

Catalytic Coatings for Active and Passive Diesel Particulate Filter Regeneration

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Summary. This paper will give an overview how catalytic coatings are applied in diesel particulate filter systems to support filter regeneration by soot oxidation with nitrogen dioxide or oxygen. Catalytic coatings can be placed on a catalyst substrate in front of a diesel particulate filter, on a filter, or in a combined system on both. Strategies and conditions for successful filter regeneration of those systems will be discussed.

Keywords. Heterogeneous catalysis; Kinetics; Oxidations; Nitrogen dioxide; Soot oxidation.

Introduction

Diesel engines combust diesel fuel to convert its chemical energy into mechanical power. The primary combustion products of diesel fuel are carbon dioxide and water. More than 99% of diesel emissions consist of CO₂, H₂O, and the portion of air left over from the combustion process. As real diesel combustion is not ideal, a fraction of a percent of the total diesel emissions are unwanted combustion by-products [1]. These pollutants are mainly particulate matter (PM), nitrogen oxides (NO_x = NO and NO₂), hydrocarbons (HC), and carbon monoxide. Of those, PM emissions are seen as perhaps the most critical. They are of major concern regarding negative health [2–6] and possible climate effects [7–10].

The most effective method to control PM emissions from diesel engines is applying diesel particulate filter (DPF) systems. They are very effective in filtering PM of all sizes out of diesel emissions [11–17]. The main technical challenge for DPF systems in automotive applications is their regeneration from the soot they retain from the exhaust gases. For a large variety of applications ranging from passenger cars, city busses, garbage trucks, delivery trucks, in-door fork lifters, construction machines, tunnel- and mining equipment, to locomotives, various

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DPF systems with soot regeneration technologies are in use today [13, 18]. Whatever the regeneration method, catalytic coatings play a major role in supporting it.

Fundamental Principles of DPF System Regeneration

Particulate matter consists of an agglomeration of primary soot particulates (mainly elemental carbon), adsorbed hydrocarbons (VOF), water, sulphuric and nitric acid, and engine oil derived components like Ca, P, or Zn [19]. The ratio of these components, the microstructure and properties of PM depend on the combustion conditions, the fuel and oil used, and whether and which aftertreatment device is present in the exhaust system.

When trapped in a DPF all of the components present in particulates except the normally very small amount of inorganic oil derived residues can be converted into gaseous products by evaporation (water), decomposition (H_2SO_4 , HNO_3), or oxidation (VOF, soot (=mainly C)). Therefore all technologies commonly used for DPF regeneration are based on some heat treatment and the oxidation of soot to CO_2 . From each regeneration a small amount of "oil ash", which typically consists mainly of zinc phosphate and calcium sulphate, remains in the filter and has to be mechanically removed during vehicle service.

The microstructure of particulate matter influences its reactivity against oxidation [20]. However, a much greater influence on the rate at which PM can be oxidised comes from the concentration and the reactivity of the applied oxidising agent. In diesel exhaust emissions there are two oxidising gases present, which are suitable for soot oxidation: oxygen and nitrogen dioxide. Both play an important role in DPF regeneration. There is much more O_2 present in diesel exhaust emissions than NO_2 , but NO_2 is much more active than O_2 . The difference in reactivity between O_2 and NO_2 as oxidising agent for soot can be seen in Fig. 1, which shows the temperature-ranges at which NO_2 and O_2 start to combust soot.

Oxygen Based Soot Oxidation

The oxygen comes from the charge air left over from the diesel combustion process and its concentration in diesel exhaust emissions is in the order of around 10%. Exhaust temperatures above 550°C are required for soot oxidation by O_2 . With the

