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

Ragini Ramdas, Ewa Nowicka, Robert Jenkins, David Sellick [1], Catherine Davies, Stan Golunski*

Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK

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.

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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 NOx, 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 NOx 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 NOx/carbon ratio and the exhaust-gas temperature are much lower. At present, the only practical means of regenerating a particulate

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
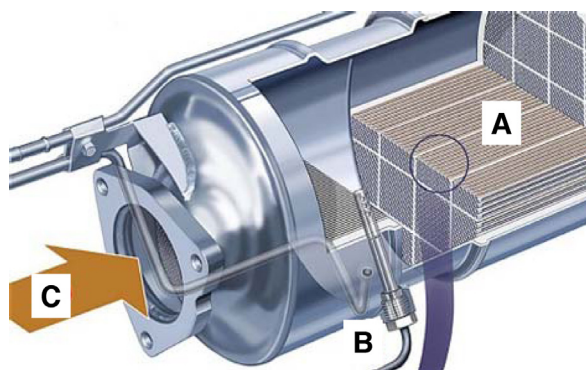
show here, even this combination of silver and potassium is not effective for the complete combustion of the soluble organic fraction of the soot. The 3- and 4-ring polyaromatic compounds, which account for most of the organic fraction, have low volatility and reactivity, and require a further catalyst component that will activate them into reactive surface species as they desorb from the particulate.

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.
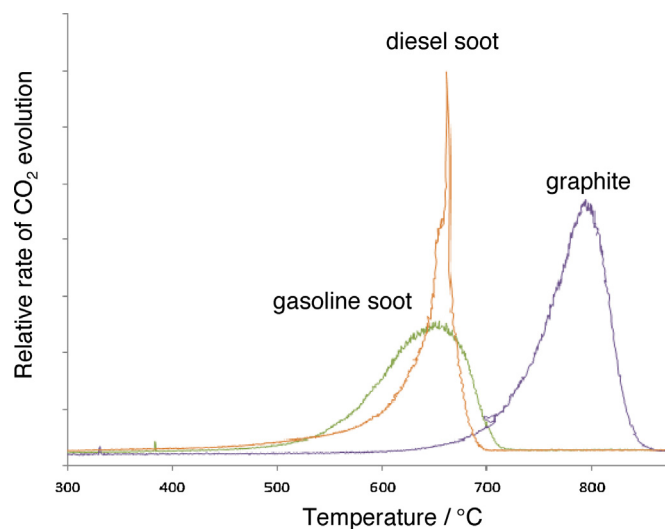

Fig. 1. An actively regenerated diesel particulate filter (courtesy of the UK daily telegraph). A passive soot combustion catalyst, coated on the filter walls (A) would reduce or completely eliminate the need to inject fuel (B) into the exhaust gas entering the filter (C).

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.
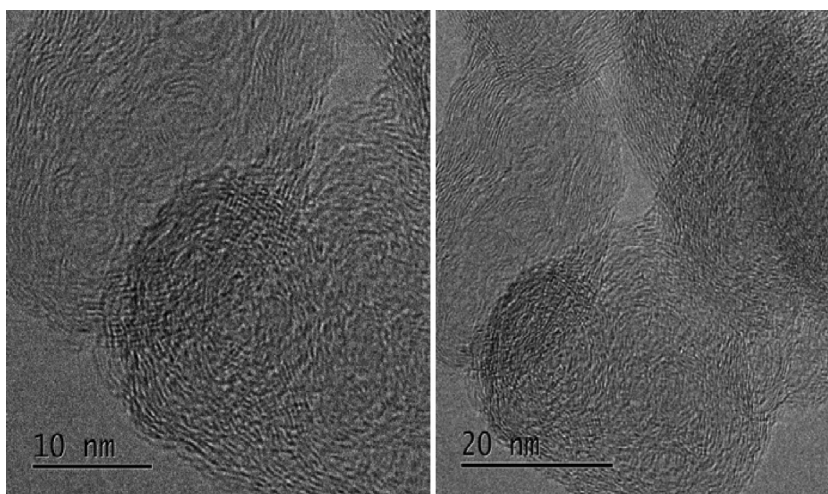
Fig. 3. TEM of diesel soot, showing the presence of distinct spherules within the primary particles.

