

An Investigation into the NO₂-Decoupling of Catalyst to Soot Contact and Its Implications for Catalysed DPF Performance

Barry W. L. Southward and Stephan Basso

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ABSTRACT

A study of the impact of the exhaust environment and catalyst composition on the performance of direct soot oxidation catalysts has been performed. In agreement with previous studies it is noted that contact efficiency between soot and catalyst dictates soot oxidation rate, with tight contact required for low temperature soot oxidation. However it is shown that contact efficiency is not a static feature and under application conditions a 'De-Coupling' of intimately mixed catalyst and soot can occur in-situ, resulting in loss of contact efficiency and activity. The mechanism of 'De-coupling' has been investigated and demonstrated to arise from the ubiquitous NO₂-mediated soot oxidation mechanism. It is proposed that incomplete filter regeneration by NO₂ dictates the requirement for active filter regeneration due to retention of residual soot, physically 'distant' from the washcoat. Conversely it is shown enhanced, and in some cases complete, low temperature catalysed soot combustion is possible by application of appropriate washcoat formulations which overcome the deleterious impact of NO₂-decoupling. The benefits of this new generation of formulations are demonstrated in engine dynamometer soot loading and regeneration trials.

INTRODUCTION

In the last thirty years increasingly stringent legislative limits have been introduced to regulate the various emissions from both petrol and diesel internal combustion engines [1]. In the case of diesel vehicles this has necessitated the control of both gaseous and solid emissions, namely the control of particulate matter (soot) emissions. To date it has been possible to meet all legal requirements via engine-related control measures only [2]. However the stringent targets embodied in, for example, Euro 5 or Euro 6 [3] necessitates the introduction of the Diesel Particulate Filter (DPF), aka the 'Wall-Flow Filter'.

To this end there have been extensive efforts to develop appropriate washcoat formulations to affect enhanced catalytic function with respect to the main chemistries

required of the filter viz, promotion of soot oxidation via 'in-situ' NO₂ generation, CO and hydrocarbon slip control (in continuous or soot regeneration modes) and the direct catalytic promotion of the rate of soot oxidation, [2,4-14]. In the case of development of catalysts for the direct oxidation of soot a wide variety of catalyst coatings have been examined including ceria-zirconia containing mixed oxides [4-7], so-called 'molten salt' catalysts based upon alkali metals e.g. potassium [8], perovskites [9] and spinel oxides [10]. Additional efforts have addressed the introduction of base metal or organometallic fuel additives to affect lower soot combustion temperatures [11].

However, to date, there is still debate as to the nature and magnitude of the benefits derived from the catalyst washcoat within the DPF architecture. Clearly the washcoat is beneficial in providing a supplementary emissions control function to decrease normal CO and HC emissions as well as providing an effective means to control slip during active regeneration [2,4]. Similarly much data and experience have shown that active washcoats can facilitate the generation of NO₂ 'in-situ'; the NO₂ thus formed initiating the soot combustion process at much lower temperatures than molecular oxygen [6,7,12,13].

In contrast any benefits of the washcoat with respect to the direct catalysis of soot combustion is a matter of much conjecture. The problem herein is many-fold. Firstly, one may consider the catalytic combustion of soot as a homogeneous catalytic process and hence a unique challenge within the field of emissions control. Secondly, this homogenous combustion catalysis suffers from a fundamental mass transfer limitation arising from the highly limited mobility of soot once contained within the filter cake. This mass transfer limitation has been widely examined and has led to the introduction of the terms 'tight' and 'loose' contact to describe the effective interactions between soot and washcoat dispersions [14]. Based upon an examination of the effectiveness of conventional non-molten salt washcoats it has been thus argued that under normal operating conditions of the catalyst coated DPF that contact between catalyst and

soot is at best 'loose' and hence direct soot oxidation catalysis is highly limited [15-16]. Finally, the local catalytic combustion/regeneration event must be considered within the entire topological regime of the filter, a highly complex 3-dimensional environment subject to considerable heterogeneity with respect to temperature, flow, reagent concentrations, presence of segments/cement boundaries and filter cake thickness amongst many variables. Indeed the complexity arising herein represents an enormous challenge to the experimentalist to ensure that 'clean' and reproducible studies are executed to enable the examination and comparison of candidate washcoat materials. In this area the experimentalist is well supported by the large body of theoretical and modelling studies addressing the manifold issues of soot deposition processes and characteristics, soot re-distribution, soot oxidation and the translation of these aspects from the micro to the macro scale [17-19].

