

NO₂ Reduction, Passive and Active Soot Regeneration Performance of a Palladium-Base Metal Coating on Sic Filters

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ABSTRACT

Silicon carbide diesel particulate filter (DPF) is now recognized as the most effective and robust way to reduce not only the mass but also the number of emitted particles on diesel passenger cars. Widespread use of expensive catalytic platinum containing coatings has contributed to increased harmful NO₂ emissions.

A novel low cost palladium-base metal coating, BMC-211, was developed which assists soot regeneration by oxygen transport and which actively removes NO₂ still having comparable passive and active soot regeneration properties. The novel coating was tested against a traditional commercial platinum coating on a modern series produced car, on chassis dynamometer and on engine test bench. The test results obtained demonstrate that palladium-base metal coating has significantly lower NO₂ emission during NEDC tests compared to traditional Pt-coating, both for fresh and aged samples, and showed at least the same performance concerning passive regeneration, forced regeneration, pressure drop, regulated NEDC emissions and secondary emissions. The silicon carbide filter material is not mechanically affected by the coating.

INTRODUCTION

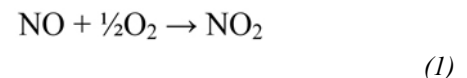
PRESENT TECHNOLOGY STATUS

Diesel engines are recognized as energy efficient for passenger cars but have inherent particulate matter emission problems. The particulate matter emission has been solved by

the implementation of silicon carbide wall flow filters, but increased emission of NO₂ and the high usage of expensive precious metals have required further improvements. NO₂ is toxic [1] and air quality limits proposed by EU are exceeded in many cities in Europe. The present technology is to a great extent based on exhaust system configurations as:

Engine→DOC→cDPF→Exhaust

where DOC is a diesel oxidation catalyst and cDPF is a catalyzed diesel particulate filter. The present use of both platinum containing DOC and cDPF has contributed to the increased emission of NO₂ into ambient air. Over platinum catalysts, NO from the engine is converted to NO₂ by reaction (1)



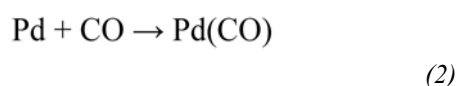
The generated NO₂ over the platinum catalysts has partly been used for passive PM regeneration of the c-DPF. However, due to the difficult management of the NO₂:PM ratio, a large part of the generated NO₂ will always be emitted from the vehicle.

LOW NO₂ FILTER CATALYSTS

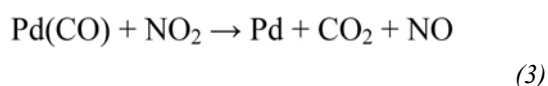
In order to reduce the NO₂ formation on the filter and actively remove the surplus of NO₂ on the filter, a novel palladium-base metal oxide filter coating was developed and tested in engine bench and demonstration taxis [1] and [2]. Palladium has, in contrast to platinum, a low tendency to

form NO₂ according to the reaction scheme (1). The passive PM regeneration by NO₂ can to a high degree be substituted by soot combustion on base metal oxides. It is known that oxygen stored in the lattice of base metal oxides directly oxidizes soot [3] and, in a recently published environmental TEM study [4], it is shown how soot particles are transported to contact the lattice of model base metal oxide for oxidation. The above knowledge was used in the development of novel palladium-base metal catalyst filter coating that actively reduces NO₂ [1], [2] and [4]. The mechanism for the NO₂ reduction requires both the presence of base metal oxide and palladium:

CO formed from soot or hydrocarbon oxidation is adsorbed on palladium



with a subsequent oxidation by present NO₂



The NO₂ reduction performance of the BMC catalytic formulation has in all studies been proved to be robust to high temperature and is in this study compared with a traditional Reference Pt filter coating, concerning active and passive regeneration - and emissions.

ADVANCED SIC FILTER MATERIALS

Silicon carbide diesel particulate filter (DPF) is now recognized as the most effective and robust way to reduce not only the mass but also the number of emitted particles on diesel passenger cars [5]. Saint-Gobain recrystallized silicon carbide (RSiC) filters have an assembled design as shown in Figure 1. Single segments are extruded with wavy cell geometry [6]. The standard Saint-Gobain material has a microstructure with 47% porosity and a mean pore size of 15 µm.