2.2. Catalytic materials

The composition of our base catalyst (referred to as Ag–K/CZA throughout the following text), which had been optimised for the combustion of graphitic carbon during a parametric study of the preparative variables, has been shown to maintain its activity during repeat testing [16]. It was prepared by co-precipitating the support material with an atomic composition of $Ce_{0.35}Zr_{0.15}Al_{0.5}O_{1.75}$ (i.e. Ce/Zr = 7/3) from a mixed aqueous solution of the precursors – ammonium cerium(IV) nitrate (Sigma–Aldrich, purity $\geq$ 98.5%), zirconyl oxynitrate hydrate (Aldrich, 99%), aluminium nitrate nonohydrate (Sigma–Aldrich, $\geq$98%) - using aqueous Na_2CO_3 (Alfa Aesar, 99.5%) as the precipitant. The dried support was then impregnated with aqueous solutions of $AgNO_3$ (Aldrich, 99.99%) and K_2CO_3 (Alfa Aesar, 99.5%) to achieve a loading of 2 wt% Ag and 10 wt% K, before drying (110 °C for 16 h) and calcining at 500 °C (5 h; flowing air).

The additional component, required to target the polyaromatic compounds within diesel soot, was prepared by incipient-wetness impregnation of 2.5 wt% Pt on SiC. Platinum(II) acetylacetonate (Sigma–Aldrich, 99.99%; 0.0504 g) was dissolved in toluene (6.5 cm^3) and added to silicon carbide powder (Sigma–Aldrich, 200–450 mesh; 1 g). The resulting paste was dried (110 °C for 16 h), ground to a fine powder and calcined at 500 °C (5 h; static air). The Pt/SiC component and the Ag–K/CZA catalyst were thoroughly ground together using a mortar and pestle in a mass ratio of 1:2 (Pt/SiC:Ag–K/CZA), which was the optimum ratio identified in a separate study [16].

2.3. Physical characterisation of soot samples and catalysts

The bulk structure and reducibility of the catalysts were determined by XRD and TPR, respectively, as part of an extensive characterisation study [16]. The surface structure and composition both of the catalysts and soot samples were examined by transmission electron microscopy (TEM), using a JEOL microscope equipped with a high-resolution (0.02 nm) digital camera and elemental mapping capability. Additionally, the proportions of crystalline and disordered carbon in the bulk of the soot and graphite samples were measured using a Renishaw inVia Raman microscope.

2.4. Catalyst testing

In our tests of combustion activity, the catalyst was mixed with soot in a mass ratio of 10/3 (catalyst/soot), by shaking the two powders together in a vial to establish the type of loose contact that is considered representative of the catalyst-soot contact in a catalysed soot filter [9]. Evolved gas analysis was carried out during temperature-programmed heating of a 0.4 cm^3 packed bed of the mixture, while a gas stream was fed through the bed at a gas-hourly space velocity of 30,000 h^{-1}. Several different gas-feeds were used to evaluate the effect of inert and oxidising atmospheres on the rate of formation and the composition of the evolved gases: (i) non-oxidising standard (100% He); (ii) oxidising standard (10% O_2, 90% He), (iii) synthetic air (20% O_2, 80% He), (iv) synthetic diesel exhaust (8% O_2, 1% CO, 0.01% C_3H_8, 0.024% C_3H_6, 0.03% NO, balance N_2). The same methodology was used to study the uncatalysed combustion of graphite, synthetic soot, diesel soot and gasoline soot.

Due to the complexity of the evolved gases, the usual practice of continuously monitoring the exit stream by mass spectrometry [17] could not be used. Instead, it was either analysed for CO and CO_2 by gas chromatography and FTIR (while the bed was being heated at a rate of 5 °C min^{-1}), or it was passed through a trap that contained acetone and was cooled by an ice-acetone bath. The evolved organic gas-phase molecules were trapped while the catalyst + soot mixtures were heated (at 40 °C min^{-1}) to a temperature of 300, 400, 500 or 600 °C and held at the maximum
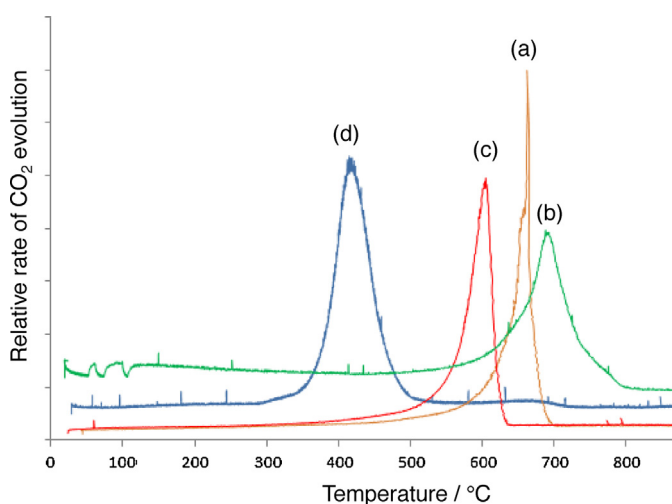

Fig. 4. Rate of combustion of (a) diesel soot alone, and diesel soot when loosely mixed with (b) powdered cordierite, (c) γ-Al_2O_3 and (d) Ag–K/CZA catalyst. As measured by rate of CO_2 evolution during temperature-programmed heating under 10% O_2 in helium.

