



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

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ABSTRACT

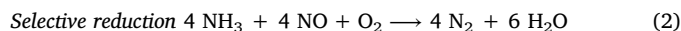
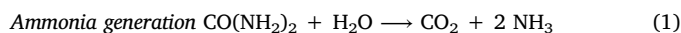
One of the outstanding challenges in diesel exhaust catalysis is to integrate oxidation chemistry, soot filtration and NO_x reduction in a single aftertreatment unit, while avoiding the need for fuel injection to regenerate the filter. Here we show that destruction of trapped soot can be initiated catalytically 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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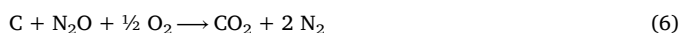
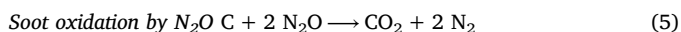
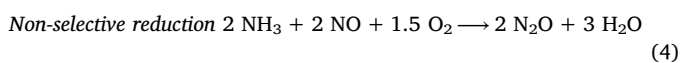
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Previous work has shown that the temperature for complete oxidation of diesel particulate can be lowered by > 250 °C through the use of a silver catalyst [11,12], potentially eliminating the need for fuel injection into the exhaust as a means of regenerating 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

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