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DOI:

[10.1016/j.apcatb.2018.07.072](https://doi.org/10.1016/j.apcatb.2018.07.072)

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Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Davies, C, Thompson, K, Cooper, A, Golunski, S, Taylor, S, Bogarra Macias, M, Doustdar, O & Tsolakis, A 2018, 'Simultaneous Removal of NO_x and Soot Particulate from Diesel Exhaust by *in-situ* Catalytic Generation and Utilisation of N₂O', *Applied Catalysis B: Environmental*, vol. 239, pp. 10-15.
<https://doi.org/10.1016/j.apcatb.2018.07.072>

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Simultaneous removal of NO_x and soot particulate from diesel exhaust by *in-situ* catalytic generation and utilisation of N₂O

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ARTICLE INFO

Keywords:

Diesel exhaust
NO_x Reduction
Soot oxidation
Nitrous oxide
Silver

ABSTRACT

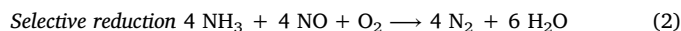
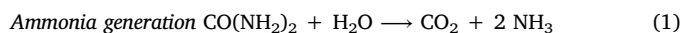
One of the outstanding challenges in diesel exhaust catalysis is to integrate oxidation chemistry, soot filtration and NO_x reduction in a single aftertreatment unit, while avoiding the need for fuel injection to regenerate the filter. Here we show that destruction of trapped soot can be initiated catalytically at 200 °C when its oxidation is coupled with non-selective NO_x reduction (using NH₃ as reductant), which acts as an *in-situ* source of N₂O. In laboratory tests over an extended temperature range (up to 800 °C), using supported silver as a catalyst for both non-selective NO_x-reduction and soot oxidation, the conversion of immobilised soot to CO₂ can be resolved into four consecutive steps as the temperature rises: catalysed oxidation by N₂O; non-catalysed oxidation by NO₂; catalysed oxidation by O₂; non-catalysed oxidation by O₂. Initial engine tests indicate that the critical first step (C + N₂O) can be replicated in a diesel exhaust.

1. Introduction

Effective control of air pollution leads to substantial benefits whether measured in terms of human wellbeing or in value to the economy [1]. On the other hand, in major cities throughout the world, the cost of long-term exposure to the combination of fine particulate (sub-PM_{2.5}) and NO₂ in the atmosphere is currently being counted in hundreds of thousands of lost human life-years, while the number of hospital admissions attributable to the effects of short-term exposure to these pollutants amounts to many thousands per year [2]. Although the major causes of pollutant-related mortality and morbidity arise from respiratory and cardiovascular conditions, there is increasing evidence of wider health effects, including cognitive impairment arising from fine particulate crossing the blood-brain barrier [3]. The primary source of these localised pollutants is road traffic, with diesel vehicles being implicated more than gasoline (petrol) vehicles. The detrimental effects now overshadow the environmental benefits of higher fuel economy and lower CO₂ emissions that enabled modern diesel vehicles to achieve high market share, particularly in Europe. Many governments are now at the point of scheduling the phasing-out of conventional diesel and gasoline vehicles, and yet it will be several decades before most vehicles are electrically powered.

The exhaust-gas from a spark ignition gasoline engine, operating

under stoichiometric air/fuel conditions, can be treated highly effectively in a single catalytic converter, but there is no equivalent integrated technology for the diesel engine [4]. Instead, diesel vehicles are fitted with multiple units, which consecutively remove carbon monoxide and hydrocarbons, soot, and NO_x [5]. A four-way system, in which all the regulated pollutants would be controlled in a single unit [6,7], would be expected to have the performance benefits associated with lower weight and back-pressure, and with faster warm up, than the combination of existing technologies. Two of the most difficult functions to integrate are the regeneration of a filter (by complete oxidation of trapped soot to CO₂) and the selective catalytic reduction (SCR) of NO_x to nitrogen (in which the selective reductant is ammonia generated *in-situ* from aqueous urea via decomposition and hydrolysis reactions [8]; Eqs. (1) and (2)). On diesel passenger cars, the trapping of soot particulate and the SCR reaction are carried out under the normal exhaust-gas temperatures, typically between 100 and 360 °C [9,10], whereas the oxidation of soot Eq. (3) is induced by catalytic combustion of injected fuel which generates a large exotherm in the exhaust system.



