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A Diesel Oxidation Catalyst with Low T50 Properties and a Wide Operating Temperature Range

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ABSTRACT

AirFlow Catalyst Systems has developed a unique low temperature washcoat material, which is ideally suited for use in Diesel Oxidation Catalyst (DOC) applications. A key feature of this DOC is its ability to efficiently oxidize CO and hydrocarbons at the diesel exhaust temperature levels, with lower than traditional PGM loadings. In addition to T50 values that are below 200^{o}C for these exhaust gases, this DOC shows thermally stable operation across the full diesel exhaust temperature range. DOC components with this washcoat material can be readily manufactured using ceramic or metal substrates in a single pass process without changes to current processing equipment.

Data showing the T50 characteristics of this DOC component, as well as results of accelerated aging and engine tests will be presented.

KEYWORDS: Diesel Oxidation Catalyst (DOC), catalytic oxidation, T50, low temperature, CO oxidation, hydrocarbon oxidation, washcoat, Pt catalyst, X-ray diffraction, scanning electron microscopy, hydrothermal aging

I. INTRODUCTION

Pollution emitted by diesel engines contributes greatly to our nation's air quality problems. Increasingly stringent environmental regulations are exerting pressure on diesel engine manufacturers to reduce polluting emissions from their exhaust systems. Carbon monoxide (CO), hydrocarbon mixtures (HC), nitrogen oxides (NOx), and particulate matter (PM) all contribute to serious health problems [1]. The diesel oxidation catalyst (DOC) is effective for the control of carbon monoxide (CO), hydrocarbons (HC), and the soluble organic fraction (SOF) of particulate matter in the exhaust stream of diesel engines [2].

As DOC technology has progressed to the point where CO and HC emissions can be reliably mitigated, there remain issues of cost and low temperature activity (i.e., low light-off or T50). The exhaust temperature of diesel engines is much lower than that of gasoline engines. Maximum diesel exhaust temperatures rarely exceed 350^{o}C.

Therefore, there is less thermal energy to facilitate the catalytic destruction of the exhaust pollutants. When a cold diesel engine starts it can take several seconds for the exhaust temperature to reach the temperature where the catalytic processes begins and conversion of pollutants to harmless gasses occurs. It is important to begin the conversion of CO and hydrocarbons as soon as possible after engine start to minimize exhausting these pollutants to the atmosphere. In diesel applications this requirement is generally achieved by use of high precious group metal (PGM) loadings.

Recent development activity at our laboratory, starting with the license for a low temperature CO oxidation catalyst from NASA, has produced a cost effective, technically advanced washcoat material for diesel applications. Trademarked Active-X™ this DOC has excellent thermal durability and low light off temperatures for CO and hydrocarbons oxidation, while requiring substantially less PGM to achieve the required catalytic activity. Platinum is being used as the catalyst of choice in most DOC applications in the industry. However, at a current cost of $1,200 per ounce, using Active-X as the washcoat support reduces the amount of platinum necessary for the required low temperature light off, thereby reducing cost of the exhaust system.

II. EXPERIMENTAL

A. Materials

AirFlow's Active-X™ washcoat powder, a multi-component oxide material with a surface area of ca. 200 m^2/g, was prepared as previously described [3].

The final DOC monolith was prepared by milling an aqueous suspension of the washcoat (to give a particle size distribution with D_{50} = 2.5 microns and D_{90} < 15 microns) and applying the resulting aqueous slurry to the flow-through cordierite substrate (6" diameter x 4" long / 400 cpsi), followed by drying and then calcining at 450^{o}C for 1 hour. Washcoat coverages were ca. 2.6 g/in^3. The desired Pt loading was then applied by a dip coating process using a soluble platinum nitrate complex and calcining the coated substrate at 450^{o}C for 1 hr.

B. Characterization of Materials

X-Ray Diffraction Measurement: The X-ray scans were recorded on a Scintag, Inc. theta-theta diffractometer (model PAD-X) with a solid-state Ge detector using copper k-alpha radiation. The voltage and current were 45 kV and 40 mA, respectively, and step scans with a step size of 0.02 degrees and a preset time of 0.3 sec/step were used. The detector had a 0.3 degree receiving slit.