Figure 1. Saint-Gobain Assembled RSiC Filter (144 mm outer diameter)

Recrystallized silicon carbide filter is a fuel economy optimised technology: benefits of the material (porosity, thermo-mechanical properties and robustness) offer reduced fuel penalty from low backpressure, high soot loading operability, and increased regeneration interval. RSiC filters used for this study are specifically designed for washcoat accommodation with a minimal impact on backpressure.

EXPERIMENTAL

CATALYZED FILTERS

Samples of commercial Saint-Gobain SG3 silicon carbide wall flow filters with 180 cells/inch², 350 µm wall thickness and geometric dimensions (given as diameter × length) of 144 mm × 254mm (4.1 l) were used for the experiments and validation.

The filter samples were coated with 40 g/l of the novel base metal-palladium catalytic coating according to a patent application [7] and canned in a test car with OEM spare parts. The palladium content of the coating was 1.1 g/l Pd. This catalytic coating is referred to as BMC-211.

The platinum containing filter reference samples with the same dimensions as given above were supplied canned with the new OEM test car and as OEM spare parts for the car model. The Reference coating contains both platinum and palladium close to the same overall precious metal level as above.

For accurate measurements of filter inlet/outlet temperatures and filter pressure drop as a function of time during soot loading, forced regeneration and NEDC tests, the canned filters were additionally equipped with inlet and outlet thermal and pressure sensors.

Aged filter samples of the two above formulations (Reference and BMC-211) were also tested, since ageing may influence

their performance. In order to secure the exact same ageing conditions on Pt-Reference coating and BMC-211 coating and to save project time, a severe hydrothermal off-line accepted ageing procedure was chosen according to the literature [8]:

16 hrs at 790°C in air with 10% v/v water vapour

COLD FLOW BACKPRESSURE MEASUREMENT

Backpressure measurement was carried out on specific Superflow™ test rig at 300 and 600m³/hr air flow (room temperature and atmospheric pressure air intake).

ENGINE BENCH TESTING

Soot loading slope

The tests were performed on a commercial 2.0-liter 103 kW, common rail injection, turbocharged diesel engine. The engine is equipped with a post injection system to increase exhaust gas temperature during the regeneration phase. A Diesel Oxidation Catalyst (DOC) is placed just in front of the DPF which is located in an under-floor position at about one meter downstream of the turbocharger.

Prior to starting any tests, each new filter was canned and stabilized. This stabilization was performed on the engine bench at 4000 RPM and under full load conditions, for 30 minutes, in order for the temperature within the filter to be higher than 640°C (no post injection needed for this step). Then, the filter was loaded with soot under steady-state conditions (3000 RPM, 25 Nm). The loading time depends on the desired amount of soot, which is checked by weighing the filter at 150°C before and after soot loading. Backpressure is recorded during the loading step; final filter soot loading is checked from the loaded filter mass. The backpressure curve versus soot loading is reported as soot loading slope.

SiC filter robustness

The severe regeneration test, intended to create a strong thermal field with high temperatures and temperature gradients, consists in a drop to idle step [9] as soon as the soot combustion starts. The protocol used is divided into two main phases:

- Start of regeneration by post injection at 1700 RPM 95 Nm. The temperature in front of the DPF is about 640°C. As soon as the filter pressure drop starts to decrease, the engine is switched to idle.
- Idle phase to strengthen soot combustion. Thermocouples (type K, 0.5 mm diameter) are placed inside the DPF to measure temperatures and gradients (Figure 2).