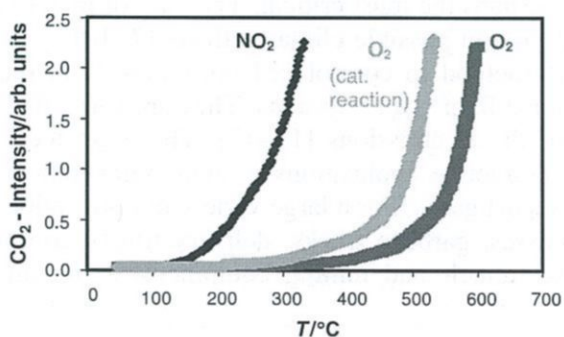


Fig. 1. Soot combustion (to CO_2) by NO_2 and O_2 as a function of temperature

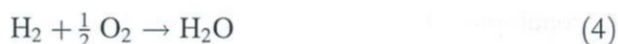
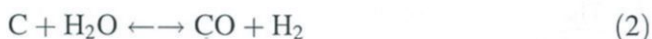
application of so-called “fuel borne catalysts” (FBCs), which precursors are added to the diesel fuel, the required temperature can be lowered to around 400–450°C [21–33]. Alternatively oxygen could be “activated” by applying non-thermal plasma to generate ozone [34], which could then be used to combust soot at low temperatures [35]. However, this approach has not been used in commercial applications yet.

Chemistry of Oxygen Based Soot Oxidation

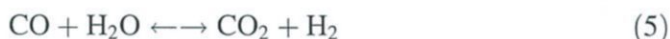
If the temperature exceeds 500°C soot oxidation by oxygen becomes significant (Eq. (1)).



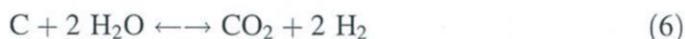
The kinetics of soot oxidation is also influenced by the presence of water vapour and adsorbed species like hydrocarbons on the soot surface. A possible influence from water vapour could come from the steam reforming reaction (Eq. (2)) which could be followed by the oxidation of CO and H₂ to CO₂ and water according to Eqs. (3) and (4).



The CO of Eq. (2) could also react with water in the water gas shift reaction (Eq. (5)).



The combination of Eqs. (2) and (5) results in Eq. (6).

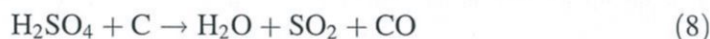


The presence of CO₂ could lead to carbon removal according to Eq. (7) towards the *Boudouard* equilibrium [36], which could be followed by the oxidation of CO to CO₂ (Eq. (3)).



Adsorbed hydrocarbons could help to ignite the soot by its easier oxidation. The oxidation of these adsorbed HCs could lead to local exotherm generation heating up the soot locally to its combustion temperature. Additionally, when HCs are desorbing or burning off from soot particulates, the surface area of the soot particulates accessible to oxygen increases. This activates the soot for its easier combustion.

Whereas sulphur in the fuel has a negative effect on the NO₂ formation and PM emissions (see later), it might have also beneficial effects for the soot oxidation itself. Sulphuric acid adsorbed on particulate matter becomes more concentrated, when the temperature comes close to its boiling point (338°C). H₂SO₄ is a strong oxidant and might support the soot oxidation according to Eq. (8).



This reaction might become more important, after a long period of passive regeneration at low temperatures, when some H_2SO_4 has been accumulated within the soot layer.

Nitrogen Dioxide Based Soot Oxidation

NO is formed under the high-temperature, high-pressure in-cylinder conditions from the nitrogen and oxygen present in the charge air during the diesel combustion. NO_2 forms from NO by reaction with excess oxygen. During the expansion stroke of the piston the temperature decreases rapidly within the combustion chamber, but the NO concentration does not decrease to the NO/ O_2 / NO_2 equilibrium concentration as NO is kinetically relatively stable under these conditions [37]. Figure 2 shows the NO_2 concentration at thermodynamical NO/ NO_2 / O_2 equilibrium (Eq. (9)) for the temperature range from 0–700°C under typical diesel O_2 concentration levels.



The concentration of nitrogen oxides in diesel exhaust gas is around 0.01–0.1%. That is 2–3 orders of magnitude lower than the O_2 concentration. 80–95% of the nitrogen oxides leave the engine as NO and only 5–20% as NO_2 .

