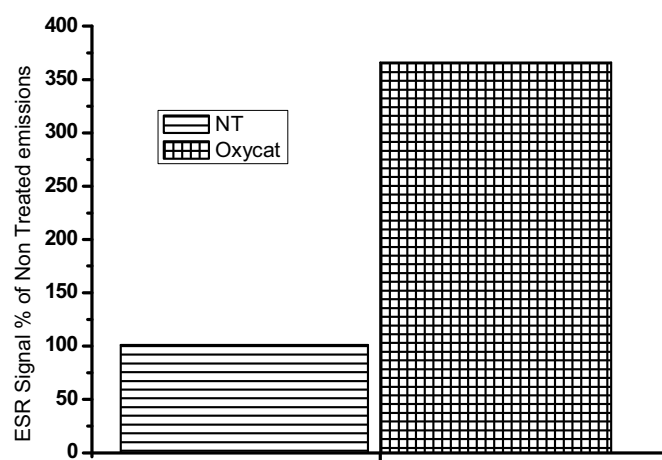


Figure 1. ESR Signal Resulting From Gas Phase to Biological Fluid Containing CPH as a Spin Probe

Using an acellular system, we assessed the capacity of gaseous NO₂ to interact with CPH dissolved in biological fluids and showed that electron spin resonance (ESR) signal increased as a function of NO₂ gas phase concentration. This NO₂-induced increased signal could be almost totally mitigated by using anti-oxidant agents as ascorbic acid, reduced glutathione, or sodium dithionite. Figure 2 shows the impact of antioxidant on ESR signal induced by 5 ppm NO₂, 5mM ascorbic acid, 5mM reduced glutathione, and 5mM dithionite.

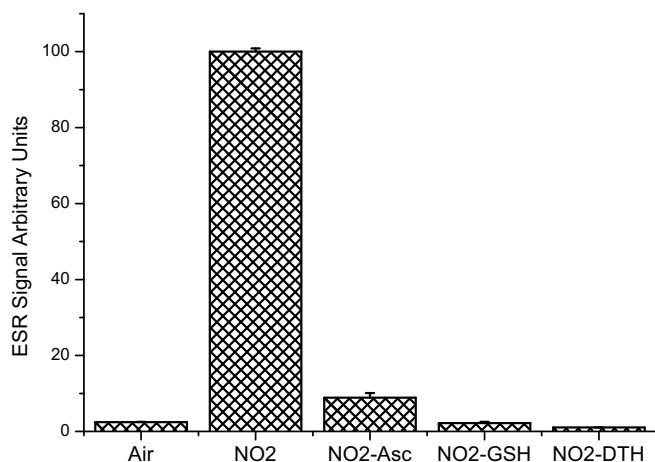


Figure 2. Impact of Antioxidant On ESR Signal

Interestingly enough, experimental studies show that exposure to Diesel engine emissions lead to decreased glutathione and anti-oxidant agent concentrations in the lung lining fluid [2] as well as decreased intracellular glutathione levels in organotypic cultures of lung tissue [3]. In the latter experiments, the observed changes were associated with the aerosol NO₂ content. Recent experiments at INSERM showed that in a rat model of chronic cardiac insufficiency, inhalation of NO₂ could mimic the observed impact of oxidation catalysis-treated emissions on cardiac electrophysiology recorded by continuous telemetry [4] thus pointing out the potential role of NO₂, beside particulate matter as being a rising active trigger of cardio-respiratory responses to traffic emission exposure which have been reported in epidemiologic studies [5].

NO₂ is a well known airborne toxic substance with a variety of health impacts as extensively reported in the World Health Organization (WHO) air quality guideline update 2005. On this basis increasing NO₂ emissions from the Diesel engine tailpipe should be considered a new health concern. Increased NO₂ atmospheric concentrations in the proximity of ground transportation traffic have been reported in the City of London, in several German cities, and in Paris. This development represents a rising source of concern. As discussed by [6], these concerns are mainly due to the onset of platinum based oxidation catalysis for Diesel emission aftertreatment strategies.

The study described below represents a potentially interesting method for NO₂ abatement while keeping efficient PM, CO, and HC removal efficiencies.

DPF CATALYTIC FORMULATION

Catalyzed diesel particulate filters (cDPF) are currently an important part of diesel exhaust systems. The role of the catalytic coating on a diesel particulate filter is to assist passive soot regeneration by directly oxidizing soot either by oxygen or indirectly by forming more NO₂. In addition, the catalytic coating has the function of oxidizing hydrocarbons and carbon monoxide both under passive and active (forced) DPF regeneration.

So far, the main technical solutions have utilized NO₂ as low-temperature soot oxidation agent [7] as described in the following equations:



where trapped soot is symbolized by C (carbon). One way of quantifying passive soot combustion is by the so-called balance point temperature (BPT), which is the temperature at which soot accumulation on the filter is balanced by soot combustion. Soot oxidation by NO₂ has been reported to result in a BPT as low as 250°C [7], which is sufficient to rely only on passive regeneration of the soot during many driving patterns. However, since the NO₂/soot ratio for the reactions (1) and (2) is nearly impossible to manage in practice, a surplus of NO₂ relating to soot combustion may be formed, resulting in an increased NO₂ emission from the vehicles' tailpipe.