temperature for 1 h. The contents of the trap were heated to evaporate the acetone before the organic fraction was re-dissolved in acetonitrile (1 cm^3). Samples of the resultant solution (injection volume: 5 μl) were then analysed by HPLC on an Agilent Technologies 1200 series chromatograph. A standard calibration mixture of polyaromatic hydrocarbons (Sigma–Aldrich) was used to ensure the accurate identification and quantification of the aromatics. It contained 10 μg–cm^{-3} of the following 16 compounds: naphthalene, acenaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzanthracene, chrysene, benzofluoranthene, benzofluoranthene, benzopyrene, dibenzanthracene, benzoperylene, indenopyrene. A reverse phase system with a solvent mixture of water and acetonitrile as the mobile phase (flow-rate of 1 cm^3 min^{-1}) was used for separation on a Zorbax Eclipse Plus phenyl-hexyl 4.6 × 150 mm, 3.5 μm column. The column temperature was kept constant at 25 °C.

The gas chromatograph used for CO_2 analysis was a Varian Star instrument, fitted with a Poropak-Q column and a thermal conductivity detector; CO was measured using a Gasmet FTIR gas-phase analyser with a 400 cm^3 high-temperature (180 °C) sampling cell. To simplify calculations of the carbon mass-balance, the evolved gas analysis was correlated with separate measurements of the change in mass. Thermogravimetry was carried out by heating 10 mg of the soot or catalyst+soot mixtures at 10 °C min^{-1} from 30 to 900 °C under circulating air in a Setaram Labsys TGA-DTA/DSC thermal analyser.

3. Results and discussion

3.1. Non-catalytic combustion of real and synthetic soot

The widespread use of commercially sourced carbon, as a soot mimic during catalyst development for exhaust particulate control, is usually justified on the grounds that incomplete hydrocarbon combustion invariably forms elemental carbon in its thermodynamically stable sp^2-hybridised form. Even when real soot is used [e.g. 18], the effect on the organic compounds within the solid particulate is generally ignored, because these compounds are expected to be oxidised more readily. The overall combustion rate of exhaust soot is assumed, therefore, to be determined largely by
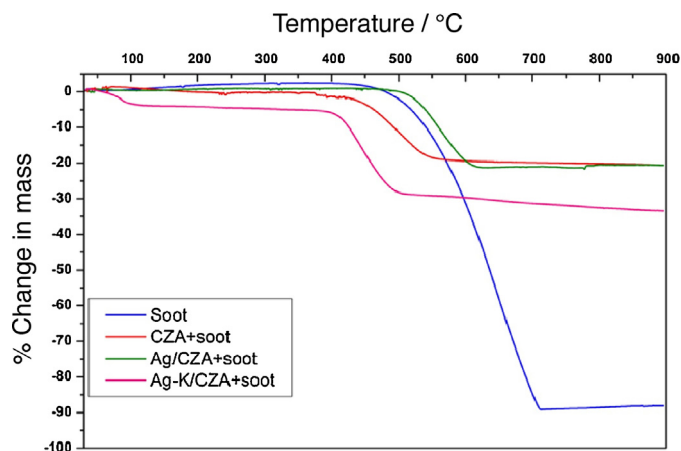

Fig. 5. Effect of adding Ag and K on the catalytic activity of CZA, as measured by thermogravimetry.

the combustion of the elemental carbon fraction, which is thought to be the slower process.

Our tests show that there are clear differences between the reaction profiles for the uncatalysed combustion of different types of real and synthetic soot samples (Fig. 2). Although the soot produced by diesel and gasoline engines combusts over a similar temperature range, diesel soot gives rise to a very sharp peak, which is consistent with the fast combustion of the 'soot cake' that takes place during active regeneration of a diesel particulate filter. Significantly, both types of real soot combust at temperatures about 150 °C lower than graphite. Based on accepted wisdom, the higher rate of combustion of the real soot samples would be attributed to the presence of condensed and adsorbed organic compounds, which are expected to be more reactive than elemental carbon.