In this paper we shall present an examination of the impact of the exhaust environment and compositional factors on the performance of candidate materials for the direct catalytic oxidation of soot. An analysis of the activities of single powders with simple thermogravimetric studies, the characteristics of mixed washcoat powders on the synthetic gas bench (SGB) and performance of fully formulated washcoated monolith filters on the engine dynamometer (dyno) and vehicle will be presented. From the data collated, a model describing the phenomenon of 'De-coupling' and requirements for realisation of active direct soot combustion catalysts will be proposed.

RESULTS AND DISCUSSION

PART 1: INITIAL SCREENING STUDIES

Figure 1 compares the thermogravimetric (TGA) δm versus temperature performance (Perkin Elmer TGA7 ramp rate 10 °C/min in air purge of 20 ml/min) of a conventional mixed oxide / Oxygen Storage (OS) material CeZrLaPrO₂ 1 [4] for the direct catalytic combustion of synthetic soot (Printex U, a low soluble organic fraction (SOF) soot analogue from Degussa A.G. see [14,15]) under conditions of 'loose' (mixed by spatula) and 'tight' or intimate contact (mix-milled in paint shaker for 15 minutes). The data are further contrasted with the response for the homogeneous combustion of Printex U. The data is clear and unambiguous; the prerequisite for efficient direct soot combustion catalysis is high contact efficiency, in agreement with previous studies [14,15]. The sharp response in the case of good contact is seen as a manifestation of a thermal cascade process arising from the specific mass and heat transfer phenomena present with the TGA. However, once intimate contact is lost the T_{max} (temperature of maximum rate of soot combustion) increases from 405 °C to 590 °C. Moreover comparison of the shape of the three responses is informative; in the case of loose contact there is bi-modal combustion profile reflecting the presence of limited domains of higher contact (peak

at ca. 410 °C) and large areas of practically zero contact, which correspond well to homogeneous combustion, albeit promoted by the exotherm generated by the tight contact combustion process.

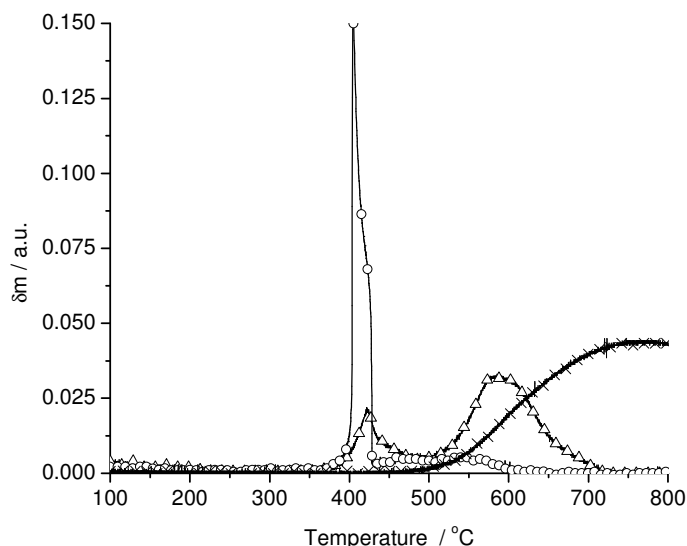


Figure 1: Impact of 'Contact Efficiency' on oxidation of Printex U. Key: O – OS + Soot with intimate mixing, Δ – OS + Soot without intimate mixing, X – Homogeneous Soot Oxidation without catalyst.

From these initial observations a screening study of the performance of candidate washcoat materials for the combustion of 'real' diesel soot (obtained via collection from dyno exhaust gas) has been performed. Figure 2 illustrates a very limited selection from this screening. From these experiments the following conclusions may be drawn. Firstly, direct soot oxidation requires high contact between soot and redox active catalyst, hence the performance of a conventional oxidation catalyst (Pt-CeO₂-Al₂O₃) is identical to homogeneous combustion. Secondly, the composition and characteristics of the redox oxide has a direct impact on the soot oxidation process, a finding confirmed in independent studies [4-7]. Hence the activity follows a general trend of:

Low Ce binary oxide < intermediate Ce binary oxide < tertiary oxide < quaternary oxide

Thirdly, the data confirm that the state of the cerium oxide is also critical; hence the activity of CeO₂-doped solid solution is lower than the non-doped solid solution. The importance of the Ce state is further emphasised by comparison of the two quaternary mixed oxides. The material CeZrLaPrO₂ 1 offered the best activity within the study and characterisation confirmed this material to be high surface area, mesoporous and single phase cubic fluorite material [4]. In contrast, the sample CeZrLaPrO₂ 2 (of comparable composition but produced by an alternate method) displayed the worst performance of any of the redox oxides examined, a characteristic attributed to the heterogeneous nature of this material since it was found to exhibit multiple fluorite phases via XRD. The presence of multiple phases or the

onset of phase disproportionation are undesirable based on previous studies which demonstrated maximum OS functionality and active oxygen donation is observed for phase pure materials, doped with appropriate levels of rare earth metal oxides to maintain phase and surface area stability and also promote oxygen ion conductivity [4,20].