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<https://doi.org/10.1016/j.apcatb.2018.07.072>

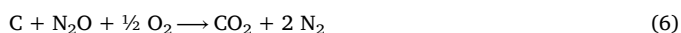
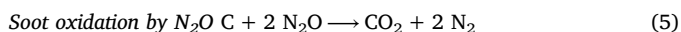
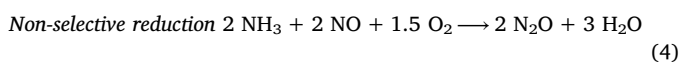
Received 15 April 2018; Received in revised form 22 July 2018; Accepted 27 July 2018

Available online 29 July 2018

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Previous work has shown that the temperature for complete oxidation of diesel particulate can be lowered by > 250 °C through the use of a silver catalyst [11,12], potentially eliminating the need for fuel injection into the exhaust as a means of regenerating soot filters on passenger cars. In common with other workers in the field [13–16], we have been investigating the potential for coupling catalytic soot oxidation with SCR. Although we were expecting this to require a combination of catalysts with high performance for each separate function, we have found that a silver catalyst can reduce NO_x to N₂ while at the same time oxidising soot, at the low temperatures typical of diesel exhaust, despite it being a poor (ie non-selective) SCR catalyst in the absence of soot. This effect arises because the non-selective product of SCR is N₂O Eq. (4), which we have found to be effective at initiating the oxidation of trapped soot Eqs. (5) and (6) in the presence of silver. As the exhaust-gas temperature rises, N₂O formation diminishes as initially NO_x reduction becomes more selective and then the direct oxidation reactions of NO and NH₃ predominate, but soot removal can continue through the well-established oxidation routes in which NO₂ and O₂ are the oxidants.



2. Experimental

The design of our experimental study consisted of preparing a range of catalysts (supported silver, platinum and vanadia) with distinct functionality for exhaust treatment, and testing them for their ability to reduce NO_x in a simulated fuel-lean exhaust gas, before we evaluated their performance for the simultaneous removal of NO_x and elemental carbon. Finally, we coated the best-performing catalyst onto a diesel particulate filter, which was tested under real exhaust-gas.

2.1. Catalysts

A silver formulation known to be active for soot combustion [12] was prepared by co-precipitating a support material with an atomic composition of Ce_{0.35}Zr_{0.15}Al_{0.5}O_{1.75} (i.e. containing Ce/Zr molar ratio of 7/3, or 47% Ce and 13% Zr by weight) from a mixed aqueous solution of the solid precursors (ammonium cerium(IV) nitrate, purity ≥ 98.5%, from Sigma-Aldrich; zirconyl oxynitrate hydrate, 99%, Aldrich; aluminium nitrate nonohydrate, ≥ 98%, Sigma-Aldrich) using aqueous Na₂CO₃ as precipitant (solid 99.5%, Alfa Aesar). After drying the support material (110 °C for 16 h), it was impregnated with an aqueous solution of AgNO₃ (solid 99.99%, Aldrich) to achieve a loading of 2 wt% Ag, before the fully formulated catalyst was dried (110 °C for 16 h) and calcined at 500 °C (5 h; flowing air) in preparation for testing. This catalyst is subsequently referred to as Ag/CZA.

A broad-acting oxidation catalyst was prepared by dispersing platinum, with a loading of 2 wt%, on an alumina support. Aqueous platinum tetrachloride (11.5 cm³, 3.48 g cm⁻³, Alfa Aesar) was heated to 90 °C with constant stirring, before γ-Al₂O₃ (1.96 g, 0.0192 mol, Merck) was added and stirred until there was no excess liquid present. The resulting white paste was then dried at 110 °C for 16 h, before being calcined at 500 °C for 5 h. This catalyst is subsequently referred to as Pt/Al₂O₃.