Electron microscopy of the diesel soot (Fig. 3) showed that the typical particulate matter was comprised of primary particles (average diameter: 22.6 ± 6.0 nm) with the classic onion-skin structure [19] consisting of concentrically wound nanocrystalline graphite [20] (domain sizes between 2 and 3 nm) that is often reported for exhaust particulate, carbon black and macroscopic graphite. Raman spectroscopy, which is very effective at
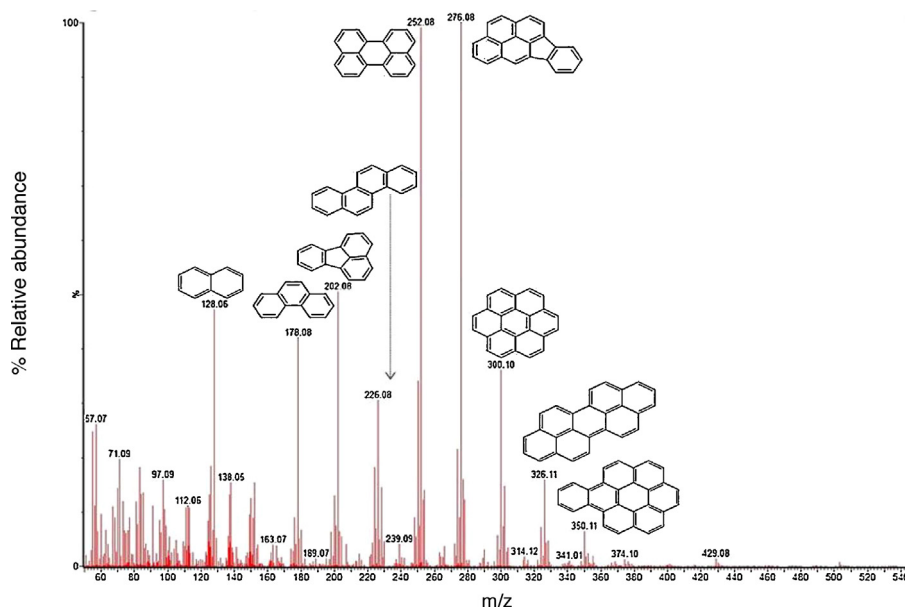

Fig. 6. Mass spectrum of organic species evolved during flash-desorption from diesel soot.
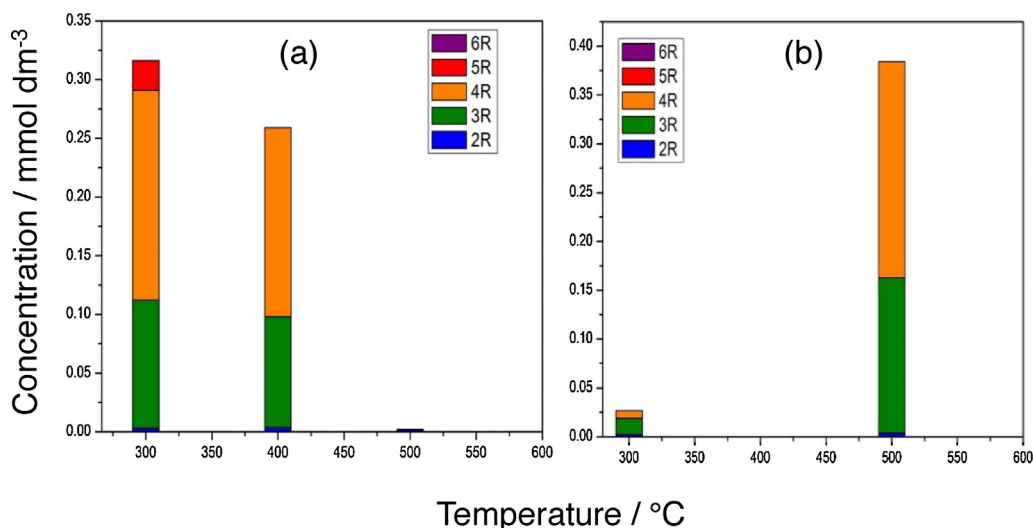
Fig. 7. Concentration of evolved polyaromatic hydrocarbons trapped in acetone, during heat treatment of diesel soot under synthetic exhaust gas in (a) absence of catalyst, and (b) presence of Ag–K/CZA catalyst. (Each bar represents the heating of a fresh sample to the temperature indicated; R refers to the number of rings in the polyaromatic molecules.)

detecting the amorphous forms of sp^3 and sp^2 hybridised carbon (often referred to just as disordered carbon [21]) indicated that the soot was not entirely crystalline, but this was also the case for commercial graphite. In fact, the intensity ratios of the characteristic Raman peaks [22] for disordered carbon (D: $1350\,cm^{-1}$) and crystalline graphite (G: $1575\,cm^{-1}$) differed by only 4% between the soot (D/G = 1.62) and the graphite (D/G = 1.56). The physical characterisation was, therefore, consistent with the explanation that the higher reactivity of real soot is due to the presence of the entrapped organics, and not because its structure differs substantially from that of commercial graphite.

However, when we tested a sample of graphite impregnated with phenanthrene (one of the major organic constituents that we have identified) in a ratio that is representative of that found in diesel soot, the presence of the organic shifted the peak maximum to a higher temperature (see below). Although this does not eliminate the possible promoting role of entrapped organic compounds, it suggests to us that the lower combustion temperature of real soot indicates the importance of (a) local disorder in the nanostructure (e.g. at points where partial oxidation by either O_2 or NO_2 has already taken place), and (b) the self-catalysing effect of the

inorganic components (usually referred to as ash [7]) within the particulate.

