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THE ROLE OF CATALYST IN THE REDUCTION OF DIESEL PARTICULATE EMISSION

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Abstract

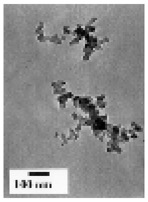
In this paper a brief overview about diesel emissions and those environmental and health effects are presented. Strategies to control diesel emissions, including engine adjustment, fuel reformulation, and exhaust after-treatment systems are briefly discussed with emphasis on catalytic diesel soot abatement technologies. Types of catalysts reported in literature in the last decades are reviewed. Challenging topics in catalysis of diesel soot oxidation conclude this paper.

Key Words: diesel emissions, soot oxidation,

A. Diesel emissions, environmental effect and its legislation

Diesel emissions

To the present day, diesel engine's excellent fuel economy remains one of its strongest selling points in the automotive market. Unfortunately, the practical application of combustion engines, including diesel engines, encounters incomplete combustion, which leads to the emission of severe pollutants. Non-ideal mixing of fuel and air creates pockets of excess fuel, where solid carbonaceous soot particles (the solid and the soluble organic fraction, SOF) are formed [1-3]. Associated with carbonaceous soot, adsorbed hydrocarbon, small amounts of sulfate, nitrates, metals, trace elements, water, and unidentified compounds make up of diesel particulate matter (PM). A Transmission Electron Microscopy (TEM) images, and the schematic structure and composition of a typical diesel particulate system are shown in Figure 1.



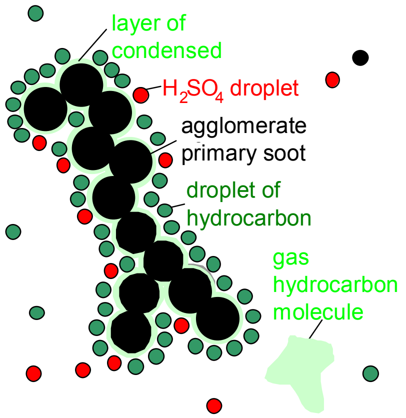


Figure 1. a. TEM micrograph of particulate matter <10 mm (PM10) collected by impaction for 30 s after [4], b. Schematic representation of diesel soot and its adsorbed species.After [5, 6]

Adsorbed hydrocarbon, sulfate, and water act as "glue"; this causes the particles to agglomerate and as a result a shift of the particle size and mass distribution upward is observed [5]. Diesel PM is typically composed of 50% to 75% elemental carbon (EC), depending on the age of the engine, deterioration, heavy-duty versus light-duty, fuel characteristics, and driving conditions. The hydrocarbon portion of diesel PM originates from unburned fuel, engine lubrication oil, and low levels of partial combustion and pyrolysis products and will typically range from 19 - 43 %.

Together with particulate emissions, CO, hydrocarbon (HC), and NO_x are emitted as gaseous diesel exhaust pollutant. As with the formation of soot, CO and HC are the results of incomplete combustion. In contrast with soot formation, NO_x is created where the air/fuel ratio is more stoichiometric and high temperatures are generated [6]. The output range of the main pollutant components, the temperature and the exhaust mass flow rate are summarised in Table 1. For the pollutants the lower value can be found in new clean diesel engines while the higher numbers are characteristic for older engines [7-11].

Table 1. Typical conditions of diesel exhaust gas [9-14]

	CO (vppm)	HC (vppm)	SO_2 (vppm)	NO_x (vppm)	PM (g/m^3)	Exhaust temp. K	Exhaust flow-rate m^3/h
Passenger car	150-1500	20-400	10-150	50-1400	0.01-0.1	373-635	40-50
Heavy- duty truck	nq.	nq.	nq.	50-1600	0.05-0.25	373-723	15-125

nq = not quoted

Environmental and health effect of diesel particulate emissions

Particulate matter from diesel engine emitted directly to the air is an origin of air pollution. Together with bio-mass combustion, fuel combustion contributes to the high level of soot particles in the lower troposphere [12]. In the urban area, where exposure to diesel exhaust may be especially high, diesel engine can be a dominant source of particulate matter [13]. The presence of soot as air pollutant has serious consequences for the human health. In general, particles inhaled by humans are segregated by size during deposition within the respiratory system [14,15]. Diesel particulate matter smaller than 10 µm, PM10, not only penetrates deeper and remains longer in the lungs than larger particles, but also contains a quantity of organic materials that might have significant long-term health effects.