An ammonia-SCR catalyst, with a composition of 2 wt% V₂O₅ and 6 wt% WO₃ supported on TiO₂, was prepared by dissolving ammonium metavanadate (0.064 g, 5.48 × 10⁻⁴ mol, ≥ 99%, Sigma-Aldrich), oxalic acid (0.099 g, 1.10 × 10⁻³ mol, ≥ 99%, Aldrich) and ammonium metatungstate hydrate (0.159 g, 5.38 × 10⁻⁵ mol, ≥ 99%, Fluka) in 5 cm³ of de-ionised water. The solution was brought to a temperature of

90 °C under constant stirring, before titanium oxide (2.3 g, 0.0288 mol) was added. The resulting suspension was stirred for 30 min while maintaining the temperature at 90 °C, until all the excess water had been absorbed or evaporated to leave a brown paste. The remaining solid was dried under static air at 110 °C for 16 h, before being calcined for 5 h at 500 °C. This catalyst is subsequently referred to as V₂O₅-WO₃/TiO₂.

2.2. Laboratory test procedure

Having established that carbon black (Cabot Black Pearls 2000) was a consistent mimic for the elemental carbon component of diesel soot (see Supplementary Information), samples taken from a single batch were used throughout the laboratory tests in this study.

The catalytic reduction of NO_x and the oxidation of soot were studied by passing a gas mixture containing 500 ppm NO, 500 ppm NH₃ and 8% O₂ (by volume) in nitrogen at a flow rate of 200 cm³ min⁻¹ either through 0.25 g of catalyst (equivalent to a gas-hourly space velocity of 40,000 h⁻¹) or through a mixture of 0.025 g carbon black and 0.25 g catalyst, while the temperature was increased at a rate of 7 °C min⁻¹. The carbon + catalyst mixture was prepared by shaking the two powders together to form the loose contact typical of that between the catalytic washcoat and the trapped soot in a catalysed soot filter [17]. In the tests on catalyst alone, the maximum temperature was 500 °C, whereas the temperature was ramped to 800 °C when carbon black was present, and the maximum temperature was then held until all the carbon had oxidised. Although the gas mixture was intended to be representative of a diesel exhaust-gas to which NH₃ (hydrolysed urea) had been added, CO₂ and H₂O were deliberately excluded, so that their formation could be used to track the oxidation of the carbon black. All gas concentrations shown were measured (in mol-ppm) using an FTIR gas analyser (Gaset), except for the concentration of N₂ which was calculated from the nitrogen balance.

2.3. Catalysed diesel soot filter

A batch of the Ag/CZA catalyst (prepared as described above) was dispersed in dilute nitric acid (3 vol% concentrated HNO₃ in distilled water), before the resultant slurry was stirred for 4 h. A silicon carbide diesel particulate filter (length: 4.5 in. diameter: 1 in. cell density: 200 cps; wall thickness: 0.012 in.) was then dipped repeatedly into the slurry, which adhered to the inner surfaces of the filter channels. Any excess of catalyst in the channels was forced out by blowing a controlled air flux through the filter. Finally, the catalyst-coated filter was calcined in static air at 600 °C for 3 h. From weighing the calcined filter, the catalyst loading was found to be 8.4 wt%, while the thickness of the catalyst coating was observed by electron microscopy to be about 100 μm (see Supplementary Information).

2.4. Engine test procedure

A experimental single-cylinder direct injection diesel engine was used to test an uncoated diesel particulate filter and the catalyst-coated filter. The engine calibration was kept the same in all tests, and to reduce test-to-test variability and ensure steady state operation, the engine was warmed up until the oil temperature reached 60 °C, before carrying out the testing at 1500 rpm and 15 Nm (3 bar IMEP). The filter was mounted in a tubular reactor which was positioned at the centre of a tube furnace (see schematic in Supplementary Information), which was programmed to maintain the exhaust-gas temperature at the filter inlet at 300 °C. Exhaust gas from the engine was fed through the filter, while the pressure drop across it was continuously monitored. The soot-particulate size distribution in the exhaust gas, upstream and downstream of the soot filter, was measured using a scanning mobility particle sizer (comprising a TSI series 3080 electrostatic classifier, a 3081 differential mobility analyser and a 3775 condensation particle