In exhaust systems without oxidation catalysts NO is oxidised to NO_2 mainly only after leaving the tailpipe as the reaction of NO with O_2 is very slow under these conditions. The presence of an oxidation catalyst can speed up the NO oxidation reaction and increase the NO_2 -share of NO_x downstream of the catalyst, where the NO_2 can then be utilised for soot oxidation. An alternative, but not yet

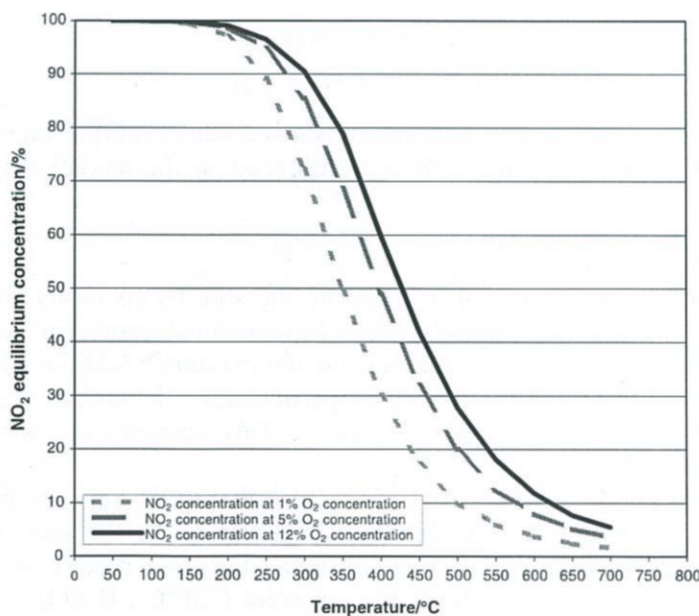


Fig. 2. Equilibrium NO_2 concentration for various (diesel emissions typical-) oxygen concentrations as a function of temperature

commonly applied way to increase the rate of the NO oxidation is the application of a non-thermal-plasma reactor [34, 39–42].

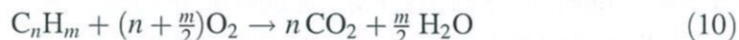
NO₂ oxidises soot to CO₂ at reasonable rates at temperatures as low as *ca.* 250°C [43].

Design of Diesel Oxidation Catalysts (DOC) for Nitrogen Dioxide Based Soot Regeneration Strategies

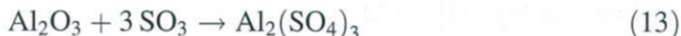
A DOC typically consists of a ceramic (most common is cordierite) or metallic (most common is stainless steel) substrate with geometric surfaces of a few square meters. To increase the surface area for a good distribution of the precious metal catalyst material (most common is Pt for DOCs) a so-called “washcoat” consisting of a thermally stable high surface area metal oxide (with a few hundred square meters surface area per gram, *e.g.* Al₂O₃) is used. The main function of the washcoat is to stabilise the fine dispersed catalyst material against sintering, but can also be used to enhance the catalytic activity or protect it against poisoning. The aim is to use as much washcoat material as possible without compromising the backpressure behaviour of the catalyst too much. The typical range for washcoat loading is between 3 and 300 g/dm³ catalyst volume with typical metal loadings of 0.1–10 g/dm³ catalyst.

Reactions Catalysed by DOCs for NO₂ Based Soot Regeneration

Besides of the NO oxidation further reactions taking place over the DOCs are the oxidation of CO according to Eq. (3) and hydrocarbons (HCs) according to Eq. (10).



As CO and HC compete with NO for the active sites on the catalyst, a very high activity for all these oxidation reactions is desired. When sulphur-containing species like SO₂ are present in the diesel exhaust, they will also be oxidised over the DOC to eventually form sulphuric acid and sulphates (Eqs. (11)–(13)).



Equation (11) competes with Eq. (9) and therefore limits the NO₂ formation. The formation of sulphuric acid (Eq. (12)) can block the active sites and the formation of washcoat component sulphates (*e.g.* Eq. (13)) can destroy its functionality. Another disadvantage of sulphuric acid and sulphate formation is that sulphuric acid and sulphates can pass DPFs and are measured as particulate matter in legislated emission tests. Therefore the sulphur contents of the diesel fuel as well as the sulphur contents of the engine oil have to be minimised.

Chemistry of Nitrogen Dioxide Based Soot Oxidation

The chemistry of nitrogen dioxide based soot oxidation has been subject to several studies [20, 44, 45]. In recent synthetic gas studies with carbon black exposed to a

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