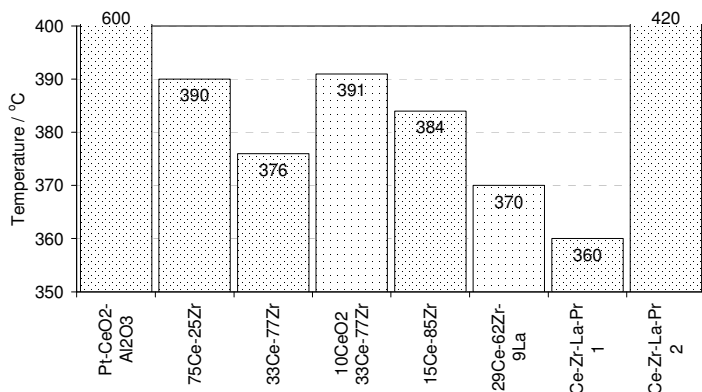


Figure 2: Effect of OS composition on the efficiency of catalysed soot oxidation for intimately mixed OS-Diesel soot as determined by TGA.

PART 2: MINI FILTER SCREENING STUDIES

Based on the promising data obtained in the TGA studies the performance of candidate compositions were examined in interim scale studies. In these studies 'mini-filters' (NGK cordierite C611, 300 cpsi, 0.3mm wall thickness, porosity 59%, mean pore size 20-25um, 44.45mm round * 152.4mm long, 0.236 L volume) were washcoated with representative formulations of mixed oxide or mixed oxide plus alumina at target washcoat loads of 0.45 g/in³ and 30gcf (g per ft³) Pt (0.75% Pt).

The coated parts and blank references were wrapped in mat and loaded in metal retaining sleeves, weighed after mat burn-out (2h 550 °C in static oven) and loaded into a converter can specially designed to accommodate three mini-filters: 2 coated parts plus 1 blank cordierite as internal reference. The parts were soot loaded on the engine dyno using a Chevrolet 6.5L diesel engine. Soot loading was performed at 1100 RPM, 30-32 Air to Fuel ratio (A/F), a Mass Air Flow (MAF) of 21 g/sec and a target filter inlet temperature of 200 °C. The soot produced was characterised as containing significant SOF. During loading backpressure was constantly monitored using a δP sensor and flow was controlled using a butterfly valve. In all cases soot-loading rate was ca. 4g / hour with total loading times of 3-4 hours.

Upon completion of the soot loading cycle the parts were removed from the can, weighed and loaded, still in the metal retaining sleeve, into a synthetic gas bench (SGB) unit for soot regeneration. Soot regeneration consisted of a simple temperature ramp (15 °C/min) in a reactive gas

environment comprising 10% O₂, 10% steam, 500ppm CO, 100ppm NO, balance N₂ at a total flow of 30 L/min. Figures 3-5 show representative data for 3 parts simultaneously loaded with Diesel soot as part of these studies.

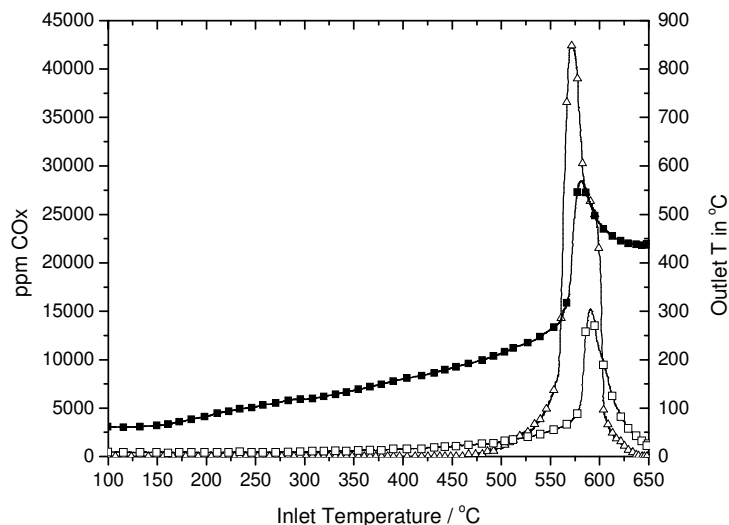


Figure 3: Soot burn out of blank 'Mini-Filter' Key: Δ – CO₂ evolution, – CO evolution, $\blacksquare$ - Outlet temperature.

