

Investigation of the Impact of Real-World Aging on Diesel Oxidation Catalysts

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ABSTRACT

Real-world operation of diesel oxidation catalysts (DOCs), used in a variety of aftertreatment systems, subjects these catalysts to a large number of permanent and temporary deactivation mechanisms. These include thermal damage, induced by generating exotherm on the catalyst; exposure to various inorganic species contained in engine fluids; and the effects of soot and hydrocarbons, which can mask the catalyst in certain operating modes. While some of these deactivation mechanisms can be accurately simulated in the lab, others are specific to particular engine operation regimes.

In this work, a set of DOCs, removed from prolonged service in the field, has been subjected to a detailed laboratory study. Samples obtained from various locations in these catalysts were used to characterize the extent and distribution of deactivation. The arsenal of techniques used to characterize the samples included probe reactions of NO and C₃H₆ oxidation, as well as a set of pre-treatment conditions, targeting at removing various contaminants, including hydrocarbons, soot, sulfur, and phosphorous.

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INTRODUCTION

Diesel oxidation catalysts (DOCs) are used in a variety of diesel aftertreatment systems, enabling them to meet stringent exhaust emission regulations. Precious metals, especially platinum (Pt) and palladium (Pd) are the primary active DOC components, with their loading and ratio depending on the specific target application [1]. Key functions of DOC include oxidation of hydrocarbons (HC) for the sake of gaseous HC slip mitigation, reduction of the organic portion of the particulate matter, and increasing the exhaust temperature; as well as oxidation of carbon monoxide (CO), and of nitric oxide (NO). In particular, NO to NO₂ oxidation is beneficial for various NO_x reduction technologies, such as lean NO_x trap (LNT) and selective catalytic reduction (SCR) [2,3]. Also, NO₂ produced by DOC provides crucial contribution to passive regeneration of diesel particulate filters (DPF).

However, practical applications expose DOCs to a variety of long-term and short-term performance degradation factors. Commonly, being the most up-stream aftertreatment element, the DOC can be exposed to different organic or inorganic species, including HC, soot, and chemical contaminants such as P, S, Ca, Zn, Na and K, originating from various engine fluids. Although typically present in small quantities, long-term accumulation of chemical contaminants could

potentially cause significant loss of DOC performance. Furthermore, in the systems where the DOC acts as a source of elevated temperature for downstream elements by oxidizing additional fuel injected for this purpose, either in-cylinder or via exhaust dosing, the DOC is intermittently exposed to high surface temperatures, unevenly distributed across the catalyst.

Thermal aging of oxidation catalysts, representing an irreversible deactivation mechanism, has been a subject of several previous studies [4, 5, 6, 7]. Sintering of precious metals is commonly believed to be the underlying reason for DOC performance loss, observed upon high-temperature exposure. The added complication in understanding of this deactivation mechanism in real-world systems arises from large temperature gradients across the operating DOC, especially when acting as a catalytic combustor for heat generation. A study by Shakir et al. [8], using IR-camera to measure the surface temperature of a model Pt/Al₂O₃ oxidation catalyst during the reaction of C₃H₆ oxidation, showed that local surface temperatures can exceed the temperatures measured by conventional methods by over 100°C. Furthermore, the location of peak temperature spot in the catalyst was found to move with aging, resulting in an overall complex aging profile. As a consequence, even when the general behavior of a given catalyst formulation is well

understood in the lab, predicting or in fact interpreting its real-world thermal aging is often difficult, due to the large temperature gradients and lack of accurate catalyst surface temperature measurements in-use.

