

## LOW TEMPERATURE OXIDATION CATALYST DEVELOPMENT AND APPLICATIONS

Joseph A. Holroyd  
Director, Technical Sales/Marketing  
AirFlow Catalyst Systems  
183 E. Main Street Suite 925  
Rochester, NY 14604  
e-mail: [jholroyd@airflowcatalyst.com](mailto:jholroyd@airflowcatalyst.com)

### ABSTRACT

#### LOW TEMPERATURE OXIDATION CATALYST DEVELOPMENT AND APPLICATIONS

Low temperature washcoat material, suited for use in Diesel Oxidation Catalyst (DOC) and Catalyzed Diesel Particulate Filter (CDPF) applications can enhance the performance of these components. A key feature of washcoat material with enhanced catalytic activity for DOCs is the ability to efficiently oxidize CO and hydrocarbons at the diesel exhaust temperature levels, with lower than traditional PGM loadings. In addition to T50 conversion values that are below 200°C for these exhaust gases, this material shows thermally stable operation across the diesel exhaust temperature range. Data showing the T50 characteristics of this DOC component, as well as results of accelerated aging and engine tests will be presented. CDPF components manufactured with this catalyst lower the burn-off temperature of soot from the substrate, providing a passive soot removal system. Data showing low temperature soot burn-off will be presented.

Components for DOC or CDPF applications with this catalyst material can be readily manufactured using ceramic or metal substrates in a single pass process without changes to current processing equipment.

### INTRODUCTION

Diesel Oxidation Catalysts (DOC) and Diesel Particulate Filters (DPF) applied to vehicles manufactured from 2007 forward will encounter lower temperature exhaust out of the engine. In order for catalyst to be effective, they require a threshold temperature to “light-off” (LOF) and convert the noxious gases and particulate matter (PM) to harmless gas and water.

Light-off behavior and performance of a catalyst is not only a function of catalytic formulation and coating density but also of operating conditions. LOF is generally defined as the temperature at which the conversion rate of gaseous constituents reach the 50% conversion level. The DOC components used in this work consisted of Cordierite flow-through monoliths and metal foam material coated with Active-X™ washcoat material (2g/in<sup>3</sup> loading) and a platinum catalyst. Active-X is a proprietary washcoat supplied by AirFlow Catalyst Systems which provides low temperature T50 values for CO and hydrocarbons (i.e., below 200°C).

Diesel emission control catalysts are typically manufactured by applying a washcoat to a substrate material of a cordierite or metal material. The washcoat increases the surface area upon which the precious metal catalyst is applied. Aluminum oxide is a typical washcoat material. However, more sophisticated washcoats that lower the light off temperature of the catalyst are now common in the industry.

## 1. WASHCOAT BACKGROUND

Washcoat material is applied to various substrate materials to increase the surface area for application of precious metals as a catalyst. There are many formulations for washcoats, depending on the substrate material and the desired performance of the catalyst.

The quality and durability of the catalyst coating on the substrate material is highly dependent on the washcoating process. Therefore, the procedures for this process are guarded as trade secret by most manufacturers.

Various washcoat characteristics have different effects on the coating quality. Depending on the application, particle size can vary from less than 1 micron to several microns. The percent solids content of the slurry can be varied for certain applications. For instance, in coating certain metal foam materials, percent solids is critical. Other parameters such as pH and viscosity of the slurry and the percent solids all have an impact on the final washcoat coating.

AirFlow Catalyst Systems has designed a custom state-of-the-art Synthetic Gas Reactor (SGR) system (Figure 1) to facilitate the development of new washcoats and catalyst material compositions. The system is used to evaluate the characteristics and performance of catalysts for a variety of applications.

## 2. TEST SETUP

The Synthetic Gas Reactor provides simulated exhaust gas mixtures that can be very closely controlled. This high resolution FT-IR based gas analyzer is designed to monitor automobile and diesel catalyst combustion exhaust at 5 Hz sampling frequencies. The analyzer allows gas flows exceeding 100 L/min and no back pressure or acoustic gas cell noise is generated that could degrade the data collection. Over twenty gases can be qualified simultaneously at this frequency. Samples containing up to 30% absolute water content can be monitored without chillers. Detection limits of 1 ppm or less are achievable with this analyzer.

The reactor is also used to age catalysts to determine durability limits of coated substrates. The system is

capable of hydrothermally aging substrates up to 1000° centigrade.