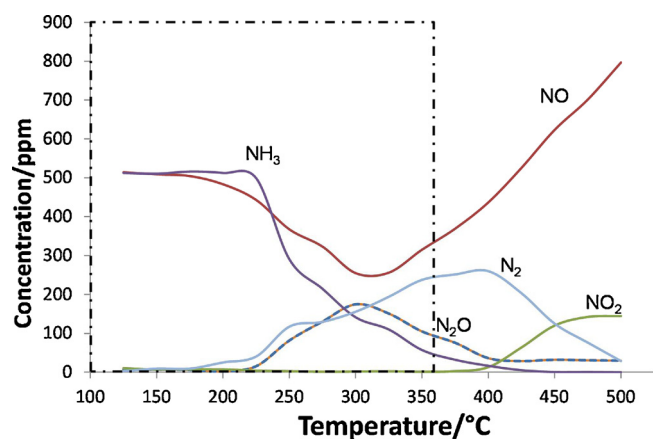


Fig. 1. NO_x-reduction performance of Ag/CZA tested in a simulated exhaust gas containing NH₃ as reductant, with dotted line indicating typical 'temperature window' for diesel exhaust emitted by passenger cars.

counter). In common with the laboratory tests, the concentrations of the gas-phase species were measured using an FTIR gas analyser (MKS MultiGAS 2030 series).

3. Results and interpretation

3.1. In-situ generation and utilisation of N₂O

When a silver soot-combustion catalyst, Ag/CZA, was tested for its ability to catalyse the reduction of NO_x by reaction with NH₃ in the absence of soot, the NO concentration decreased by 50% between 150 °C and 310 °C, before beginning to increase. This gave rise to the inverted peak for NO concentration seen in Fig. 1, which is mirrored by a positive peak for N₂O concentration over the temperature range 225–425 °C. The onset of the N₂O peak (225 °C) coincides with the temperature at which the NH₃ concentration began to decrease, while the upper limit of the N₂O peak (425 °C) coincides with the NH₃ concentration reaching zero, the NO returning to its starting concentration, and the onset of NO₂ formation. Above 425 °C, the NO concentration continued to rise (exceeding its starting concentration), while the NO₂ concentration levelled.

These results show that Ag/CZA is active for NO_x reduction over the temperature range 150–425 °C. Initially, between 150 and 225 °C when the NH₃ is not being converted, the decrease in NO concentration is due to its adsorption on the catalyst surface, an effect often observed for NO_x-reduction catalysts [18]. The subsequent rise in both N₂O and N₂ concentrations (225–310 °C) indicates that the catalyst is actively reducing the NO in the synthetic exhaust-gas by catalysing its reaction with NH₃. However, at the lowest temperatures, it clearly lacks the selectivity of the most effective SCR catalysts, which would convert the NO to N₂. As the catalyst is not active for the dissociation of N₂O below 500 °C, the decline in N₂O concentration between 310 and 425 °C indicates that it competes with NO for reduction by ammonia over this temperature range. At temperatures above 400 °C, the dominant reactions are the oxidation both of the NO and NH₃ by O₂, with the resultant release of NO and NO₂.

Significantly, no N₂O was detected between ambient temperature and 800 °C, when the same test procedure was repeated using a mixture of the Ag/CZA catalyst and carbon black (an effective soot mimic in these experiments). In place of the N₂O peak between 220 and 425 °C (seen in Fig. 1), continuous formation of CO₂ was detected, as the first of four consecutive steps (i) to (iv) in Fig. 2. As oxidation of the carbon black was the primary source of any of the CO₂ formed in this test, it can be deduced that the N₂O, produced by the non-selective reaction of NO with NH₃, is responsible for step (i) in the release of CO₂. (The small CO₂ peak visible at 250 °C corresponds to the dissociation of carbonate

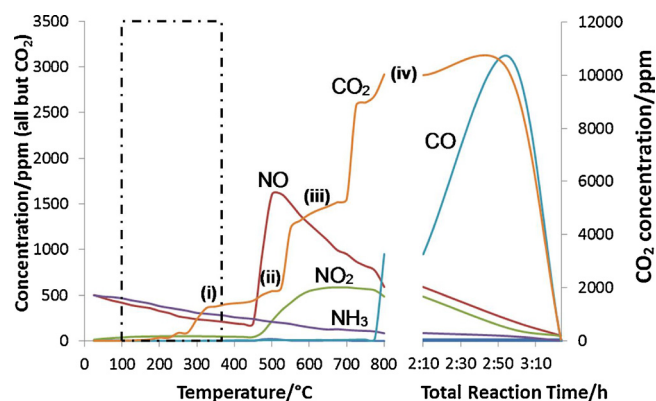
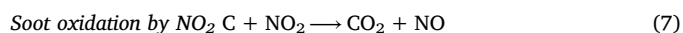