Scanning Electron Micrographs: SEMs were recorded on an ASPEX PSEM 3025 equipped with an energy dispersive X-ray analysis unit for element mapping.

C. Aging and Testing

Hydrothermal aging of the DOC was carried out by heating the monolith at 800^oC for 5 hours in a flowing gas mixture containing 10% H_2O in air at a space velocity of $25Khr^{-1}$.

Sulfur aging was done using a similar procedure but with the flow gas composition being 150 ppm SO_2, 3 % H_2O, and air at a space velocity of $24Khr^{-1}$.

Measurements of T50 values for CO and hydrocarbon oxidations were carried out by passing a standard synthetic gas mixture over the DOC monolith while increasing the temperature from 80^oC to 450^oC at a heating rate of 10^oC/min. The gas mixture, prepared using a standard gas handling system with digital mass flow controllers, contained 1060 ppm CO, 33 ppm propylene, 30 ppm decane, 100 ppm NO, 14% O_2, 5% H_2O , and 4% CO_2. A space velocity of $50Khr^{-1}$ was used in the T50 measurements

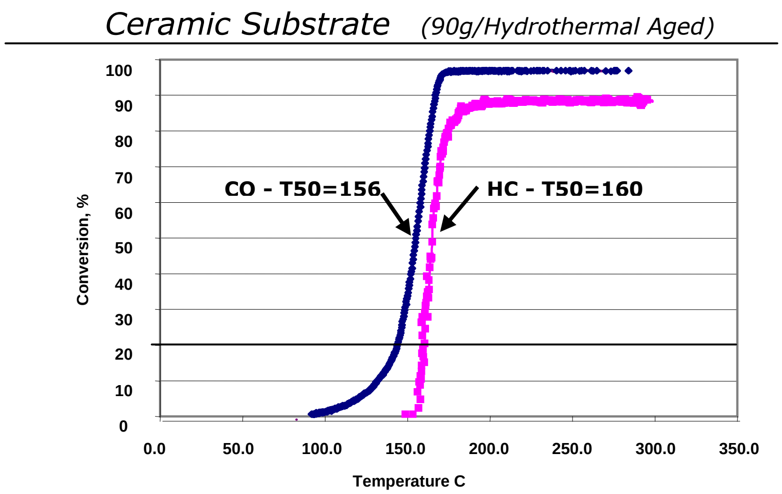
III. RESULTS AND DISCUSSION

A. Aging and Test Results

Test results demonstrate that the AirFlow's DOC, with Active-X washcoat and Pt catalyst coated on a cordierite substrate, has excellent durability and T50 values for CO and hydrocarbon oxidation below 200^oC. **Figure 1** gives the CO and hydrocarbon light-off curves for a DOC containing 90g Pt/ft3 loading which had been hydrothermally aged for 5 hours at 800^oC. The

T50 values for the CO and hydrocarbon oxidation reactions are both significantly below 200°C (i.e., 156°C and 160°C, respectively).

Figure 1: CO and Hydrocarbon Light-off Curves for an AirFlow DOC Containing 90g Pt/ft^3 and Hydrothermally Aged for 5 Hours at 800°C.



Similarly low T50 values are obtained after sulfur aging of this DOC (**Figure 2**).