**Figure 1: Synthetic Gas Reactor Set Up**

Synthetic gas reactor testing is a necessary step in the development of catalysts and diesel particulate filters. It is significantly less expensive to run laboratory tests on a reactor than to run on-engine or on-road tests to provide early development data. The system allows very precise control of the simulation gas mixture concentrations, flow rates, and other parameters.

The heart of the SGR system is a sophisticated MKS Real Time Gas Analyzer (Figure 2) composed of a high speed 0.5 cm-1 process hardened Fourier-transform (FT-IR) spectrometer. This system is unique in that it has an infrared path length of over 5 meters which provides exceptional data accuracy.



**Figure 2: MKS Gas Analyzer**

## Principle Of Operation

When a gas sample is passed through the reactor chamber (Figure 3) and is introduced to the analyzer gas cell, an infrared beam is partially absorbed by the gas species present. The spectral frequencies absorbed and their intensity are the result of the specific atoms associated with the chemical bond and strength of that bond. The absorption spectrum is unique for each infrared-active gas. The analyzer measures the absorption spectrum, and its analysis algorithm measures the concentration of each gas using pre-loaded calibrations. The system software allows for the continuous measurement, display and recording of a sample stream.

The system includes a temperature controlled circulating bath, which provides precise closed loop temperature controlled circulation to the SGR system. The bath will operate to 150°C, stable at  $\pm 0.05^\circ\text{C}$ , with a readout accuracy of  $\pm 0.5^\circ\text{C}$ .

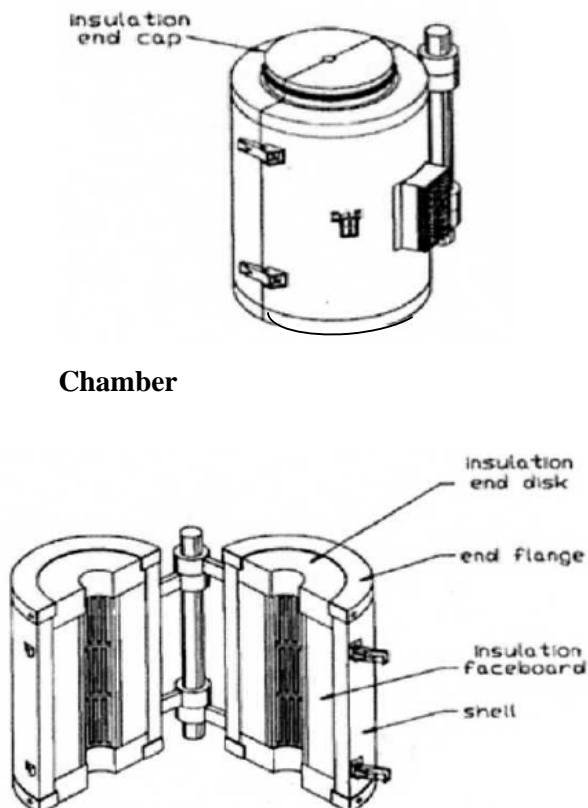


Figure 3: Reactor Heating Chamber

The reactor heating chamber shown in Figure 3 is designed to accept core samples from substrates one inch in diameter up to three inches long. The chamber has a maximum heating capacity to 2200°F (1200°C).

## 3. DESIGN FEATURES

The critical features for low temperature oxidation catalyst development are: 1) obviously, quick low light-off; 2) durability; and 3) low cost.

1) The following charts (Figures 4 & 5) indicate low temperature light-off obtained with a proprietary washcoat material, Active-X™. As the exhaust temperature of a diesel exhaust approaches 100°C the catalyst becomes active. Depending on the PGM loading, the oxidation sequence quickly reaches the point of 50% conversion, known as the T50 point. This can be as low as 100°C.

Figures 4 & 5 show the light-off curves (CO and hydrocarbon) for ceramic core samples with typical formulations. These light off curves were measured on the synthetic gas reactor (SGR) with a standard gas mixture typically used in such tests (10% O<sub>2</sub>, 4% CO<sub>2</sub>, 5% H<sub>2</sub>O, 100 ppm CO, 30 ppm propylene, 30 ppm propane, 100 ppm NO – balance N<sub>2</sub>) and a space velocity of 50Khr-1. Samples were hydrothermally aged in air with 10% H<sub>2</sub>O for 10 hours at 700°C and a space velocity of 25Khr-1.