The growing awareness of the effects of pollutants on the environment and human health has made the legislation on the emission of, among others, diesel-powered vehicles more and more stringent. The authorities have formulated regulations for diesel exhaust emissions worldwide. Since 1986 in Japan, since 1987 in California USA, and since 1992 in Europe, diesel engine emissions have to comply with the emission standards. Complete and updated emissions standards for all types of diesel engine can be found, for example in [16,17]. In Figure 2 the European PM and NO_x standards for passenger car are given.

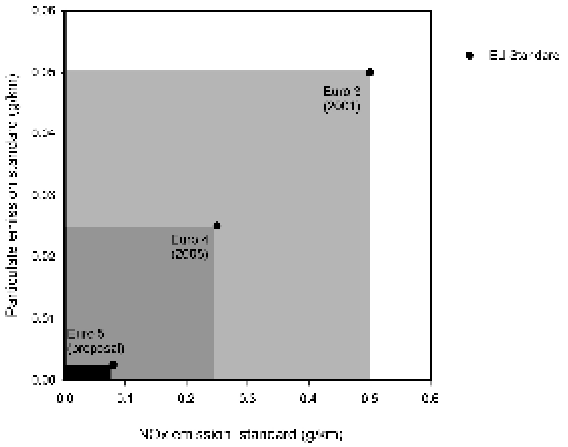


Figure 2. Diesel emission standards for passenger car.

B. Diesel Emission Control Strategy

Engine adjustment and fuel reformulation have greatly contributed to the reduction of PM emission. It is, however, anticipated that particulate reduction via engine modification and fuel reformulation will not meet to the future standards. Diesel engines with exhaust after-treatment seem to be a standard feature of future diesel exhaust. In the early 1980s, great advances were made with diesel particle-trapping techniques. The wall-flow monolith was developed and it was found that particulate emissions could be controlled without having to make engine adjustments. The introduction of wall-flow monolith filter has been proven capable to reduce diesel particulate mass emission up to 98% [18]. Accumulation of particulate matter in the filter will create back pressure and has to be regenerated (combusted). The regeneration can be achieved by active or passive regeneration. Additional control strategy by using a device in the exhaust line (exhaust after-treatment) completes the control strategies.

The main part of diesel PM regeneration is the oxidation of the solid carbonaceous particles, the soot. In an active regeneration system, a monitor system to observe the pressure build-up in the trap due to the deposited soot in combination with a trigger system to execute specific action to regenerate the filter has to be installed. A variety of specific action has been studied, for example a post fuel injection, electric heater, and microwave regeneration [19,20]. In passive regeneration, exhaust conditions of normal vehicle operation are utilised to keep the system in function. However, the reactivity of the trapped soot under observed exhaust conditions is rather low. A temperature over 775 K is generally required to oxidise the soot to CO_2. Unfortunately, the average exhaust temperature is not high enough for the oxidation of soot. Catalytic diesel soot oxidation is believed to be a solution. Furthermore, complexities associated with catalytic soot oxidation are high. In the following section, various catalytic systems developed for the oxidation of soot will be discussed.

Catalysts for the oxidation of diesel soot

In the last two decades, a number of materials have been explored as catalysts for diesel soot oxidation. The fact that in diesel exhaust O_2 is available excessively (4-10%), has influenced the development of catalyst for the oxidation of soot. The exploration for the catalyst was initially focussed on the direct contact between catalyst and soot in order to decrease the C-O_2 reaction temperature, which is generally, as mentioned before, above 775 K for the non-catalytic soot oxidation. Furthermore, the catalytic oxidation of soot is slow, since the solid soot particles are large and, when deposited, immobile. They cannot penetrate into the catalyst's micropores or mesopores where catalytic processes usually take place. Soot oxidation takes place only on the filter walls of the particle filter where the catalyst has been deposited.

