

Why Pt-Ce-soot generated from fuel borne catalyst is extremely active in soot oxidation?

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Introduction

Diesel engines are the most preferred for heavy-duty applications and light-duty trucks due to its high torque and superior fuel economy, therefore, decreasing CO₂ emissions. Diesel engine exhaust gases contribute, however, significantly to urban and global air pollution. Emissions of hydrocarbon (HC) and CO from diesel exhaust gases are low and can be easily converted by using diesel oxidation catalyst (DOC). Further improvements in modern diesel engine design and combustion process will lead to decreased emissions of both NO_x (NO+NO₂, mainly present as NO) and particulate (soot or carbon particulates). Improvements in diesel fuel properties and combustion processes alone will not meet the legislation of Euro V (2008) and US'7 and US'10 (2007, 2010) for both NO_x and soot. Soot can be collected on a filter and active and passive filter regeneration strategies are being used in practice to burn soot. During most of the diesel engine operation period the exhaust gas temperatures are below 300°C and that temperature is too low for initiating continuous un-catalysed soot oxidation with O₂ or NO₂. The two most popular technologies to decrease soot oxidation are i) catalysed soot filter, converts NO to NO₂, that oxidises soot, and ii) fuel-borne catalyst, that oxidises soot with mainly O₂ as well as NO. A variety of fuel borne catalysts are proposed and some of them have been implemented in practice. Ce and Ce-Fe fuel borne catalysts mainly oxidise soot by utilising the 'lattice oxygen', and decreases soot oxidation temperature by about 100 and 175 °C, respectively. Bimetallic fuel borne catalysts containing ultra low concentrations of Pt-Ce are shown to decrease the balance point temperature (where soot oxidation rate is equal to soot deposition rate) to around 275- 300 °C [1]. This is the **lowest balance point** achieved among the many combinations of fuel additives and catalysed soot filters studied so far. In this presentation, besides from known benefits of fuel borne catalysts in soot oxidation, various mechanistic aspects for very high efficiency of Pt-Ce fuel borne catalyst in soot oxidation, compared with other fuel borne catalysts/catalysed soot filter systems will be discussed.

Results and Discussion

Ce (50 ppm), Pt (10 ppm), Pt-Ce-soot (2 ppm Pt and 30 ppm Ce) and Fe (44 ppm) containing soot is generated from the respective fuel borne catalysts in a real diesel engine. Soot containing fuel borne catalysts are also characterised and compared with model printex-U soot. Oxidation of different soots is studied at different reaction conditions (with O₂, NO+O₂ and NO₂ and with and with out adding Pt/Al₂O₃ catalyst).

It is found on one hand that: 1) Fe-, Ce- and Pt-Ce-soot can be oxidised at lower temperature with O₂, compared with Pt-soot and 2) the opposite trend is observed with NO+O₂. NO is oxidised to NO₂ more efficiently over Pt-soot, compared with Fe-, Ce- or Pt-Ce-soot, and this Pt-soot decreased soot oxidation temperature by about 150°C. On the other hand when different soot samples are mixed with similar amount of Pt/Al₂O₃ catalyst and the reaction is carried out with NO+O₂, Pt-Ce-soot is found to show significantly higher soot oxidation rates

(Fig. 1a), compared with all the soot samples. Jelles et al. [1], based on similar experiments and results proposed that NO₂ decomposed to NO and adsorbed oxygen over CeO₂ and such adsorbed oxygen will significantly enhance soot oxidation rate. Fe-, Cu- and printex-U soot did not create such adsorbed active oxygen and, therefore, showed lower soot oxidation activity.

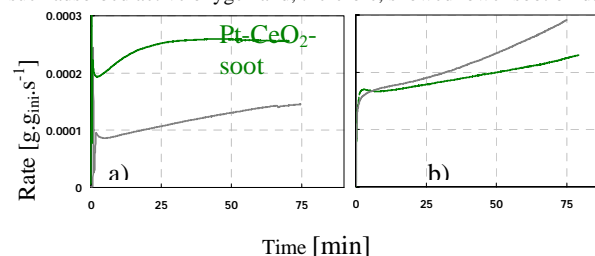


Fig. 1. Different Soot oxidation at 350°C with 500 ppm NO₂ in gas phase; a) in the presence of oxygen and b) in the absence of oxygen

When NO₂ alone is used as feed gas, the rate of printex-U, Fe-, Cu-, Ce- and Pt-Ce-soots are similar (example in Fig. 1b). If only ceria is able to create this adsorbed oxygen species then it would have shown higher soot oxidation rates. This is clearly not the case and, therefore, the mechanism proposed by Jells et al. [1] cannot fully explain the very efficient soot oxidation mechanism over Pt-Ce-soot.

From soot oxidation studied under different reaction conditions and with different fuel borne catalysts it is found that Pt-Ce- fuel-borne catalyst is highly efficient only when NO₂+O₂ or Pt/Al₂O₃+NO+O₂ are present. The main reaction, that takes place under these reaction conditions over ceria, is the formation of surface nitrates. These nitrates are found to oxidise soot at very low temperatures (even below 300°C) in comparison with gas-phase NO₂. Combination of Pt and Ce stimulates this surface nitrate formation and its subsequent migration to soot surface will dramatically increase the soot oxidation rate. Fe, Cu and Pt fuel borne catalysts do not form extensive surface nitrates and the main reactions over these catalysts are the direct soot oxidation with NO₂ and O₂. These oxidation are less effective compared with decomposition of cerium nitrates.

Conclusions

Based on the experimental results it is concluded that the oxidation activity of the species with decreasing order is: 1) nitrates, NO₃⁻; 2) NO₂, 3) lattice oxygen, and 4) gas phase oxygen. The hypothesis is formulated that all possible oxidation species present in the exhaust gas and on the catalyst surface can be efficiently utilised in Pt-Ce-soot oxidation in comparison with any of the known catalytic system. Furthermore, various parameters, such as efficient high temperature NO recycles to NO₂, and soot characterisation will be discussed in explaining the lowest balance point observed during real engine applications. These new insights into soot oxidation mechanism can lead to new catalyst formulations and control technologies and/or strategies.

References

1. S. J. Jelles, M. Makkee, J. A. Moulijn, Topics in Catalysis 16 (2001) 269.