3.2. Catalysed combustion of diesel soot

In a passive system that will rely mainly on exhaust-gas O_2 as the oxidising agent, the combustion catalyst will be coated onto the walls of an extruded or sintered ceramic filter. In the laboratory, the interaction of the catalyst with the soot trapped in such a filter is usually simulated by lightly mixing the two powders to produce a homogeneous mixture in which the catalyst is present in excess [4].

As can be seen in Fig. 4, the rate of diesel soot combustion can be changed even by mixing the soot with powdered materials that are known to have low or negligible catalytic activity for oxidation reactions. Cordierite – one of the inert ceramic materials used to make soot filters – delays the onset of soot combustion, probably by quenching the oxygen-containing radicals (especially OH [8]) that can initiate combustion; while the presence of γ-Al$_2$O$_3$–the high surface area support material used to disperse catalytically active phases – accelerates combustion, probably through the opposite
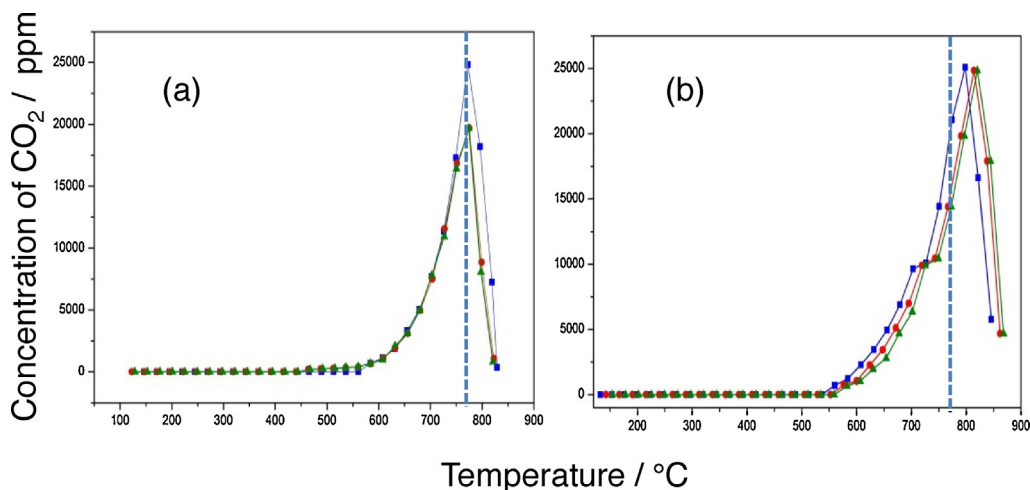

Fig. 8. Rate of combustion of (a) graphite and (b) synthetic soot (graphite + phenanthrene). As measured by CO_2 evolution during temperature-programmed heating under 20% O_2 in helium. (Each trace represents a new sample from the same batch.)
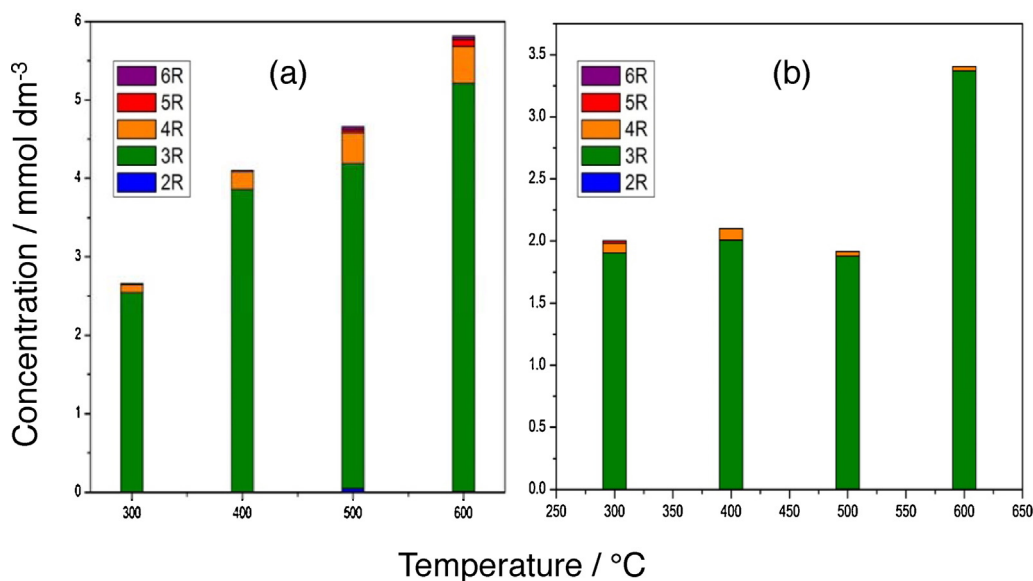
Fig. 9. Concentration of evolved polyaromatic hydrocarbons trapped in acetone, during heat treatment of synthetic soot under 20% O_2 in helium in (a) absence of catalyst, and (b) presence of combined Ag–K/CZA + Pt/SiC catalyst. (Each bar represents the heating of a fresh sample to the temperature indicated; R refers to the number of rings in the polyaromatic molecules.)

process of dissociating some O_2 molecules into free radicals that can form the reactive species.