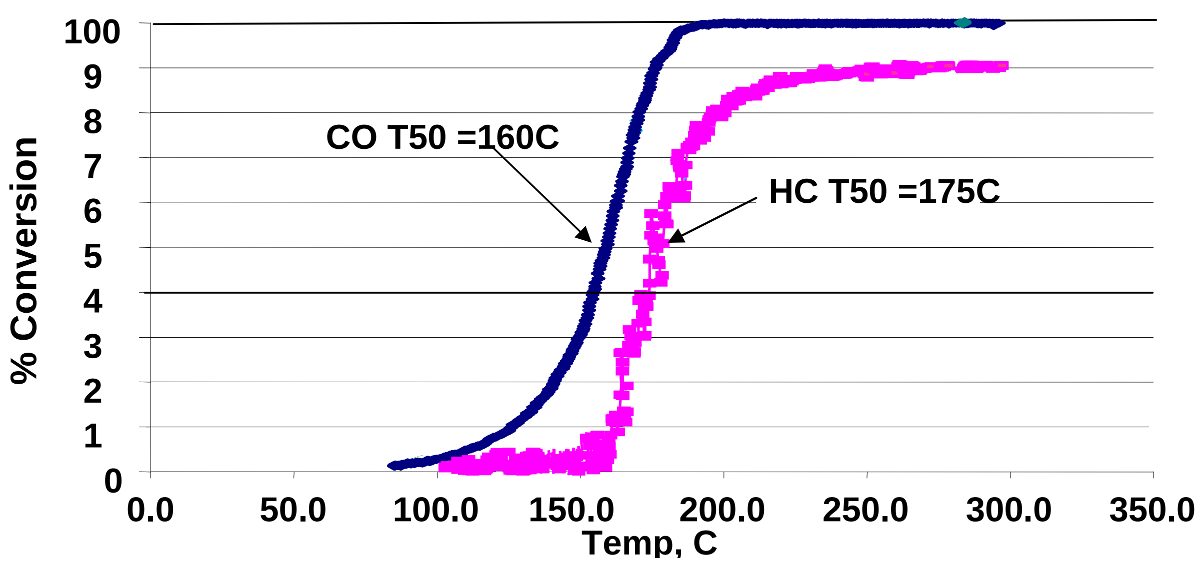
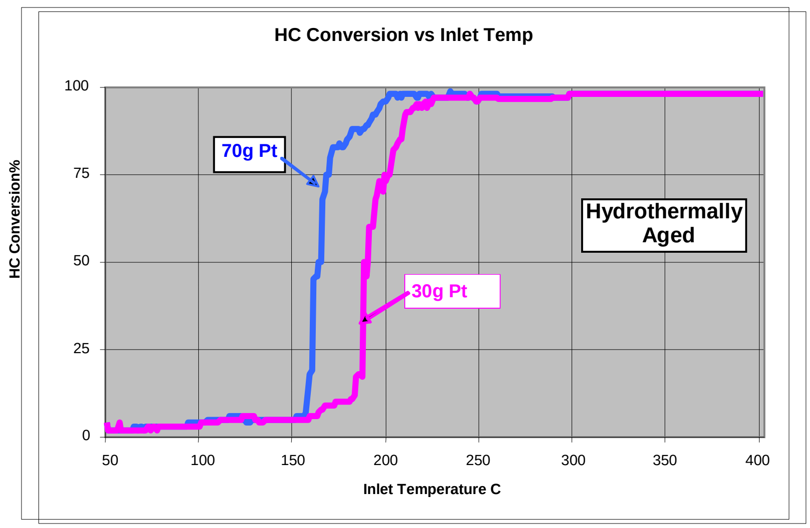


Figure 2: CO and Hydrocarbon Light-off Curves for an AirFlow DOC Containing 90g Pt/ft^3 and Sulfur Aged for 18 Hours at 300°C.