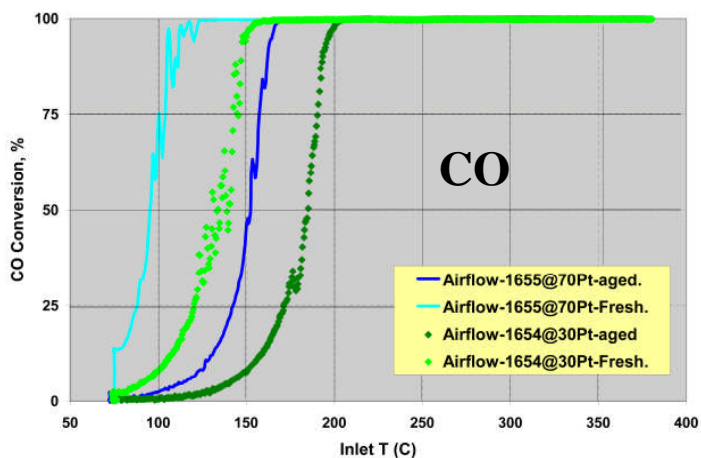
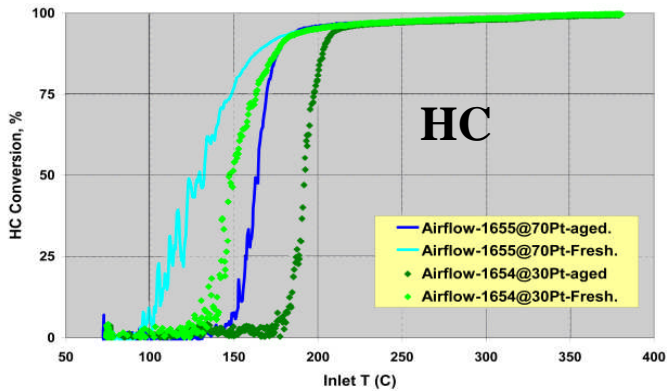


Figure 4: Carbon Monoxide Conversion



**Figure 5: Hydrocarbon Conversion**

2) Durability is affected by several key factors including temperature excursion, loss of surface area, a decline in exposed metal area (sintering), and build up of carbon deposits. To be effective a diesel oxidation catalyst must retain effectiveness in a temperature range of 100 to 900°C.

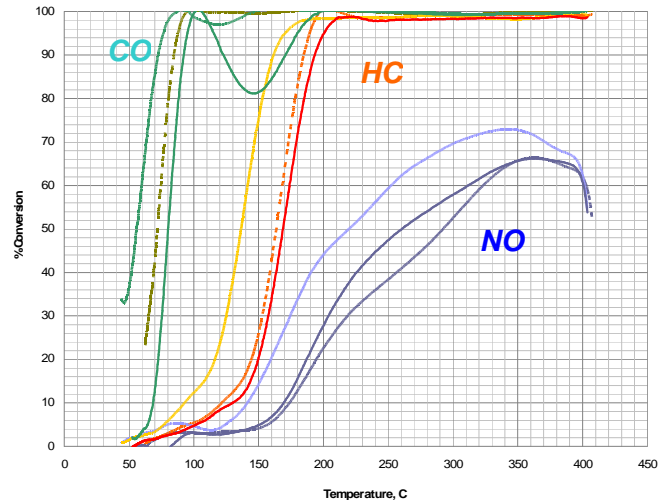
Decline in catalytic performance is often due to loss of surface area. This can be induced by high temperature excursion and/or the presence of certain gas species (particularly steam). The BET method (named for Branauer, Emmett and Teller) is used to detect changes in surface area resulting from various substrate pretreatments.

Catalyst de-activation can occur through a decline in the exposed metal area, even though the total surface area of the catalyst may not change perceptibly. A technique of X-ray diffraction (see Figure 7) and scanning electron microscope imaging (Figure 8) are used to determine PGM particle distribution.

3) In any production design, cost is typically an overriding factor. Application of a low light-off catalyst that also requires low precious metal loadings to perform well is a goal of catalyst developers. The Active-X™ material used in these experiments was compared to a variety of other catalysts by third party customer tests and showed superior performance with as little as one half as much precious metal loading.

