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Using real particulate matter to evaluate combustion catalysts for direct regeneration of diesel soot filters

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ABSTRACT

The particulate produced by internal combustion engines has a complex composition that includes a large proportion of porous soot within which condensed and adsorbed organic molecules are trapped. However, many studies of the catalytic combustion of particulate are based on the assumption that commercially produced carbon can be used as a reliable mimic of engine soot. Here we show that soot removed from a diesel particulate filter is rich in the polyaromatic molecules that are the precursors of the solid particulate. Through a combination of solvent extraction and evolved gas analysis, we have been able to track the release and transformation of these molecules in the absence and presence of combustion catalysts. Our results reveal that, although the rate of combustion of the elemental carbon in diesel soot is higher than that of graphite, deep oxidation of the polyaromatic molecules is a more demanding reaction. An active and stable Ag–K catalyst lowers the combustion temperature for elemental carbon by >200 °C, but has little effect on the condensed polyaromatic molecules. The addition of a secondary catalyst component, with aromatic-oxidation functionality is required to target these molecules. Although the combined catalyst would not enable a completely passive regeneration system for diesel passenger cars, it would improve the efficiency of existing active systems by reducing the amount of fuel-injection required for trap regeneration.

1. Introduction

Despite its long history, the compression-ignition diesel engine has only come to prominence in the passenger car market over the past 25 years. Its higher efficiency coupled with the higher energy density of diesel fuel can result in a 20% reduction in CO_2 emissions and a 40% improvement in fuel economy, when compared to a similarly sized spark-ignition gasoline (petrol) engine [1]. Although these environmental and cost benefits are narrowing with improvements in gasoline-engine technologies, they nevertheless explain why over 50% of all new cars sold in the UK, and 55% sold in the EU15 countries, now have diesel engines [2]. Legislation requires that both gasoline and diesel cars meet exacting standards for the release of carbon monoxide, hydrocarbons and NO*x*, however diesel cars have additionally been required to control the mass of particulate. In the EU, the limit for particulate emission currently stands at 4.5 mg per km, corresponding to a >95% reduction since legislation was first introduced in 1993 [3].

Two aftertreatment strategies have been commercialised for controlling the release of soot particulate from diesel vehicles. Both require the use of a filter, made from extruded cordierite or sintered silicon carbide [4], which is either continuously or periodically regenerated. The continuous process of self-cleaning relies on the carbon content of the trapped soot particulate being oxidised by reaction with the NO_2 in the exhaust gas passing through the filter (as first reported by Cooper and Thoss [5]). Although a catalyst is used to ensure that as much as possible of the NO_x present in the exhaust is in the form of NO_2 when it comes into contact with the soot, the $C + NO_2$ reaction itself is non-catalytic. This combination of NO-oxidation catalysis and soot filtration provides a highly effective aftertreatment system for heavy-duty vehicles, such as buses and trucks, where there is enough NO*x* emitted by the engine, and the exhaust gas is hot enough to enable the $C + NO_2$ reaction to persist throughout most of the drive cycle. However, this strategy cannot be used on-board diesel passenger cars, where both the NO*x*/carbon ratio and the exhaust-gas temperature are much lower. At present, the only practical means of regenerating a particulate

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filter in the exhaust pipe of a diesel car is by creating a sufficiently large exotherm to enable the carbon in the soot to combust. During this process of active regeneration (which dates back to the work of Goldenberg [6]), fuel is intermittently injected into the hot exhaust as it enters an oxidation catalyst, with the resulting adiabatic temperature rise inducing combustion of the soot within the filter (Fig. 1). Again, this system combines catalysis with filtration, but here the combustion of trapped soot occurs by the uncatalysed reaction of $C + O_2$ at high temperature.

There are two major shortcomings of active regeneration:

(i) On short journeys, the exhaust-gas temperature may not reach the threshold required to trigger fuel injection into the exhaust, which can then lead to severe blocking of the filter.

(ii) There are cost and CO_2-emission penalties associated with the repeated injection of fuel into the exhaust stream.

These shortcomings could be avoided by developing a catalysed passive regeneration strategy that makes use of the continuous high concentration of O_2 present in diesel exhaust gas. The challenge lies in finding a soot-combustion catalyst that can be incorporated into a particulate filter, where it would activate O_2 and deliver the reactive oxygen species to the retained particulate, so that the carbon content would be converted to CO_2 at typical exhaust-gas temperatures for passenger diesel cars (180–400 °C).

Although much is already known about the process of soot particulate formation in engine exhaust [7] and the mechanisms for soot combustion [8], our understanding of the complex relationship between catalyst composition, soot speciation, and combustion activity during catalytic regeneration of a filter is still poorly developed. In fact, for nearly 20 years (since the first exploratory study by Moulijn and co-workers [9]), the identification of potential combustion catalysts for the passive regeneration of filters by reaction with O_2 has been largely based on screening experiments, in which graphitic carbon (such as carbon black or printer carbon) has been used as a mimic for diesel soot. These have shown that among the most promising catalytic materials are alkali and alkaline earth metals [10], reducible metal oxides [11] including CeO_2 [12], and supported precious metals [13].