Fig. 2. Performance of Ag/CZA when mixed with carbon black (10/1 by mass) and tested in a simulated exhaust gas containing NH₃ as reductant. The temperature was increased linearly to a maximum of 800 °C, before being held until carbon oxidation was complete. The four steps of carbon oxidation are highlighted (i) – (iv). Dotted line indicates typical 'temperature window' for diesel exhaust emitted by passenger cars.

and hydrogencarbonate species initially present on the catalyst surface.) As the maximum concentration of CO₂ exceeded that of the 'missing' N₂O during the first step, it implies that storage of N₂O (or of a precursor) on the carbon preceded the onset of the C + N₂O reaction. These processes must take place as the N₂O is being formed, because feeding N₂O does not lead to the same effects, even when the Ag/CZA catalyst is mixed with the soot (see Supplementary Information).

The subsequent step-changes in CO₂ concentration (seen in Fig. 2) can be explained by the known effects of the other two potential oxidising agents: O₂ (already present in the simulated exhaust gas) and NO₂ (which can be formed from the NO in the simulated exhaust gas and from the NH₃ added as reductant). The step between 450 and 525 °C is consistent with the direct (non-catalytic) reaction of soot with NO₂ being the predominant oxidation route in this temperature range, leading to the formation of CO₂ and NO Eq. (7) [19]. This interpretation is substantiated by the corresponding test in the absence of soot (Fig. 1), which showed a crossover temperature of just above 400 °C for the disappearance of N₂O and the appearance of NO₂. The next step (525–700 °C) closely matches the position of the peak in the mass lost during the catalytic oxidation of soot by O₂, while the final step (> 700 °C) matches that for the non-catalytic reaction with O₂ [12]. Overall, the four steps in CO₂ production seen in Fig. 2 correspond to the following sequence of reactions by which the elemental carbon in soot can be consumed: (i) catalysed oxidation by N₂O, (ii) non-catalysed oxidation by NO₂, (iii) catalysed oxidation by O₂, and (iv) non-catalysed oxidation by O₂. Clearly, Ag/CZA provides the functionality for both of the catalysed oxidation reactions, as well as being active for the non-selective catalytic reduction of NO_x, through which the N₂O is formed.



When Ag/CZA was replaced by Pt/Al₂O₃ (a platinum catalyst which can be used for a variety of combustion reactions [20–22] and for NO_x reduction using hydrocarbons [23,24]), its performance in the absence of soot showed that it is even less selective for NO_x reduction to N₂ than Ag/CZA (compare Figs. 1 and 3). Whereas the N₂-selectivity of Ag/CZA was close to 50% between 220 and 300 °C, and increased to 100% between 300 and 425 °C, the predominant product of NO_x reduction was N₂O over the entire temperature range when the catalyst was Pt/Al₂O₃ (Fig. 3). However, despite the high activity of the Pt/Al₂O₃ catalyst for the non-selective reduction of NO_x at low temperatures (N₂O formation reached a maximum at 200 °C), it did not show any measurable activity for the oxidation of soot below 450 °C (Fig. 4), with the disappearance of the N₂O being accounted for by its storage by the soot.

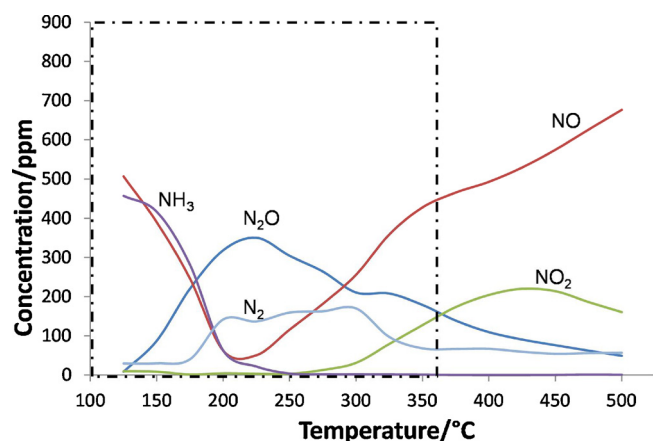


Fig. 3. NO_x-reduction performance of Pt/Al₂O₃ tested in a simulated exhaust gas containing NH₃ as reductant. Dotted line indicates typical 'temperature window' for diesel exhaust emitted by passenger cars.