Direct contact oxidation catalysts

The development of a direct contact soot-oxidation catalyst is problematic, since it is difficult to realise a direct contact with the solid soot. Inui and Otowa [21] and Löwe and Mendoza-Frohn [22] were among the first to realise that the contact of deposited soot on a catalytic filter is poor. Neeft et al. [23,24] systematically investigated the effect oft the degree of physical contact has on catalytic soot combustion. They mixed soot and catalyst powders with a spatula and defined that as loose contact; they did the same with a mechanical mill and defined that as tight contact; they filtered diesel soot from an exhaust stream on a bed of catalyst particles and defined that as in-situ contact. Combustion temperature differences as large as 200 K can be found between loose and tight contact samples of one catalyst. It is clear that Neeft et al. measured apparent activities that were a function of the intrinsic activity and the degree of physical interaction. They found that with the in-situ samples, the combustion temperatures were similar to the combustion temperatures of the loose contact samples and concluded that the contact that arises during practical conditions is similar to loose contact (Figure 3).

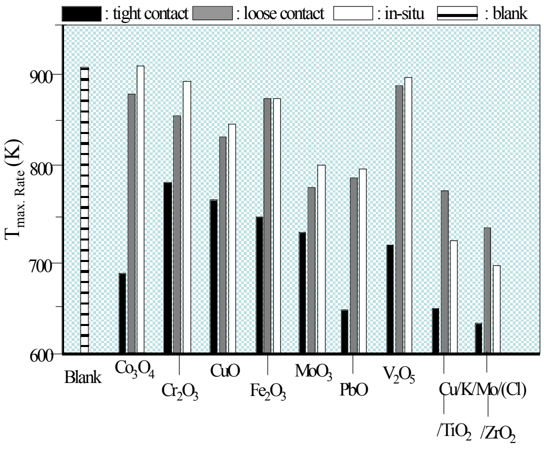


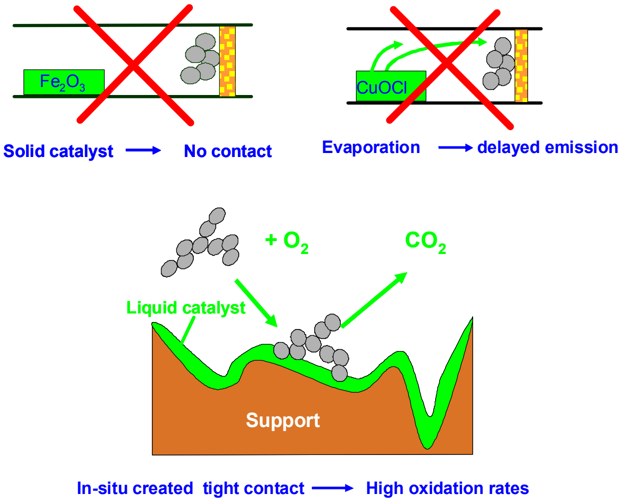
Figure 3. Comparison between combustion temperature of soot collected on catalyst powder (in-situ) and tight and loose contact combustion temperature.

This is, of course, unfortunate. Various reasons exist why tight contact mixtures are more reactive: (1) the catalyst will have more contact points with the soot; (2) the catalyst particles will be smaller and better dispersed; and (3) Mul et al. [25] found that the type of contact controls the mechanism that is occurring. They found that for V_2O_5 and MoO_3 a redox and spillover mechanism occurs simultaneously in tight contact and discussed that in loose contact, only the spillover mechanism will occur. They expected that for soot oxidation in a catalytic filter, oxygen spillover would be the predominant mechanism.

Ahlström and Odenbrand [26] and Moulijn and co-workers [27–30] reported mobile catalysts that did not evaporate during soot oxidation. This type of liquid contact occurs in both laboratory test and pilot plant scale. These types of mobile materials, like $Cs_2SO_4.V_2O_5$ (melting point of 647 K), $CsVO_3.MoO_3$ (melting point of 650 K) and KCl-KVO_3 (melting point of 760 K), demonstrate high activity in the oxidation of soot [27-30]. The activity is thought to be due to the in-situ tight contact between soot and catalyst in its molten state. However, the stability of this type of liquid catalyst might be too low under severe exhaust conditions. Figure 4 shows the different types of contact, namely the solid catalyst, the mobile catalyst and the liquid catalyst are presented.