Our standard catalyst in this study, Ag–K/CZA, was a multi-component formulation containing precious metal (Ag) and alkali metal (K) dispersed over a co-precipitated combination of CeO_2, ZrO_2 and γ-Al_2O_3. The design rationale was based on combining the known functions of the individual components:

(i) Ag provides fixed active sites which can dissociate O_2 and deliver reactive oxygen species [23]. It is also effective for activating other potential oxidising agents present in exhaust gas, such as NO and NO_2 [24]. In the presence of a reducible metal oxide, such as CeO_2, it promotes both reduction of the oxide (oxygen release) and its re-oxidation (oxygen storage), enabling the complete redox cycle to take place at lower temperatures [25].

(ii) K provides mobile active sites [26], which should enhance the degree of contact between the catalyst and the soot particles (which are too large to penetrate into the pore structure of the catalyst). The major role of the potassium, therefore, is to transport reactive oxygen to the immobilised soot particles.

(iii) CeO_2 provides a reservoir of reactive oxide ions [27]. Although diesel exhaust gas is rich in oxygen, the diffusion of O_2 to the active sites can be severely limited when the catalyst is covered by a soot layer. Under these conditions, the ceria will have the critical role of supplying oxygen to active sites at the metal-ceria interface.

(iv) ZrO_2 stabilises the CeO_2 and enhances its oxygen storage capacity [28].

(v) The high surface area of γ-Al_2O_3 provides the underlying support for the other components [14].

As the thermogravimetric traces in Fig. 5 show, CZA alone was catalytically active, lowering the onset of diesel soot combustion by 75 °C. Although addition of Ag to CZA had the effect of suppressing the activity during loose contact testing, the combustion temperature could be lowered by as much as 100 °C by increasing the degree of contact between the soot and the catalyst. Finally, addition of K_2CO_3 to the Ag/CZA created our highly active
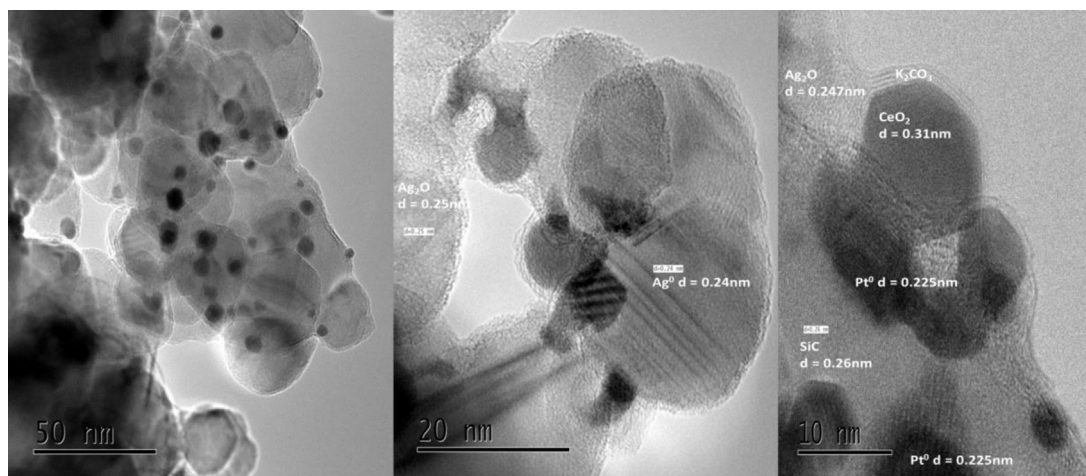