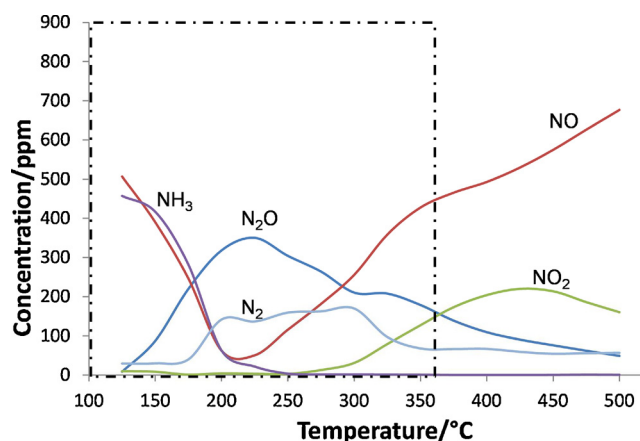


Fig. 6. NO_x-reduction performance of V₂O₅-WO₃/TiO₂ tested in a simulated exhaust gas containing NH₃ as reductant. Dotted line indicates typical 'temperature window' for diesel exhaust emitted by passenger cars.

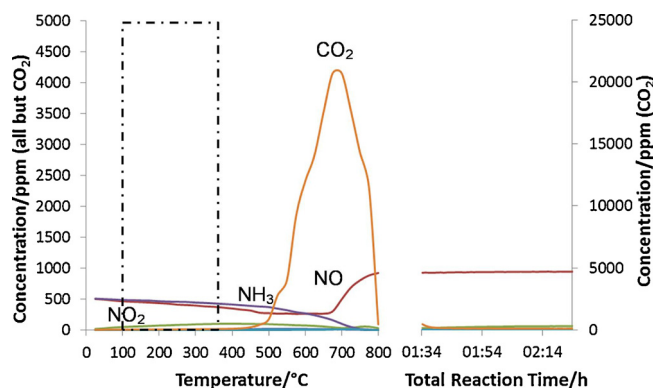


Fig. 4. Performance of Pt/Al₂O₃ when mixed with carbon black (10/1 by mass) and tested in a simulated exhaust gas containing NH₃ as reductant. The temperature was increased linearly to a maximum of 800 °C, before being held for 1 h. Dotted line indicates typical 'temperature window' for diesel exhaust emitted by passenger cars.

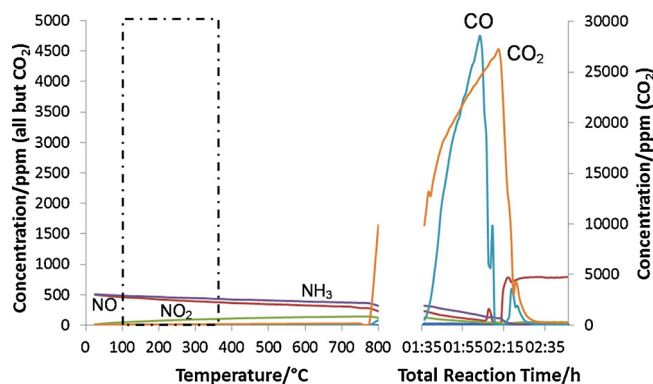


Fig. 5. Performance of V₂O₅-WO₃/TiO₂ when mixed with carbon black (10/1 by mass) and tested in a simulated exhaust gas containing NH₃ as reductant. The temperature was increased linearly to a maximum of 800 °C, before being held for 1.5 h. Dotted line indicates typical 'temperature window' for diesel exhaust emitted by passenger cars.