Figure 3 describes the results for the SGB burn out of a blank cordierite filter. Herein performance is characterised by single high temperature CO₂ and CO evolution events at ca. 575 °C, concomitant with a large exotherm measured at the outlet of the filter, responses characteristic of homogeneous soot combustion. Gravimetric analysis showed a 4g mass loss i.e. 4 grams of soot (ca. 16g/L) were removed from the part.

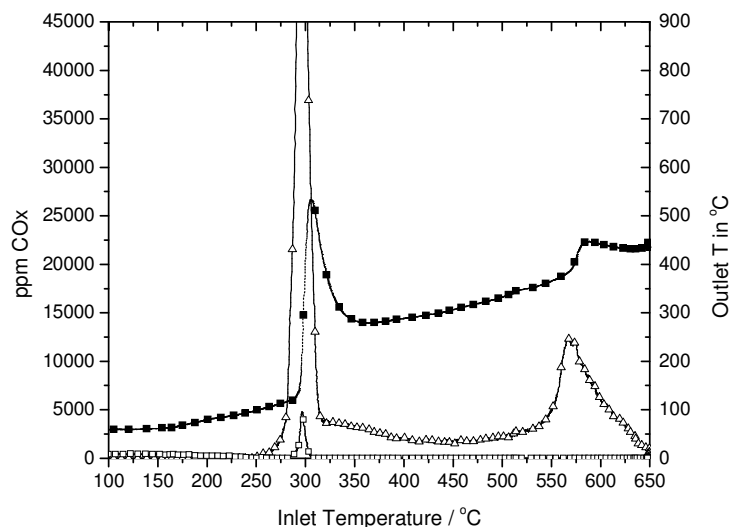


Figure 4: Soot burn out with 0.75%Pt - 49.625% - CeZrYNbO₂ - 49.625% Al₂O₃ coated filter Key: Δ – CO₂ evolution, – CO evolution, $\blacksquare$ - Outlet temperature.

This may be compared with performance of the Pt-CeZrYNbO₂-Al₂O₃ coated filter (Fig. 4). In this instance a

mass loss of 4.1g of soot was recorded. However the temperature response and soot combustion characteristics are widely different from that seen for the blank. In this case there are two clear exothermic soot combustion events, the larger event occurs at ca. 290 °C with a CO₂ peak evolution of ca. 70000 ppm, coincident with a CO evolution (CO slip) of ca. 3500 ppm, the second smaller combustion event has a CO₂ peak at ca. 575 °C of ca. 12000 ppm, with no associated CO slip. This bi-modal combustion response is indicative of a mixture of intimate and loose or filter cake soot i.e. a mixture of direct soot combustion catalysis and homogeneous combustion and is an elegant parallel to the initial TGA data (Fig 1).

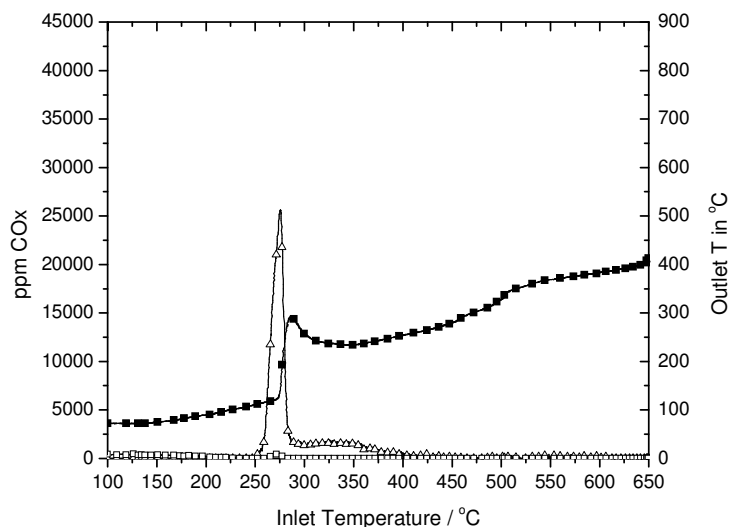


Figure 5: Soot burn out for 0.75%Pt-49.625% CeZrLaPrO₂ - 49.625% Al₂O₃ coated filter Key: Δ – CO₂ evolution, – CO evolution, ■ - Outlet temperature.