In practical operation, a DOC is also exposed to various inorganic contaminants, such as P, S, Ca, Zn, Na and K, derived from fuel, lubricating oil, and coolant. Sulfur is the most ubiquitous among these inorganic contaminants, even with ultra-low sulfur diesel fuel (ULSD), since the cumulative exposure of a catalyst over a lifetime of a heavy-duty vehicle reaches kilograms. Use of high-sulfur fuel can cause rapid decline in DOC performance, as reported by G. McCullough et al. [9]. As shown in the same paper, with ULSD the catalyst deactivation is slowed down and could be fully recovered by thermal treatment. Sodium (Na) and potassium (K) in exhaust can originate, for example, from biodiesel. It has been reported by Cavataio et al. [10] that when present on the catalyst in the following amounts - 1 wt % Na and 3 wt% Na - they degraded the three key functions of the DOC, including the CO, HC and NO oxidation. The deterioration effect increased with the weight of Na and K. These results are consistent with William et al's results [11]. Phosphorus is another well-known chemical poison, typically affecting the most up-stream catalyst in the system. It is derived from the common engine oil additive (zinc dialkyldithiophosphate, ZDDP). Depending on the mechanism of transfer into exhaust and catalyst operating conditions, phosphorus can affect the catalyst either by physical masking or via chemical poisoning [12, 13, 14, 15]. Unfortunately, the phosphorus accumulated on DOC could not be removed in-situ even under reducing atmosphere [6]. However, earlier studies had demonstrated that acid washing could effectively remove P from the surface [16, 17].

Furthermore, due to its location up-stream of diesel particulate filter, DOC can retain soot, which could lead to masking of its active sites and loss of activity. Adsorption of un-oxidized hydrocarbons, with potential additional transformation to more carbonaceous deposits ("coke"), can also contribute to the same deactivation behavior. As shown by Scott et al., the impact of this factor can be quite substantial, exceeding such long-term deactivation factors as phosphorus accumulation and thermal degradation [14]. Fortunately, this deactivation mechanism can be reversed by oxidizing soot and coke, e.g. via NO₂ oxidation at moderate temperatures or by O₂ oxidation at elevated temperatures.

Finally, superposition of these aging mechanisms, with their different spatial distributions across the DOC, adds another level of complexity to the aging process and renders it very difficult to accurately represent the aging in laboratory conditions. In this study, we have selected several field-aged DOCs, with different mileage and aging histories, as samples representing realistic aging mechanisms, and focused on decoupling these mechanisms through laboratory analysis of their catalytic performance, supported by a variety of targeted treatments.

EXPERIMENTAL DETAILS

Samples

Field-aged catalysts used in this study all belonged to the same commercial formulation, coated on a cordierite substrate with 400 cells per square inch (cpsi), and were part of the Cummins 2007 heavy-duty actively regenerated Diesel Particulate Filter (DPF) system. Their accumulated mileage is reported in Table 1. In addition, an engine de-greened DOC (Catalyst A) with 150 hours of operation and a lab-aged DOC were used as references for comparison. The lab-aged catalyst was only exposed to thermal aging, with no chemical contaminants or masking agents present. The 150-hrs engine aged sample was subjected to a number of active DPF regeneration events, but overall was expected to have minor thermal aging. It should also have had virtually no poisoning by such slowly accumulating species as phosphorus, but possibly had a limited amount of rapidly accumulating poisons or masking agents, such as sulfur, soot or stored hydrocarbons.

In order to capture axial distribution of various aging factors, four micro-cores (diameter = 0.25", length = 1") were taken from each catalyst, including front (inlet) face, rear (outlet) face, on-axis (central) and radial locations. The samples were designated accordingly as front center (FC), rear center (RC), front radial (FR) and rear radial (RR).

Experimental Setup

The micro-core samples, obtained as described above, were placed into a quartz (fused silica) reactor tube, located horizontally in a resistively-heated furnace. The required gas species, UHP grade, were blended using MKS mass flow controllers to achieve the desired gas composition. All the lines up- and down-stream of the reactor tube were heated to the temperatures above ~150°C to prevent condensation or adsorption of reactants or products. Two K-type thermocouples, shielded with sealed quartz tubes, were

Table 1. List of DOC Samples

Catalyst Designation	A	B	C	D	E	F
Mileage	~450 ^(*)	148k	171k	60k	48k	220k

^(*) Equivalent mileage, estimated from ~150hrs of test-cell operation

^(*) Equivalent mileage, estimated from ~150hrs of test-cell operation



Documents

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placed at the inlet and outlet of the catalyst monolith to measure gas temperatures at the inlet outlet of the catalyst core. Gas composition measurements were conducted using a chemi-luminescence NO_x analyzer (CAI 400HCLD, modified to accommodate low flow rates) and a Mass Spectrometer (Agilent, 5973N) to measure HC concentration.