Similarly, V₂O₅-WO₃/TiO₂ (a proven SCR catalyst for diesel NO_x control [25,26]) showed no low-temperature soot oxidation activity (Fig. 5). This was not unexpected as its high selectivity to N₂ means that it generated negligible amounts of N₂O when it was tested in the absence of soot (Fig. 6). The inability of this catalyst to release either gas-phase N₂O or NO₂, and to catalyse the oxidation of soot by reaction

with O₂, led to all the soot being oxidised in a single high-temperature step (non-catalytic combustion), which gave rise to the large CO₂ and CO peaks with onset temperatures above 750 °C (Fig. 6).

3.2. Operando testing of silver catalyst in a diesel particulate filter

When a diesel particulate filter coated in Ag/CZA was inserted into a real diesel exhaust-stream maintained at 300 °C (the temperature for maximum N₂O formation during NO_x reduction by ammonia over this catalyst), the filtration efficiency consistently exceeded 99% across the range of particulate size monitored, but only when NH₃ was added to the exhaust gas (Fig. 7). By contrast, in the absence of added NH₃, the efficiency of the coated monolith only exceeded 99% for particulate size < 75 nm, and it showed the characteristic 'dip' in the mid-range, corresponding to the region in which diffusional filtration is decreasing while the contributions from alternative mechanisms (interception and inertial impaction) have yet to reach their maxima [27]. Although these tests do not provide direct evidence for the C + N₂O reaction under operating conditions, the results are entirely consistent with the elimination of particulate within the filter when the non-selective reaction between NO_x and NH₃ is taking place. It is worth noting that the ammonia was added at two different concentrations, 500 ppm (as used in

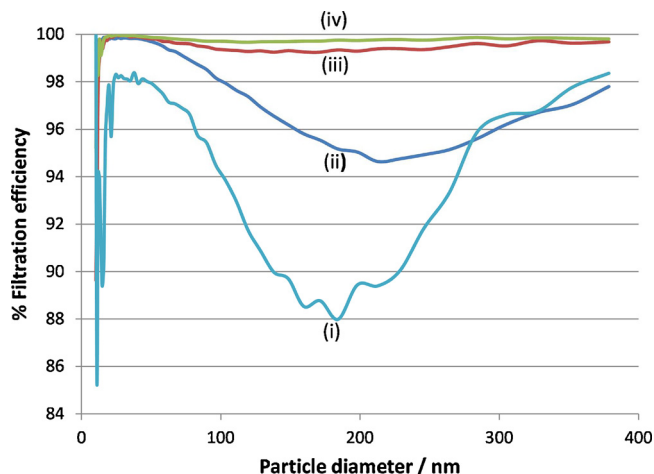


Fig. 7. Filtration efficiency of a diesel particulate filter as function of the size of soot particulate emitted by a diesel engine. Measurements made on (i) uncoated filter, (ii) Ag/CZA-coated filter, (iii) Ag/CZA-coated filter with 500 ppm NH₃ added to the exhaust gas inlet, and (iv) Ag/CZA-coated filter with 540 ppm NH₃ added to the exhaust gas inlet. The temperature of the filter was maintained at 300 °C throughout.

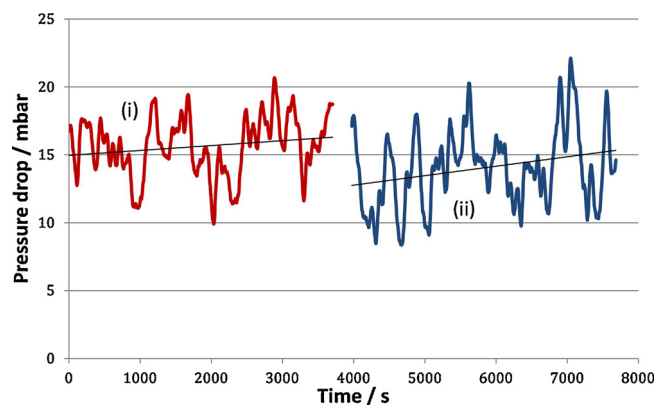


Fig. 8. Pressure drop across the Ag/CZA-coated filter as function of elapsed time, (i) in the absence of NH_3 , and (ii) when 500 ppm NH_3 was added to the exhaust gas inlet. Normalised values shown in red and blue; linear trend lines in black (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

the laboratory tests) and 540 ppm (to achieve a 1:1 stoichiometry with the NO_x released by the engine). As seen by comparing traces (iii) and (iv) in Fig. 7, the higher ammonia concentration gave a higher value for the filtration efficiency, which is consistent with a higher rate of N_2O formation and a higher rate of soot oxidation. Our interpretation is that, in these experiments, the *filtration efficiency* is in effect a measure of soot destruction and not a measure of soot retention.