Evidence for direct catalytic soot combustion is even clearer in the activity of the Pt-CeZrLaPrO₂-Al₂O₃ mini-filter (Figure 5). This sample displays a single low temperature soot combustion event/exotherm at an inlet temperature of only ca. 270 °C. Moreover the soot combustion event exhibits a marked decrease in CO₂ peak (ca. 26000 ppm) with close to zero CO slip (a peak value of ca. 500 ppm). This decreased CO / CO₂ production is consistent with the marked decrease in soot burn-out for this sample 2.6g vs the 4.0g seen for the 2 sister parts simultaneously. This may be a potential indication of continuous soot regeneration during the soot loading cycle, although the combustion of SOF during loading is also likely a contributing factor. In order to further corroborate the hypothesis of direct soot combustion catalysis the NO conversion response during the experiment was examined. This showed that conversion of NO to NO₂ or N₂O was < 5ppm at all temperatures of interest. Hence what is evident is that under the conditions employed in these studies it is possible to achieve direct soot oxidation catalysis, contra to the claims of previous studies [5-7,14,15] and the process involved is not consistent with the reported

characteristics of the NO₂-assisted CRT mechanism [6,7,12,13].

However attempts to reproduce the excellent performance for the catalysed washcoat shown in Figure 5 under a variety of loading cycles, performed at different engine set-points, was unsuccessful. Indeed, as can be seen in Figure 6, it was discovered that the performance of the washcoat appeared to be more related to the type of soot produced, flow rate during loading, exhaust composition characteristics at the different engine loading protocol than to the nature of the washcoat. This may be a practical demonstration of issues highlighted by Kostoglou and Konstandopolous [18,19].

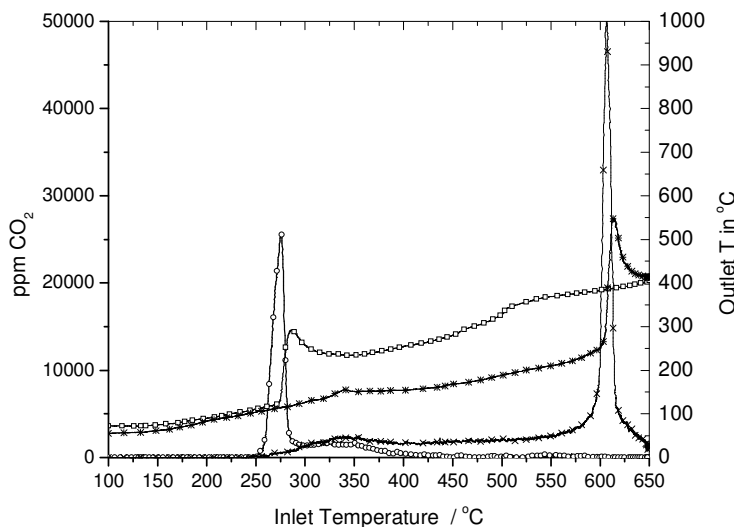


Figure 6: Impact of soot accumulation conditions on regeneration of catalysed 'Mini-Filter'. Key: O – CO₂ evolution ex low engine load accumulation, X – CO₂ evolution ex 'high' engine load accumulation, – Outlet temperature sample O, * - Outlet temperature sample X.

Hence while the lower load engine set point resulted in highly active catalyst performance, the use of higher load / MAF (63 g/s) / lower SOF / higher CO / HC / NO_x emission conditions did not. Comparison of the CO conversion profiles for the (same) catalyst in both tests indicated no loss in emissions function (CO T₅₀ = 150 +/- 5 °C). Hence the loss in performance could not be attributed to catastrophic deactivation or poisoning. A closer examination of Trace X, Figure 6 is however highly enlightening. The soot combustion characteristic can be seen to contain two features, a small low temperature (ca. 340 °C) and a large high temperature (600 °C) soot exotherm. This profile is very similar in nature to that noted in Figure 1 for the catalyst and soot under conditions of loose contact/low contact efficiency. Hence it appears that a factor or factors varying in the different loading cycles results in manifestly different modes of catalyst to soot contact and thus diametric differences in regeneration efficiency. Hence in all further studies significant effort was made to ensure high reproducibility within all testing protocols employed to provide the consistency required for meaningful comparison between tests.