A good way of improving the quality of induced self-supporting regeneration of a particle filter is by increasing the reactivity of the soot with a built-in metal catalyst. The catalyst can be incorporated during the soot-formation process. Blending a stable organo-metallic additive into the fuel (typically 10–100 ppm) is the most convenient method. These catalytic fuel additives are also known as fuel-borne catalysts, and the type of regeneration as quasi-continuous regeneration [31].

Catalytic fuel additives have often been investigated for passive regeneration. During passive regeneration, a trap regenerates itself, without the intervention of on-board diagnostic and control systems. Passive regeneration is often a continuous process, because of which, it is sometimes referred to as continuous regeneration. During continuous passive regeneration, catalytic fuel additives bring the rate of soot oxidation in equilibrium with the rate of soot deposition, which causes a constant pressure drop over the filter defined as the balance temperature. Lepperhoff et al. [31] compared cerium, iron, and copper additives. They found the lowest balance temperatures for iron and copper, which were 625 K. Jelles et al. [32] measured balance temperatures for different mixed additives to discover whether synergetic effects could play a role. They found that after some time of running on low-concentration fuel additive combinations, there was a dramatic reduction in balance temperature reduction. The reduced balance temperature was explained as follows. Platinum, which was deposited on the monolith, catalyses the oxidation of NO to NO_2. NO_2 subsequently reacted with the fuel-additive-catalysed soot. The enhanced activity was explained by assuming that each NO_x molecule is used many times, as is illustrated in Figure 5.



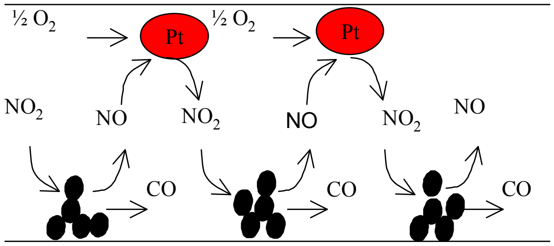


Figure 4.Types of catalyst-soot contact, namely the solid catalyst, the mobile catalyst and the liquid catalyst.

Figure 5.The multi cycle reaction of NO to NO_2 by platinum catalyst following soot oxidation by NO_2.

In the early 2000, PSA Peugeot Citroën introduced a particulate filter system on passenger car where an integrated fuel additive system is applied [33]. Now more than 500.000 units are in the market. Their particulate filter system (see Figure 6) includes:

1. A filter medium made of silicon carbide with temperature and pressure sensors.
2 An integrated fuel additive system that injects the required quantities of the cerium based catalyst (Eolys™ from Rhodia Terres Rares) whenever the fuel tank is refilled.
3 Common-rail HDi engine monitoring and control software to control filter

regeneration and self-diagnosis of the filter.

4 An integrated fuel additive system that injects the required quantities of the cerium based catalyst (Eolys™ from Rhodia Terres Rares) whenever the fuel tank is refilled.

5. Common-rail HDi engine monitoring and control software to control filter regeneration and self-diagnosis of the filter

The pressure sensor monitors filter clogging, and the engine computer initiates the regeneration when necessary. The regeneration involves post-combustion that raises the exhaust fumes to 725 K at the filter inlet. A complete regeneration requires only 2 to 3 minutes and is performed every 400 to 500 km without the driver noticing. The cerium-based catalyst additive is dissolved in a solution of 5 g cerium per 100 ml. It is injected into the fuel tank to give the diesel a content of cerium of approximately 25 ppm by weight. In Figure 6 the outline of the PSA system is given.