The solution to this problem has been to develop an alternative novel catalytic coating formulation that reduces the NO₂ emission from the cDPF. However, this formulation should still possess comparable passive soot combustion characteristic when the cDPF is placed downstream from a diesel oxidation catalyst (DOC), and also still have good hydrocarbon (HC) and carbon monoxide (CO) oxidation properties.

As precious metal for primarily HC and CO combustion palladium has been selected, since it has a low tendency to catalyze the oxidation of NO to NO₂, while still having nearly the same potential for catalyzing the full oxidation of HC and CO during passive and active regenerations. These processes are described below:



Palladium catalysts dispersed on carriers are stable at high temperature. Another important property of palladium, demonstrated in this study, is the ability to reduce NO₂, when palladium is combined with specific

base metals. Yet another advantage of palladium is that it is currently significantly less expensive than platinum.

Catalytic base metal oxide coating on the diesel filter has the potential to replace the passive soot regeneration by generated NO₂, when NO₂ is to be limited or engine-out NO_x from modern diesel engines is low. It is also known from the literature [8], [9], [10], [11] and [12] that a number of base metal oxides such as Co₃O₄, CuO, V₂O₅, Nb₂O₅, Fe₂O₃, CeO₂, Mn₂O₃, MoO₃, Cs₂SO₄, Li₂SO₄ and K₂SO₄ in combination with various carriers as Al₂O₃, La₂O₃, ZrO₂, TiO₂ and MgO have catalytic soot combustion ability. The base metal oxide coating must be optimized for durability in diesel exhaust to high peak temperatures. Some optimized compositions combust soot from around 350°C which is significantly lower temperature than the combustion in air of approximately 550°C or more. This implies that passive soot regeneration can take place using a base metal oxide catalyst on the filter without the assistance of NO₂ according to:



This catalytic soot combustion requires a good soot base metal oxide catalyst contact that is facilitated by proper design of the catalyst coating and the porous filter structure. The oxygen for soot combustion will then to a large degree originate from the base metal oxide lattice, as also demonstrated in a recent oxygen isotope study [13].

The above knowledge was used in the development work of the novel base metal-palladium DPF coating with the trade name BMC-211 tested in the current study [14]. The base metals in the BMC-211 are stable for high- temperature soot combustion and are suitable for automotive use. An indication of the performance characteristic of this coating is the fact that in addition to not producing extra NO₂, it also reduces significant amounts of NO₂ to NO at temperatures below 330°C. We have shown that the mechanism for this NO₂ removal requires both the presence of palladium and base metal on a carrier. The detailed mechanism is not fully investigated yet; however, experiments show that one plausible route is:

First oxidation of soot on the base metal oxide



or oxidation by NO₂



The CO is then adsorbed on Pd by spill over



and subsequently reacted by NO₂



CATALYST PREPARATION

A sample of commercial silicon carbide wall flow filter having 46.5 cells/cm² with a wall thickness of 0.31 mm with the geometric dimension (given as diameter×length) of 144 mm×178 mm (2.89 l) was used for the experiments. The filter sample was coated with 75.8 g/l of this novel base metal palladium catalytic coating according to a patent application [15]. The palladium content of the coating was 1.53 g Pd/l. This catalytic coating is code-named BMC-211.

EXPERIMENT

Objectives

The objectives of this experiment were to:

- 1) Characterize the impact of the DPF novel catalytic formulation on NO₂ emissions, and
- 2) Compare the characteristics of the novel DPF NO₂ emissions with other traditional DPF formulations to determine the level of NO₂ suppression resulting from the novel formulation.

Technical Approach

The technical approach involved comparing the performance of the BMC-211 DPF with three other DPFs using a high speed PSA (Peugeot) engine. The engine was a model year 2000 equipped with a common-rail injection system capable of a maximum injection pressure of 1800 Bar. Its power output was 170 horsepower with a maximum torque of 370 Nm at 1500 rpm. The engine was turbocharged and intercooled. The other three DPFs included one bare DPF, a second with 0.88g/l platinum (Pt) coating, and a third with a 1.77g/l Pt coating. This experiment was limited to the NO₂ formation evaluation rather than involve the detailed chemical analysis for the complex and lengthy list of unregulated emissions.

Five engine modes (speed and load combinations) were selected to cover the operating scope of the engine and produce various engine-out NO₂ concentrations. These 5 modes ranged from low speed, low load (LSLL) to high speed, high load (HSHL) conditions, and included low speed, high load (LSHL), high speed, low load (HSLL), and medium speed, medium load (MSML) conditions. Details of these conditions are given in Table 1 and illustrated in Figure 3.

TABLE 1. DESCRIPTION OF TEST MODES

Engine Set Points			
Mode	Speed, rpm	Load, N.m	DPF T _{in} °C
LSLL	1150	34	116
LSHL	1150	102	228
MSLL	1600	68	218
HSLL	2200	38	185
HSHL	2200	113	366