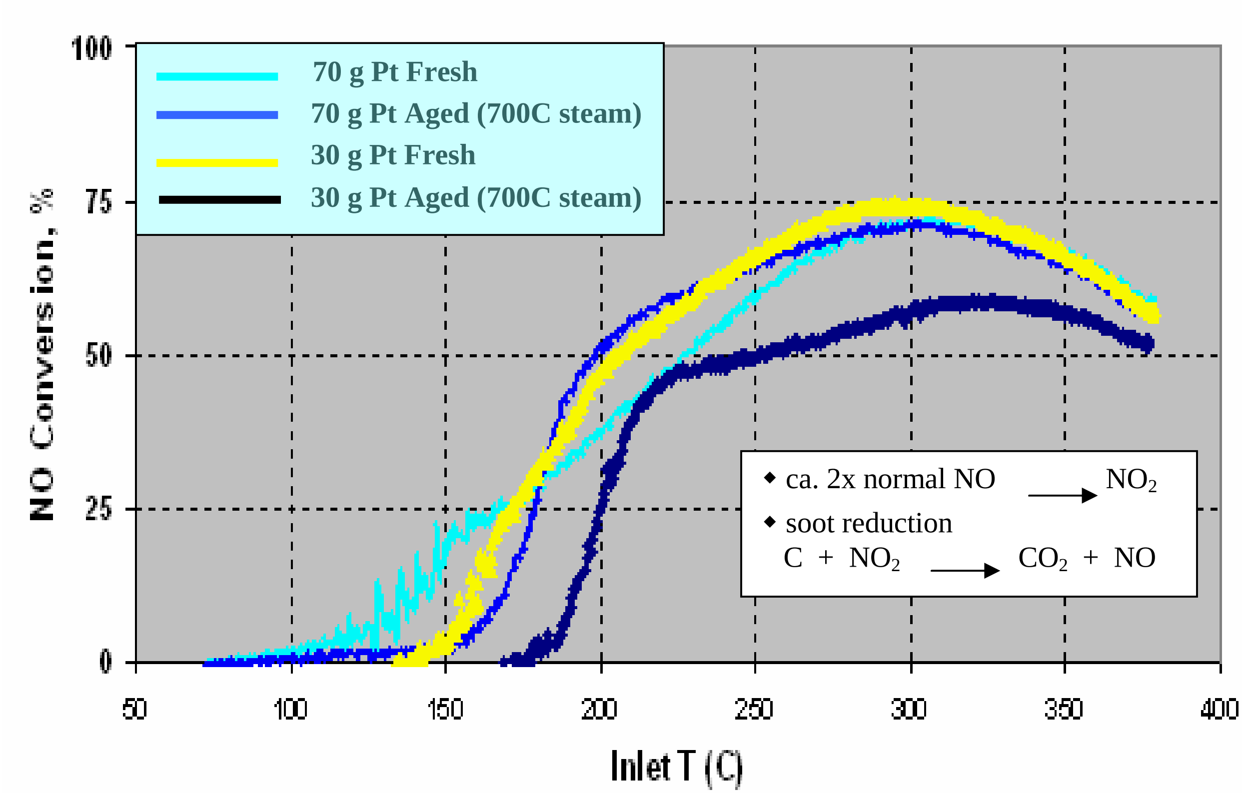
As illustrated in **Figure 3**, the low temperature activity of the AirFlow DOC is maintained even on lowering the Pt loading to 30 g/ft^3.

Figure 3: Hydrocarbon Light-off Characteristics for AirFlow's DOC With Pt loadings of 30 g/ft^3 and 70g/ft^3 After Hydrothermal Aging for 10 Hours at 700^{o}C.



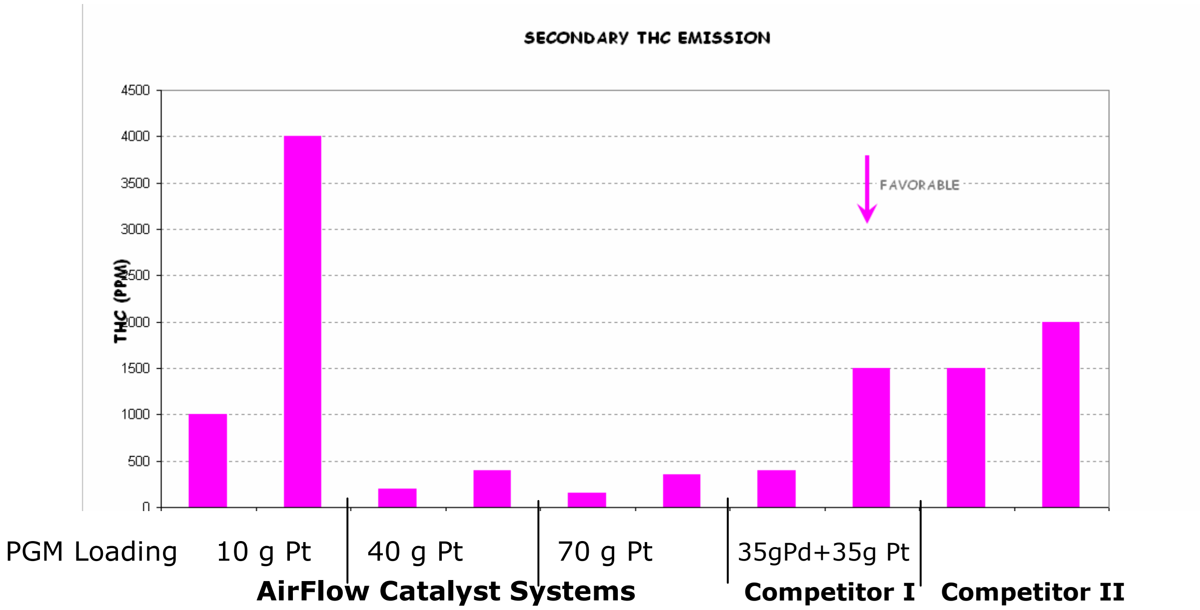
In addition, Active-X has been shown to give high NO to NO_2 conversion (**Figure 4**). This high conversion is maintained after hydrothermal aging, as well as on lowering the Pt loading from 70 to 30 g/ft^3 (**Figure 4**). This high activity for NO_2 formation is useful for soot oxidation in a downstream diesel particulate filter (DPF). Soot can be oxidized at ca. 250^{o}C by NO_2, vs ca. 625^{o}C for O_2. The use of this strong oxidizing property of NO_2 is the chemical basis of the Johnson Matthey Continuously Regenerating Trap™(CRT) [4].