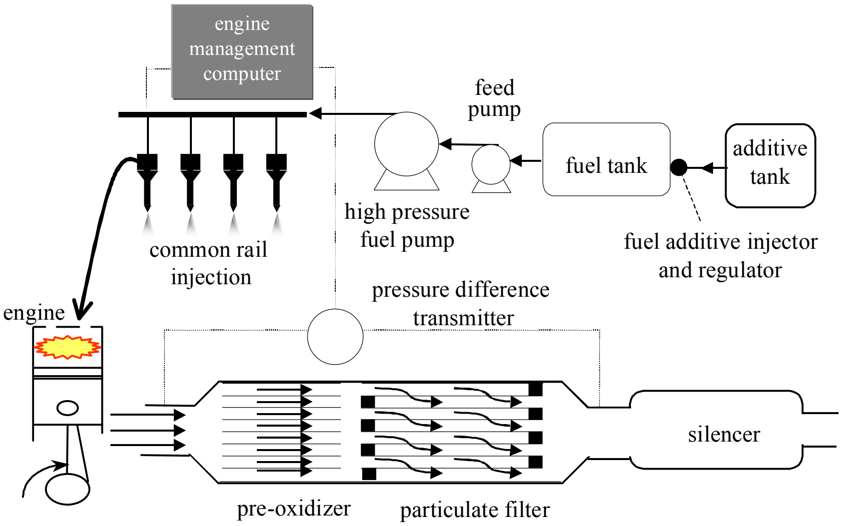


Figure 6. Schematic representation of PSA Peugeot Citroën system

Indirect Contact Catalysts

Some catalysts can oxidise soot without having intimate physical contact. They catalyse the formation of a mobile compound (NO_2, O_{ads}, etc.) that is more reactive than O_2. In the absence of physical contact, the formation of those mobile species is the main advantageous property of this type of catalyst. For indirect contact catalysts, two main reaction mechanisms are known; NO_x-aided gas-phase mechanism and spill-over mechanism.

Cooper and Thoss [34] discovered a way of using gas-phase NO_2 as an activated mobile species for soot oxidation (NO_x-aided gas-phase mechanism). The reaction of NO_2 with carbon material was published as early as 1956 [35]. They proposed that NO_2 accelerates soot combustion:

$$NO + \frac{1}{2}O_2 \xrightarrow{Pt} NO_2 \qquad (1)$$

$$NO_2 + C \rightarrow CO + NO \qquad (2)$$

$$NO_2 + CO \rightarrow CO + NO \qquad (3)$$

Some catalysts can dissociate oxygen and transfer it to the soot particle, where it reacts as it was in a non-catalytic reaction. This mechanism is known as the spill-over mechanism. Some examples exist that show that contact is not prerequisite in this reaction type. For instance, Baumgarten and Schuck [36] showed that the rate of catalytic coke oxidation can be accelerated while there is no direct contact between the catalyst and the coke, which they explained by oxygen spill-over. Baker and Chludzinksi [37] showed that Cr_2O_3 could accelerate edge recession of graphite while being motionless. Mul et al. [25] showed with a labelled oxygen study that spill-over and redox oxidation can occur simultaneously. They discussed that the dominating mechanism will depend on the degree of physical contact between the catalyst and the soot.

Continuously regenerated trap

The NO_x-aided continuously regenerated trap (NO_x-aided CRT) for trucks and buses was developed by Cooper and Thoss [34]. It consists of a wall-flow monolith with an upstream flow-through diesel oxidation catalyst, which is called, in this context, the pre-oxidiser. Figure 7 provides a schematic representation of the system. The oxidation catalyst converts 90% of the CO and hydrocarbons present to CO_2, and 20–50% of the NO to NO_2 [38]. Downstream, the particles are trapped on a cordierite wall-flow monolith and, subsequently, oxidised by the NO_2.

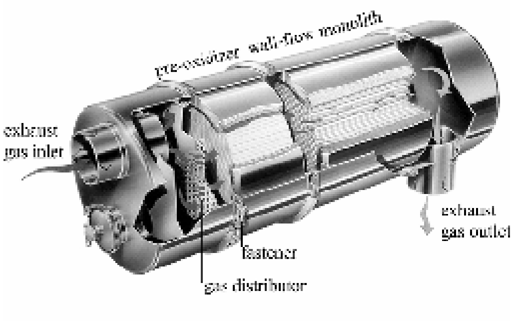


Figure 7. Illustration of the Continuously Regenerating Trapp (CRT) system and its reaction. Picture is a courtesy of Johnson Matthey.