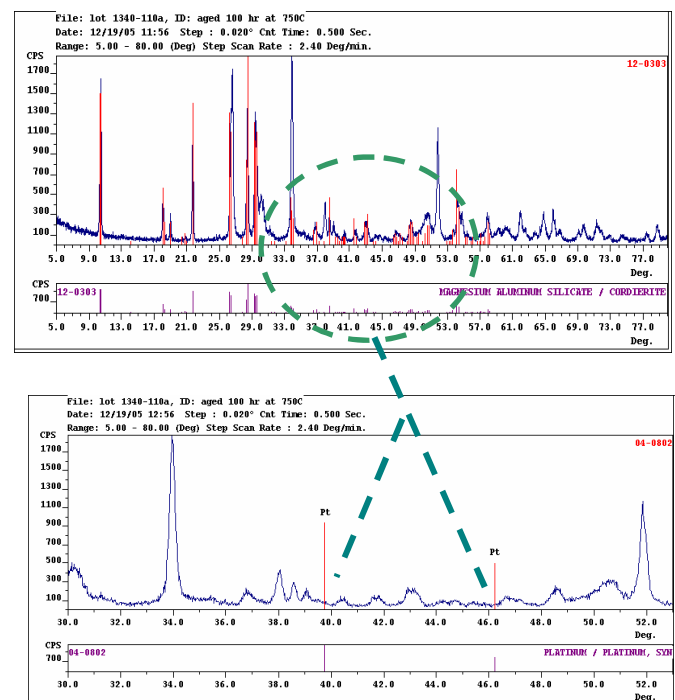
#### 4. TEST RESULTS

Certain representative examples from test results are given in the following figures to illustrate the targeted performance features.



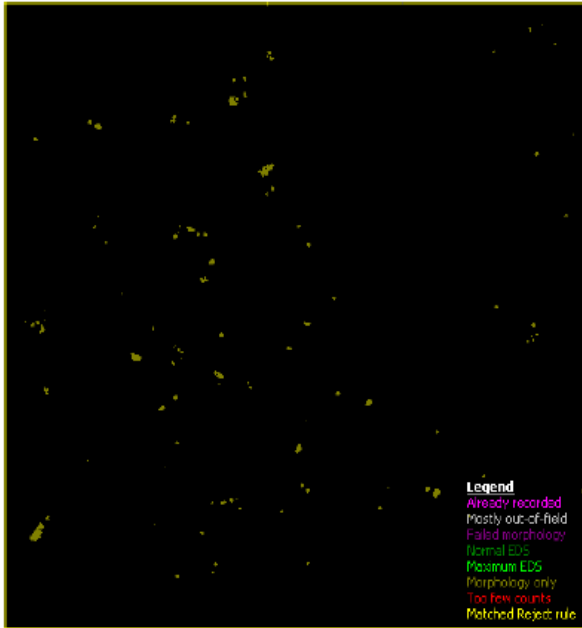
**Figure 6: Typical T50 Data**

Figure 6 indicates T50 values typical for a PGM loading of 1 gram per liter.



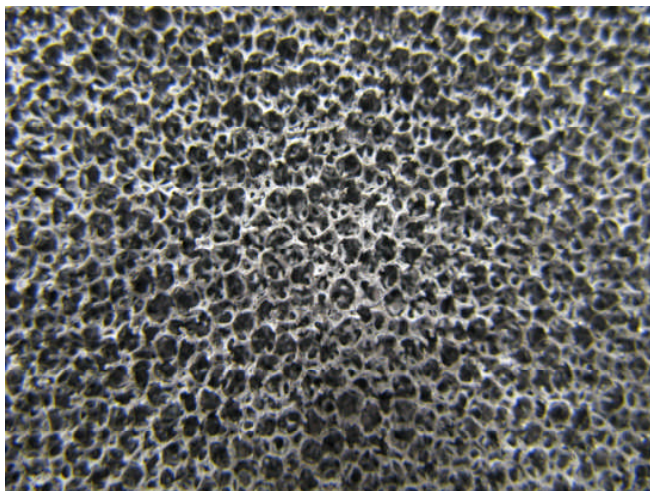
**Figure 7: X-Ray Diffraction of Substrate Coating (Absence of peaks at 39.5 and 46.2 indicates no precious metal sintering)**

Figures 7 and 8 are interesting in that Figure 7 shows no platinum present in an X-ray diffraction. However, the same material when viewed under a scanning electron microscope (SEM) shows a very fine and good distribution of platinum on the surface.