Figure 4: NO -> NO_2 Conversion Curves for AirFlow's DOC



Engine tests run on the AirFlow DOC support the superior performance and durability observed in the laboratory bench reactors. **Figure 5** shows comparative engine test results obtained for AirFlow's DOC and two DOC's obtained from other manufacturers using a 5.6L Dodge Ram engine. These results show that the Airflow DOC gives superior performance compared to the two competitor DOCs at both 70 and 30 g Pt/ft^3. Significantly, these test results show that there was no substantial decrease in performance when the Pt loading was lowered to 30 g/ft^3 in the AirFlow DOC.

Figure 5: Comparative Engine Tests (5.6L Dodge Ram) of AirFlow's DOC vs Two Competitor DOCs



B. Analysis of Aged and Tested DOC

A number of surface and bulk analytical tools have been employed to verify test data indicating excellent durability of the AirFlow DOC. The thermal durability of Active X washcoat powder has been demonstrated by X-ray diffraction (**Figure 6**). The lower set of scans corresponds to an early version of AirFlow's washcoat powder. As seen from the sharp peaks observed on thermally annealing the powder above 800^{o}C, significant crystallization occurs at these temperatures. In contrast, the top two sets of diffraction patterns, corresponding to two preparative methods for the current Active X washcoat product, show excellent resistance to thermal crystallization, even after annealing for 4 hours in air at 1000^{o}C.

