

Effect of Soot Accumulation on Light-Off Performance of Field-Aged and Accelerated Phosphorus Poisoning Diesel Oxidation Catalysts

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Introduction

The diesel oxidation catalyst (DOC) is used extensively to reduce total hydrocarbon (THC), carbon monoxide (CO) as well as total particulate matter (TPM) by targeting the soluble organic fraction of soot. Investigations into DOC deactivation mechanisms have identified three main contributors: thermal aging, fouling and poisoning. Thermal aging is very much a materials issue, whereas fouling and poisoning are directly linked to drive-train conditions. The incorporation of DOCs into advanced aftertreatment systems requires an understanding of the role soot accumulation and poisons derived from fuel and lube-oil play in deactivation to extend device lifetime. Although phosphorus derived from the lube-oil additive zinc dialkyldithiophosphate (ZDDP) has been shown to degrade three-way catalysts activity [1-3], the role of phosphorus poisoning and soot accumulation on DOC deactivation is less understood.

In the present study, the effect of soot accumulation and phosphorus poisoning on THC and CO oxidation performance of DOCs is investigated. THC and CO performance of deactivated DOCs obtained from a bus fleet as well as accelerated phosphorus poisoning DOCs are evaluated using a single-cylinder diesel engine and bench-flow reactor. Phosphorus and soot content is analyzed using XRF, EPMA, SEM and XRD.

Materials and Methods

A fresh commercially-available DOC with a 300 cps cordierite substrate and Pt/CeO₂/γ-Al₂O₃ washcoat containing 0.5 gm/ft³ Pt is used for accelerated phosphorus poisoning. In addition, three identically formulated field-aged DOCs are obtained from a high-mileage bus fleet after encountering catastrophic oil and soot contamination. A naturally-aspirated direct injection (NA/DI) single-cylinder diesel engine is used to poison and evaluate THC and CO performance. Three methods of poisoning are employed in which a total of 6.0 g of phosphorus in the form of ZDDP-doped lube-oil is injected into either the combustion chamber or directly into the exhaust manifold or mixed with diesel fuel at a rate of 0.5 g/hr. Each of these methods has been shown to produce different poisoning and fouling behavior resulting in severe DOC THC and CO degradation [4].

Core samples of 0.875" diameter and 3.0" long from fresh, field-aged and accelerated phosphorus poisoning DOCs are evaluated in a bench-flow reactor using simulated diesel exhaust gases comprising of 5% CO₂, 10% H₂O, 500 ppm CO, 300 ppm C₂H₄ and 1000 ppm NO_x at a GHSV of 80,000 hr⁻¹ over a temperature range of 200-500°C in 50°C increments. A total of four temperature sweeps are performed, alternating between increasing and decreasing temperature directions to ensure repeatability of results. XRF, EPMA, SEM-EDS and XRD analyses are used to characterize material changes induced by soot accumulation and phosphorus poisoning.

Results and Discussion

Typical CO and THC light-off curves of accelerated phosphorus poisoning DOC obtained from engine and bench-flow reactor evaluation are shown in Figures 1a and 1b, respectively. CO and THC light-off curves of field-aged DOCs are qualitatively and quantitatively similar to those of accelerated phosphorus poisoning DOCs. Engine-based evaluations produce poor light-off performance compared to the bench-flow reactor in which regeneration of THC and CO light-off performance is observed at temperatures above 350°C. Restoration to fresh DOC performance is achieved for each sample after soot removal, regardless of the amount of phosphorus accumulated as measured by XRF and EPMA. The drastic difference in light-off performance between the engine and bench-flow reactor evaluation methods are, therefore, attributed to the soot-laden exhaust gases in the engine-based testing, from which a layer of soot is invariably present on the washcoat.

SEM images of DOC washcoat contamination for field-aged and accelerated phosphorus poisoning DOCs after bench-flow reactor evaluations show the absence of soot on washcoat surfaces. The resulting ash layer appears not to inhibit THC and CO oxidation, as evidence from the light-off curves. XRF, XRD and EMPA analyses reveal that the amount and chemical composition of adsorbed phosphorus remains unchanged during the DOC regeneration indicating that, in contrast to three-way catalysts, phosphorus is not a major contributing factor to DOC deactivation. Consequently, soot accumulation on the washcoat is the key mechanism responsible for the degradation of DOC performance.

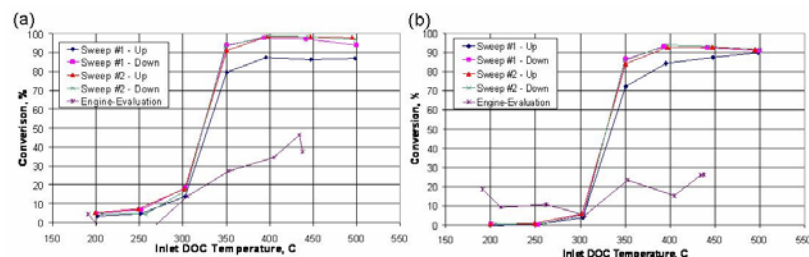


Figure 1: Typical deactivated DOC (a) CO and (b) THC light-off curves obtain from engine-based and bench-flow reactor performance evaluation.

Significance

An understanding of the roles soot and phosphorus accumulation play in DOC deactivation is achieved and provides design criteria for the implementation of DOCs in advanced automotive aftertreatment systems by improving performance and durability.

References

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