Measurements of the pressure drop through the Ag/CZA-coated filter provide support for our interpretation that the improved filtration efficiency when NH_3 was added is due to particulate oxidation, and not simply to the retention of more particulate within the filter. Although the individual pressure-drop values varied with time (giving rise to the ‘noise’ in Fig. 8) while the filter was continuously filling and regenerating, the polynomial trendlines reveal that the pressure drop was consistently lower when NH_3 was being added.

4. Conclusions – Implications for NO_x and soot particulate control

The ability of NO_2 to oxidise carbon has been exploited in explosives and pyrotechnics for centuries [28,29] and, more recently, in continuously-regenerating soot filters fitted on heavy-duty diesel vehicles [30]. It also shows potential for oxidising soot at low exhaust-gas temperatures, if the NO_2 can be formed within a catalyst pore structure in which the soot is trapped [31] (though the NO_2 is itself only reduced back to NO during this reaction). By contrast, N_2O is known to be stored by carbon [32], but is not renowned as an oxidant for soot at temperatures below the range of 400–950 °C [33]. Our results show that, despite the high affinity between soot and N_2O , a catalyst is required for the key reaction between elemental carbon and N_2O to take place at temperatures below 400 °C. A silver formulation (Ag/CZA), previously shown to be effective for soot combustion [12] (ie the $\text{C} + \text{O}_2$ reaction), has been found to be active also for soot oxidation through the $\text{C} + \text{N}_2\text{O}$ reaction. The soot oxidation specifically takes place during the in-situ formation of N_2O by the silver catalyst, during non-selective reduction of NO_x by reaction with NH_3 , suggesting that surface N_2O (or a surface intermediate in its formation) is the reactive oxidising species. Although, $\text{Pt}/\text{Al}_2\text{O}_3$ is even less selective than Ag/CZA for NO_x reduction, Pt does not have the ability to catalyse the $\text{C} + \text{N}_2\text{O}$ reaction while it is forming N_2O . When Ag/CZA is mixed with soot and tested under simulated fuel-lean exhaust gas, a sequence of consecutive oxidation steps takes place, starting with the $\text{C} + \text{N}_2\text{O}$ reaction, during which NO_x , NH_3 and soot are consumed. By contrast, $\text{Pt}/\text{Al}_2\text{O}_3$ is unable to oxidise soot at temperatures below that at which NO_2 forms, while the highly selective SCR catalyst $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ requires even higher temperatures in order to catalyse the $\text{C} + \text{O}_2$ reaction.

In the context of diesel passenger cars, the temperature range of the exhaust gas is typically 100–360 °C. Significantly, this overlaps with the temperature range (225–425 °C) over which the silver catalyst can operate bi-functionally to reduce NO_x and oxidise soot. Initial engine tests of an Ag/CZA-coated diesel particulate filter at a fixed exhaust-gas temperature of 300 °C show very high filtration efficiency and low pressure-drop, consistent with the $\text{C} + \text{N}_2\text{O}$ reaction continuously regenerating the filter. Extensive engine testing is now required to evaluate the extent of soot control together with the associated NO_x reduction over a wide range of operating conditions, and to confirm negligible emissions of N_2O as seen in our laboratory tests.

Acknowledgements

The authors gratefully acknowledge the support of RCUK through (i) the Environmental programme of the EPSRC UK Catalysis Hub (grant EP/K014706/1, EP/K014668/1, EP/K014854/1, EP/K014714/1 and EP/M013219/1), (ii) the Cardiff University EPSRC Impact Acceleration Account, and (iii) the EPSRC Centre for Doctoral Training in Catalysis (funded by EPSRC, Cardiff University and the Universities of Bath and Bristol). Information on the data underpinning the results, including how to access them, can be found in the Cardiff University data catalogue at <http://doi.org/10.17035/d.2018.0054956978>.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.07.072>.

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