Fig. 10. TEM of combined Ag–K/CZA + Pt/SiC catalyst at increasing magnification. The labels show the d-spacings used to identify the phases present.
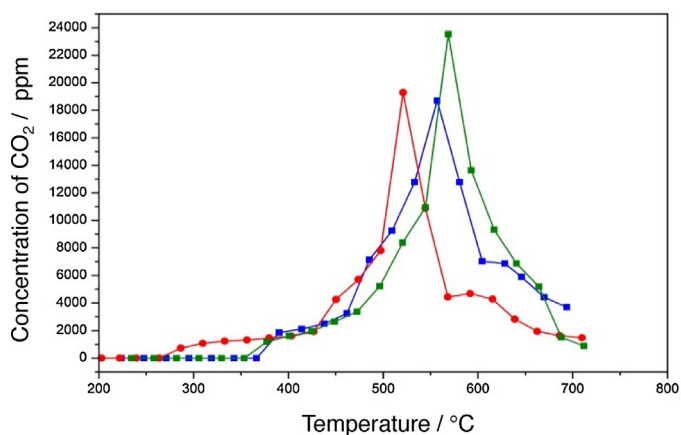
Fig. 11. Rate of combustion of synthetic soot (graphite + phenanthrene) when mixed with the combined Ag–K/CZA + Pt/SiC catalyst, as measured by CO_2 evolution during temperature-programmed heating under 20% O_2 in helium. (Each trace represents a new sample mixture made from one batch of synthetic soot and one batch of combined catalyst.)

standard, which lowered the peak temperature for soot combustion by 245 °C even during loose contact (Fig. 4). Comparative characterisation of Ag–K/CZA and Ag/CZA by XRD did not reveal any substantial differences in the bulk structure or crystallinity, but TPR showed that the presence of K_2CO_3 inhibited reduction (see Supplementary information 1). Specifically, the peaks associated with reduction of Ag_2O (maximum: 138 °C) and surface CeO_2 (onset: 410 °C) were displaced to higher temperatures (300 °C and 560 °C, respectively), suggesting that the K_2CO_3 was blocking H_2-activation sites on the Ag/CZA. It is interesting to note that, for Ag–K/CZA, both the reduction of silver during TPR and the onset of catalytic activity during soot combustion closely matched the Tammann temperature of K_2CO_3 (310 °C). These effects suggest that, as the the alkali metal becomes mobile, more of the Ag and CZA is exposed, and that as expected the degree of interaction between soot and catalyst is improved.

While thermogravimetry allowed us to track the loss in mass of the soot during uncatalysed and catalysed soot combustion, evolved gas analysis allowed us to measure the associated rate of formation of CO_2. Although carried out separately, the rate of CO_2 formation should correlate directly with the loss of mass, if all the carbon in the soot is being fully oxidised. However, during either the uncatalysed or catalysed combustion of diesel soot, the total amount of carbon present in the evolved CO_2 was lower than the total loss of mass. The deficit was consistently around 15% (see Supplementary information 2).

3.3. Speciation of the organic fraction

Our inability to close the carbon balance suggested either that some of the carbon was undergoing incomplete oxidation (to CO), or that the soot contained a high proportion of organic molecules that were released without being oxidised even in the presence of the catalyst. More extensive gas analysis showed that the concentration of evolved CO was only 2–5% that of the CO_2, and therefore could not account for the large deficit in the carbon balance. This prompted us to carry out a detailed speciation of the organic fraction, of a type that, to our knowledge, has not been reported in previous catalyst studies of soot combustion.

Elemental analysis showed that the composition by mass of the diesel soot was 91.5% C, 1% H, 0.15% N and 0.17% S, with the remainder made up of high ppm levels of a wide range of base metal oxides. After intensive solvent-extraction of the organic fraction using toluene in a Soxhlet extractor, the carbon content had

dropped to 69.5% and the hydrogen to 0.5%. This change indicates that the soluble organic fraction accounted for 24% of the mass of carbon, or 22% of the mass of soot. The proportionally higher drop in hydrogen content (from 1% to 0.5%) after solvent extraction was consistent with the expectation that the organic fraction was rich in aliphatic hydrocarbons. When we set out to confirm this by the flash-desorption of the organics from the soot into a mass spectrometer, a large number of hydrocarbons were indeed detected, but the resultant mass spectrum (Fig. 6) was dominated by a group (<10) polyaromatic molecules.

However, from the mass spectrum alone, we could not quantify the relative proportions of the hydrocarbons, nor could we deduce whether the aliphatic hydrocarbons detected were entrapped molecules or cracked products formed from the polyaromatics. This information was provided by HPLC analysis of the organic fraction dissolved in the toluene during Soxhlet extraction, which allowed us to separate and quantify 11 polyaromatic molecules. These were predominantly the following 3- and 4-ring compounds, which are intermediates in the formation of solid carbon particulate by the dehydrogenation and cyclisation of C_2 and C_3 hydrocarbons [29]: phenanthrene (0.505 mmol per g of soot), fluoranthene (0.431 mmol) and pyrene (0.396 mmol). Together the polyaromatic hydrocarbons accounted for essentially all of the organic fraction of the soot.

By trapping the volatile molecules evolved during heating of the diesel soot, we could see that the polyaromatic hydrocarbons were resistant to combustion irrespective of whether the Ag–K/CZA catalyst was present or not, hence explaining the deficit in the carbon balance that was based simply on the formation of CO_2. For example as Fig. 7 shows, in the absence of the catalyst, the polyaromatics were largely released unoxidised at temperatures below 450 °C. In the presence of the catalyst, 70% of the polyaromatics were released unoxidised, but at a higher temperature, close to that at which most of the elemental carbon had been combusted (see Fig. 4). The major of the effect, therefore, of the catalyst was to re-adsorb the polyaromatics released by the soot, and then to desorb them without combustion.