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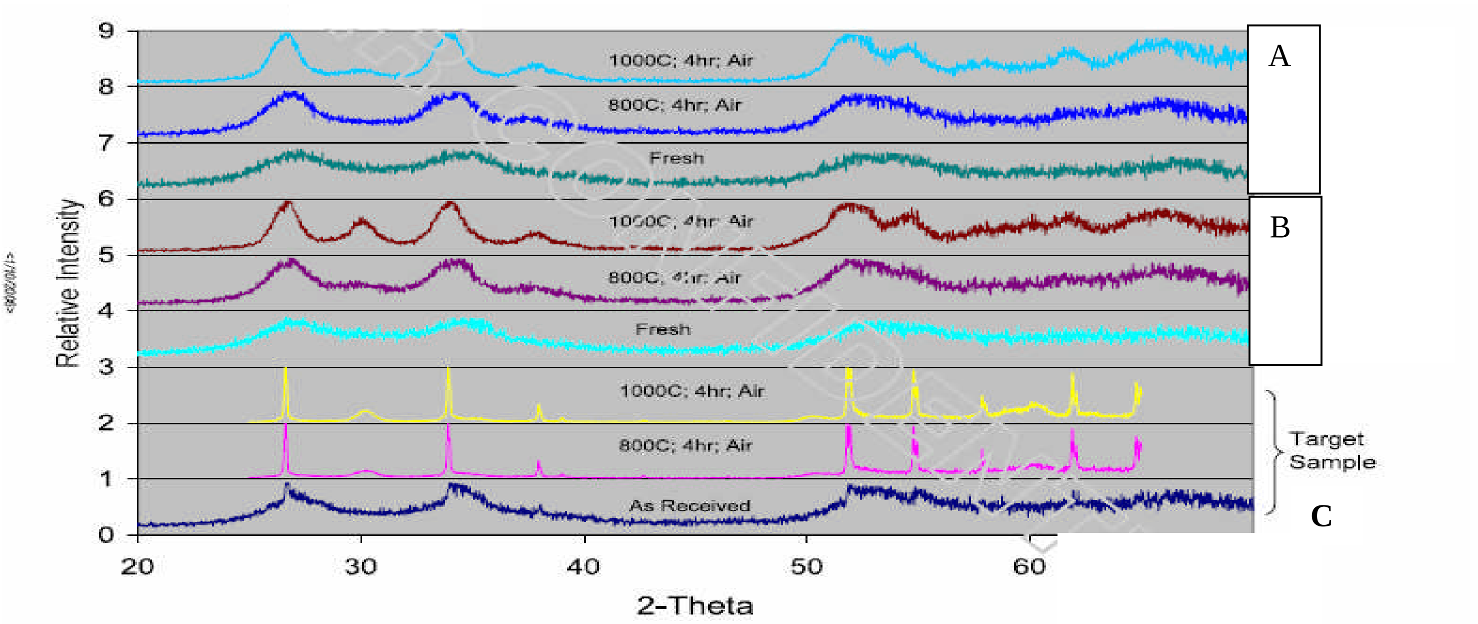
Figure 6: X-Ray diffraction Patterns of Active X Washcoat Powder (A and B), and an Earlier AirFlow Washcoat Powder (C)



The ability of Active X to stabilize applied Pt catalyst to thermal sintering has also been demonstrated by X-ray diffraction. **Figure 7** gives the X-ray diffraction pattern of an AirFlow DOC comprising a cordierite substrate coated with Active X and 70g Pt/ft^3. This DOC was hydrothermally aged for 100 hours at 750^{o}C and engine tested for 400 km (Fiat Doblo 1.9 JTD emission test). As shown in **Figure** 7, the absence of peaks due to Pt confirm that the catalyst maintains its high dispersion after these aging and test conditions. Scanning electron microscopy (**Figure 8**) further confirms the high dispersion of the Pt in this sample (i.e., Pt crystallites of ca. 100 – 400 nm in the aged and tested sample).

Figure 7: X-Ray Diffraction Pattern of Hydrothermally Aged and Fiat Doblo Engine Tested AirFlow DOC