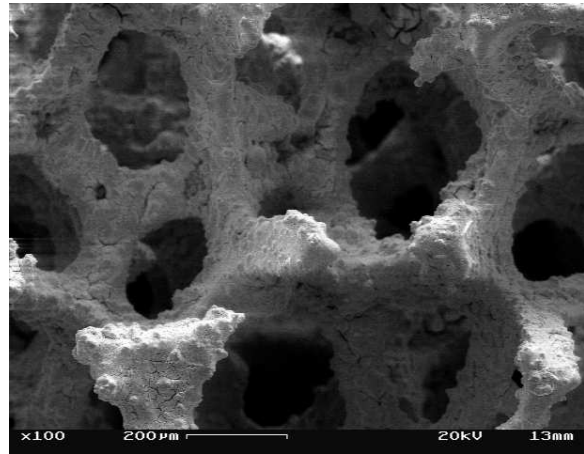


**Figure 8: Scanning Electron Micrograph (platinum particle distribution)**

**Photomicrographs of typical applications:  
Washcoat on Metal Foam Substrate**



**Figure 9: Open Pore Metal Substrate**



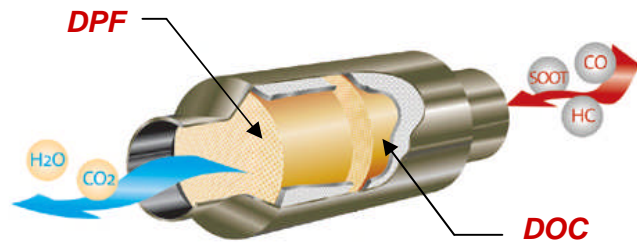
**Figure 10: Coating Magnified 100 X**

These micrographs show the control possible when applying washcoats and precious metal to unique substrates with proper preparation and control. For diesel particulate filters it is imperative to keep the pore structure open.

**CDPF Applications**

Depending on the substrate material chosen, coating of substrates for catalyzed diesel particulate filters is considerably different than for DOC applications. A low lightoff catalyst that also provides a significant exotherm is desirable for a DOC in front of a CDPF. A catalyzed DPF can reduce the temperature necessary to burn particulate matter (soot) to less than 300°C.

The washcoat consistency for a catalyzed DPF has to provide increased surface area, but not increase backpressure to the engine. Ceramic DPFs depend on wall porosity to trap and remove soot. A heavy solids count washcoat will block the pores and increase backpressure. Figures 9 & 10 show excellent washcoat coverage on metal foam material, which has proven to be very difficult to coat evenly and consistently with washcoat material.



**Figure 11 Typical Catalyst Configuration**

## 5. CONCLUSIONS

There are many demands for a low temperature light off oxidation catalysts. Low light-off temperatures for diesel oxidation catalysts are critical for cost effective efficient operation in diesel exhaust systems. For DOCs, low light-off with low precious metal loadings saves money. With platinum costing over \$2,000 an ounce and gold over \$900 an ounce, developing support washcoats that reduce the amount of precious metals required in catalysts has become a priority for manufacturers.

A DOC can also supply a high exotherm, which provides heat needed in a diesel particulate filter to change the elemental carbon to a gas.

Applying a catalyst to the DPF also enhances the conversion of PM. An even lower loading of precious metal is required in a DPF application with a DOC in front of it (Figure 11).

A washcoat is applied to the substrate of a catalytic converter to increase the surface area. Developing a low temperature catalyst requires the careful matching of the washcoat to the precious metal to be applied. Applying the proper washcoat requires a combination of chemicals milled to specific particle size, developing a slurry of the right consistency, control of the slurry pH, and control of the coating time and the drying or calcining times.

The washcoat is a key element in a catalytic converter. The precious metal needs the increased surface area provided by the washcoat to be effective. But unless that precious metal is well dispersed and stays in place (doesn't loose surface area), and has long term durability the system will fail.

Developing a winning combination of a low temperature light off catalyst formulation requiring small amounts of precious metal loading is a challenge for the catalyst industry.

## References

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## ACRONYMS, ABBREVIATIONS, DEFINITIONS

**DOC:** Diesel oxidation catalyst  
**DPF:** Diesel particulate filter  
**LOF:** Lightoff temperature  
**MFR:** Mass flow rate  
**THC:** Total hydrocarbons  
**FTIR:** Fourier Transform Infrared