In this study, our base catalyst is a multicomponent formulation containing the active phase of Ag promoted with potassium, and supported on CeO_2–ZrO_2–Al_2O_3 (CZA) for its high oxygen storage and transport properties [14]. Both potassium and silver have similar electronic configurations, which may explain the similarity in their combustion activity, but additionally ionic potassium (the form in which it is catalytically active) can be highly mobile at elevated temperatures [11]. This mobility would play an important role in ensuring effective contact between the catalytically active sites and the stationary soot particulate in a filter. However, as we show here, even this combination of silver and potassium is not effective for the complete combustion of the soluble organic fraction of the soot. The 3- and 4-ring polyaromatic compounds, which account for most of the organic fraction, have low volatility and reactivity, and require a further catalyst component that will activate them into reactive surface species as they desorb from the particulate.

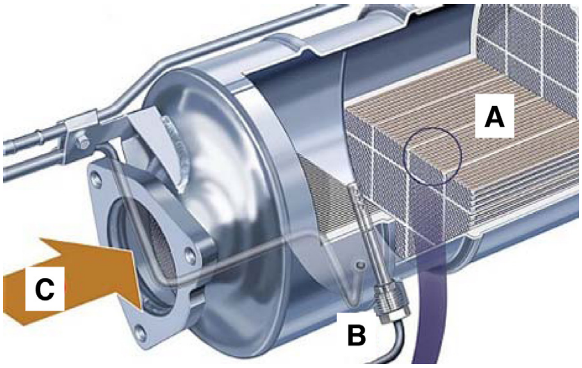

Fig. 1. An actively regenerated diesel particulate filter (courtesy of the UK daily telegraph). A passive soot combustion catalyst, coated on the filter walls (A) would reduce or completely eliminate the need to inject fuel (B) into the exhaust gas entering the filter (C).

2. Experimental

2.1. Soot samples

All experiments were carried out on samples from a single batch of diesel soot (supplied by Johnson Matthey) which had been obtained by emptying a passively regenerated diesel-exhaust filter. It was, therefore, a homogeneous mixture of particulate, which had been generated during different phases of an engine cycle and had been trapped in different parts of the filter. In view of the difficulty in sourcing gasoline soot (because of the low mass of particulate emitted by gasoline engines), a single batch was collected over two days at Loughborough University from the exhaust of a Jaguar Land Rover 2.0 L GTDi engine. Again, this was a homogeneous mixture of particulate produced over a range of engine conditions. Synthetic soot was prepared by allowing a graphitic aromatic-free carbon (Haydale GT graphite), which had been generated from CO_2, to absorb phenanthrene to achieve a carbon/aromatic ratio of 9/1 by mass.

Qualitative analysis of the volatile organic fraction of the diesel soot was carried out by mass spectrometry, using a Waters GCT Premier instrument. A sample (10 mg) of the as-received soot was placed on a solid insertion probe, which was transferred to the mass spectrometer through a vacuum lock. The sample was then rapidly heated to 400 °C (in about 10 s) to flash-desorb the volatiles, the heaviest of which could be identified from the cracking patterns in the mass spectrum produced.

A Soxhlet apparatus [15] was used for the quantitative extraction of the soluble organic fraction in 1 g of the soot. In this process, the compounds present in the organic fraction were dissolved in warm toluene (85 cm^3) over 16 h, during which the solvent was continuously re-cycled by vaporisation and condensation. The resultant solution was analysed by high performance liquid chromatography (HPLC), as described below.

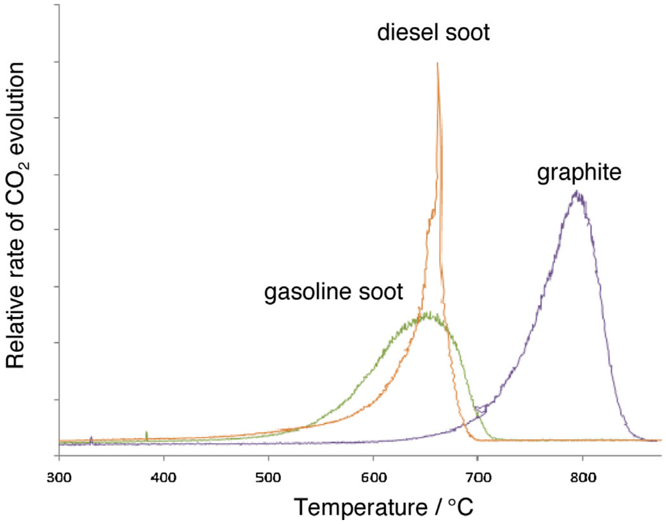

Fig. 2. Rate of uncatalysed combustion of diesel and gasoline soot samples compared to graphite. As measured by rate of CO_2 evolution during temperature-programmed heating under 10% O_2 in helium.