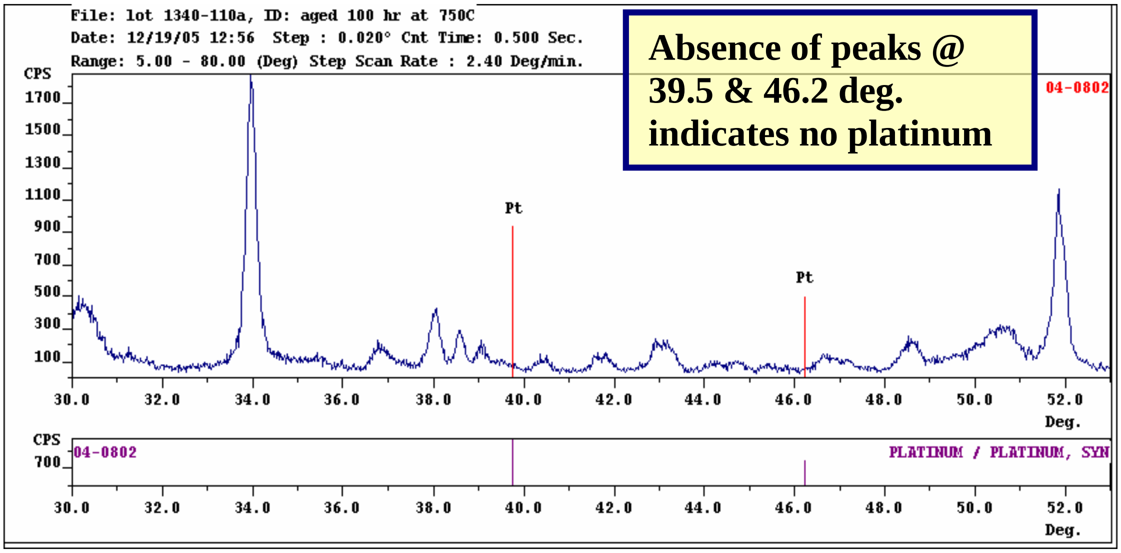
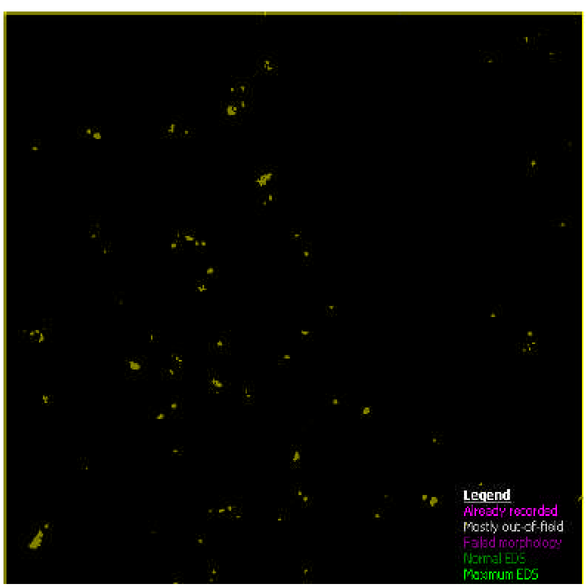
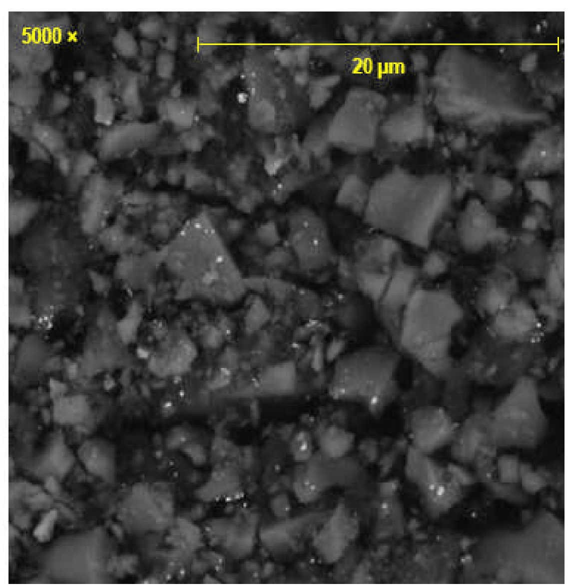


Figure 8: Scanning Electron Micrograph of Hydrothermally Aged and Engine Tested AirFlow DOC





IV. CONCLUSIONS

AirFlow Catalyst Systems has developed a superior washcoat material, Active-X™, for use as a catalyst support material in diesel oxidation catalyst components for reduction of CO and hydrocarbon emissions. When coated on a ceramic or metal substrate, with Pt catalyst, this material provides DOCs with T50 values for CO and hydrocarbon oxidations below 200^{o}C as well as NO -> NO_2 conversions two - three times the values typically observed in DOCs. These DOCs also exhibit excellent thermal durability as well as resistance to sulfur poisoning. In addition, use of this washcoat material allows significantly lower Pt loading to be used to achieve this performance (e.g., 30 g ft^3 vs the conventional 70 g/ft^3 to achieve T50 values below 200^{o}C). Engine tests have also demonstrated superior activity for this DOC. The ability of Active-X™ to promote the high dispersion of the Pt catalyst on the washcoat surface has also been demonstrated by X-ray diffraction and scanning electron microscopy studies on aged and tested DOC components.

V. REFERENCES

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