3.4. Synthetic soot

Based on our speciation of the organic fraction of diesel soot, which showed that nearly 10% of the soot mass was comprised of phenanthrene, we prepared a synthetic soot containing graphite and phenanthrene in a 9/1 mass ratio. As already mentioned (and shown in Fig. 2), the graphite combusted at a higher temperature than the elemental carbon in the diesel soot. The synthetic soot was, therefore, a far from perfect model system, but it allowed us to track the release and transformation of the phenanthrene without the confounding effects of the other polyaromatic molecules. The most obvious effects of the phenanthrene were that it gave rise to a shouldered combustion peak (as opposed to the highly symmetrical single peak for graphite alone) and it shifted the maximum rate of combustion to a higher temperature (Fig. 8). As now expected, in the absence of a catalyst, a substantial proportion of the phenanthrene was released unoxidised (Fig. 9a).

In order to target the unoxidised phenanthrene, an additional component was included in the catalyst by mixing Pt/SiC into the Ag–K/CZA (in a 1/2 ratio by mass). The Pt/SiC had been previously identified as a very effective combustion catalyst for polyaromatic hydrocarbons [16]. Electron microscopy showed that, by physically mixing the two catalysts, the Pt and Ag particles were effectively interdispersed, with the Ag present both in its metallic and oxide forms (Fig. 10). The potassium (in the form of K_2CO_3) was clearly visible by TEM as a continuous layer covering the underlying CZA support, providing a large and potentially adhesive interface with the soot.

The combined catalyst lowered the peak combustion temperature of the synthetic soot by 250–300 °C (Fig. 11). The test-to-test variability in the peak position reflects the difficulty in achieving consistent mixing between the two catalyst components and the soot. We interpret the shape of the combustion profiles in the catalysed tests (Fig. 11) to be the result of two superimposed combustion processes. The sharp dominant peak (centred at 500–600° C) is the combustion of elemental carbon, while the very broad supporting peak is the combustion of phenanthrene. Although to be confirmed, we attribute the leading edge of the broad peak to the combustion of released phenanthrene on Pt/SiC, while the tail is the result of slow combustion of released phenathrene that has been adsorbed by Ag-K/CZA. HPLC analysis of the volatiles trapped in acetone, during catalysed testing, showed that the additional catalyst component was indeed having the required effect of suppressing the release of unoxidised phenanthrene (Fig. 9b). However, this functionality still needs to be optimised (either by reformulation or by tuning the relative loadings of the two catalysts) in order to achieve complete combustion of the polyaromatic molecules.

4. Conclusions

Over the past 5 years, there has been a rapid growth in the number of active catalytic materials identified for the direct combustion of trapped soot using the O_2 that is present in diesel exhaust [26]. In common with our Ag-K/CZA catalyst, even the most active examples reported to date [12,27,30] operate within the temperature range associated with heavy-duty diesel vehicles, such as buses and trucks, for which very effective passive soot-control already exists. However, these catalysts could, in principle, be used to limit the amount and frequency of fuel injection on light-duty diesel vehicles that are fitted with actively regenerated particulate filters. Whether these or future generations of combustion catalysts are commercialised, either as a complete or partial substitute for active regeneration, does not depend solely on their ability to combust elemental carbon, though. The catalysts will additionally have to demonstrate exceptionally high durability to withstand 100,000 miles of driving, while preventing the release from the tailpipe of any carbon-containing molecules apart from CO_2.

Our work shows that, with the exception of the sulphur content (which has greatly diminished through the use of ultra-low sulphur diesel fuel), the chemical composition of modern diesel soot has changed very little from that described in the classic work of Kittleson [7]. This means that about 25% of the soot mass is made up of condensed or adsorbed polyaromatic molecules, which are the precursors of the elemental carbon within the particulate [29], and yet these are rarely taken into consideration during the screening of combustion catalysts for vehicle applications. Unlike both the current regeneration strategies, which require high temperatures and therefore can destroy the organic fraction at the same time as the elemental carbon, the release of polyaromatics during direct catalytic combustion of soot poses an emission problem in its own right [31]. This dilemma is clearly exemplified by the Ag-K/CZA catalyst. Although both active and durable for elemental carbon combustion, it is not effective for the combustion of polyaromatic hydrocarbons, with a substantial proportion being released without oxidation. The addition of Pt-containing component goes some way towards overcoming this problem, but also highlights how demanding the deep oxidation of polyaromatics can be at low temperatures.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2015.04.031.

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