The modular design of the separated and detachable pre-oxidiser and filter facilitates a high flexibility of the system, which is a great advantage for retrofitting of different buses and trucks. In each case, the optimal trap and pre-oxidiser can be chosen, which can, in many cases, save space, heat loss, back-pressure, and system costs.

The filter should produce a surplus of NO_2 in order to compensate for time intervals in which the temperature is too low for regeneration. The surplus NO_2 should not be too high because NO_2 is foul smelling in the vicinity of the vehicle, where it has not yet been diluted sufficiently with ambient air. For the environment, compared with NO, NO_2 gives no additional problems, because NO reacts to NO_2 anyway in short time scales [38].

The NO_x-aided CRT system is an effective catalytic filter that oxidises all carbon components in diesel exhaust gas, including small particles, and unregulated compounds, and it reduces the NO_x concentration by 3–8% [68]. It is a simple concept that allows for fit-and-forget usage. The temperature window of 475–725 K [39] is reasonable; 475 K is needed for CO and hydrocarbon oxidation [39], whereas 725 K relates to the chemical equilibrium between NO and NO_2, which is not favourable above 725 K. The balance temperature is actually higher than 600 K and depends on the fuel sulfur level. The temperature in the filter should be higher than 600 K for at least 40% of the time for effective filter regeneration. Because of continuous regeneration, extreme temperatures are avoided, which enhances stability; a atisfactory performance during 600,000 km [39] has been reported.

Since the system depends on NO_x, it will be uncertain if the required NO_x-to-soot ratio for successful regeneration will be met in future engines. Options to be less depended on NO_x engine out could be found by the multi-usage's of the available NO_x. Therefore, a study to optimise the oxidation of NO to NO_2 and the oxidation of soot is very important. Coating the filter section with platinum in order to re-oxidise NO produced from reaction (2) and (3) is the latest effort to optimise the system [40]. In a suitable catalytic filter, such as Pt-ceramic foam, a recycle reaction of NO oxidation to NO_2, carbon oxidation and 're-oxidation' of NO can be observed [41,42].

Diesel Particulate NO_x Reduction (DPNR) system

Recent development of the researchers at Toyota Motors is the application of spill-over catalysts [43]. On diesel soot filtration surface areas a layer of an 'active oxygen' storage metal oxide is deposited. On this layer platinum is dispersed. The 'active oxygen' is created by the conversion of gas-phase NO over the platinum into surface nitrate species. These surface nitrates will be decomposed at the interface between the soot and the active oxygen layer into very reactive adsorbed oxygen atom and NO. The NO can be re-oxidised once more to surface nitrate and the adsorbed oxygen atom is able to oxidise the deposited soot. This active oxygen is able to oxidise soot at 575 K and higher. Similar observation has been reported in a laboratory experiments [44]. The active oxygen storage material acts at the same time as a NO_x-trap. When all the soot has been oxidised the active oxygen storage material is fully converted into nitrates. CO and HC's decompose these nitrates into nitrogen. These CO and HC's are generated by running the engine rich or by additional fuel and the introduced or generated CO and HC's will be converted into CO_2 by the surface nitrates and the nitrates mainly to N_2 and to some extent also NO. In other words this type soot oxidation trap act as a soot abatement technology, but at the same time it acts as a NO_x abatement technology. The trade name of the Toyota system is DPNR and stands for diesel particulate and NO_x reduction. Simultaneously the two main pollutants of a diesel engine (soot and NO_x) are reduced.

In figure 8 the different steps of the Toyota system are illustrated. Table 3 will summarise the different diesel soot oxidation technologies.