Experimental Conditions

Catalytic behavior of the samples was probed using two reactions of practical relevance - oxidation of NO and of HC. Low concentrations of propene (C₃H₆) were used to interrogate the HC oxidation function, in order to minimize the amount of heat produced by this probe reaction. Minimal reaction exotherm improves accuracy of the catalytic activity measurements, and ensures that the catalyst surface does not experience any additional thermal aging. The results thus obtained, while qualitatively representative, would not be quantitatively correct for the entire range of hydrocarbon types and concentrations found in real-world applications. The NO oxidation function was probed using a set of isothermal steady-state measurements, while HC oxidation was probed by temperature-programmed reaction (TPRx), in recognition of the different conditions under which these

functions would play their primary role in the practical application.

The pre-treatment conditions were chosen so as to distinguish between several major catalyst deactivation modes. In particular, heating catalyst up to 450°C under lean conditions for 1 hour was used to remove adsorbed hydrocarbons and coke [18]. Subsequent heating to 600°C for 1 hour was employed to remove soot and the majority of adsorbed sulfur [19, 20].

The details of the test procedures used for laboratory diagnostics of DOCs are shown in Figure 1 and in Table 2. As-received catalyst was first subjected to C₃H₆ light-off test, which was then repeated after 450°C and 600°C treatments. Each of the C₃H₆ light-off curves were obtained by ramping catalyst temperature from 75°C to 350°C with a 10°C/min ramp rate. Finally, NO oxidation performance was measured for the “cleaned” DOC, with temperature descending from 400°C to 150°C in six steady-state steps.

An example of experimental data thus obtained is reported in Figure 2 for the lab aged DOC with 650°C, 10hrs and 700°C, 16hrs, respectively. To simplify the comparisons, the data are reported as a T_{50%} for HC light-off and T_{25%} for NO oxidation, to capture the more “sensitive” yet reproducible parts of the curves. Such evaluation was applied

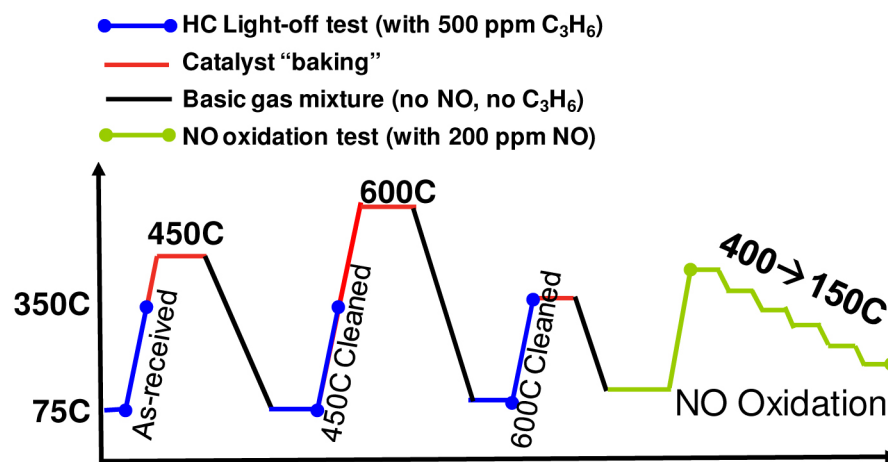


Figure 1. Schematic representation of the catalyst testing procedure

Table 2. Synthetic exhaust gas composition used in the C₃H₆ and NO oxidation experiments

Gas Species	Concentration during C ₃ H ₆ light-off	Concentration during NO oxidation
NO _x (ppm)	0	200
C ₃ H ₆ (ppm)	500	0
H ₂ (%)	0	0
CO (%)	0	0
O ₂ (%)	5	5
H ₂ O (%)	2.5	2.5
CO ₂ (%)	5	5
He	Balance	Balance
S.V., hr ⁻¹	60,000	