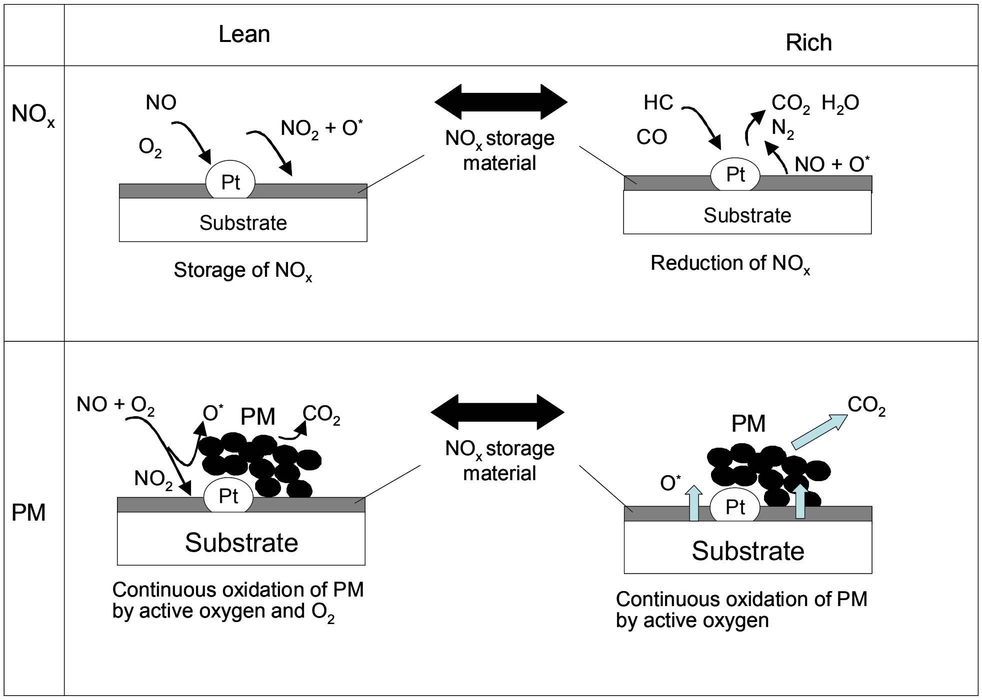


Figure 8. PM and NO reduction in DPNR system

Table 3. Classification of diesel soot oxidation catalysts

Catalyst type/Chemical process	Examples	Remarks
(1) Metal oxide catalyst;	PbO, V_2O_5, CeO_2, Ref: [21-24]	Focussed on C-O_2 based reaction Catalyst soot contact is essential; only a tight contact encounter low (625 K) oxidation temperature No application reported
(2) Catalysis by mobile material	Molten salt: $Cs_2SO_4.V_2O_5$, $Cs_2O.V_2O_5$ Volatile material: Cu/K/V/Cl, Ref: [25-32]	Based on C-O_2 reaction Establish in-situ tight contact through soot wetting by the catalyst Hydrothermal stability is low
(3) Fuel-borne catalyst	CeO_2, Pt/CeO_2, Ref: [31-32] PSA-Peugeot system Ref: [33]	Based on both C-O_2 and C-NO_2 reaction Generates fine particle Requires DPF
(4) NO_x-assisted soot oxidation	CRT system, Ref: [35-37]	Based on C- NO_2 reaction Uses Pt catalyst to generate NO_2 Operates properly in low sulphur fuel Might be threatened by the trend of lower engine out NO_x
(5) 'Active oxygen' catalyst	Toyota DPNR system	

C. Challenging topics in of diesel PM catalysis

For diesel catalytic filter relying on NO_2-soot reaction, efforts to improve the performance of catalytic system is mainly focussed on the optimisation of engine out NO_x. This caused by improvement in engine technology that tend to decrease engine out NO_x. The efforts include both filter design and type of catalyst catalysts. Further research on the use of ceramic foam, instead of flow-through monolith, as Pt catalyst support might be a future interesting topic. Combining Pt catalyst with, for example cerium could also lead to the improvement of catalytic filter performance. As has been mentioned, cerium based catalyst could increase the oxidation rate by providing additional active species, so-called active oxygen [43,44]

In view of catalyst stability and type of metals, sulphur poisoning and the use of non noble metals have become the stressing points. In countries where diesel fuel sulphur content is quite high, available technologies are threatened by sulphur poisoning. So, research to increase catalytic system stability will be an interesting one. Furthermore, the use of non noble metal catalyst is another interesting topic to solve the shortage and high price of noble metal catalyst.

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