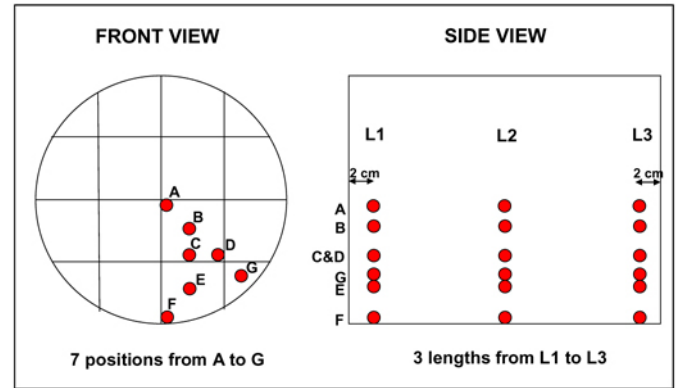


Figure 2. Thermocouples position during regeneration

The filter damage is then characterized by:

- Maximum temperature level / temperature gradient: From the thermocouple mapping of the filter, maximum temperature level and temperature gradient between individual thermocouples are recorded during regeneration.
- Ultrasonic (US) measurement: the duration for US signal to come through the filter, along longitudinal direction is measured before and after severe regeneration. The ratio called “US attenuation”, defined as “US transfer time on new filter” divided by “US transfer time on damaged filter” quantifies the filter's damage. Increase in the duration for US signal to come through the filter length, allows the number of cracks to be followed [10]. The reported results presented are the average of measurements for positions 1 to 4 (Figure 3).

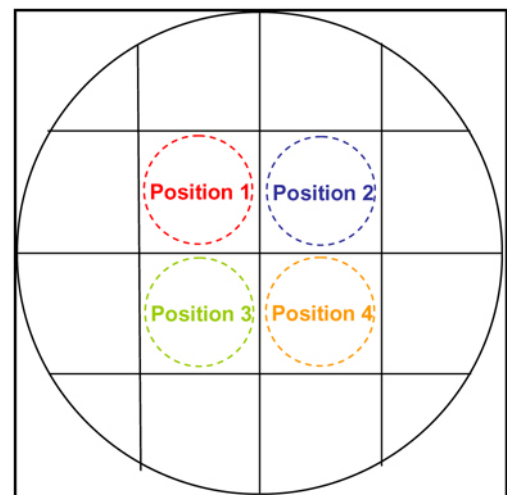


Figure 3. Positions of ultra sonic sensor

Passive soot regeneration

Passive soot regeneration was tested at a soot level of approximately 3 g/l soot as this level is considered to be the average working soot loading for a filter in application.

Like for former tests, filters are loaded with soot on engine test bench using steady state operating procedure (3000 RPM - 25Nm), up to the desired soot loading (3 g/l). The filter is initially weighed to determine precisely the soot loading before regeneration. Passive regeneration is performed on engine test bench, while operating the engine at 3000 RPM - 132 Nm during 30 minutes. Remaining soot loading on the filter is estimated by weighing of the filter at 150°C. Passive regeneration yield is determined from the decrease in soot loading before/after regeneration. Under these passive regeneration conditions, inlet temperature is at 400°C (Figure 4) and inlet NO₂ content of the exhaust gas is 200ppm with a total of 650ppm NO_x content.

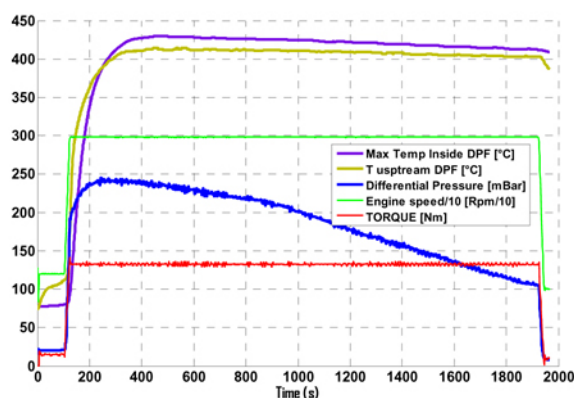


Figure 4. Passive regeneration profile: engine setting, backpressure and temperature evolution

MODERN TEST CAR

For the vehicle comparative catalyst tests, a recently introduced model of a popular mid-size diesel Euro 4 car with cDPF as standard was selected: Ford Mondeo 2.0 l Duratorq TDCi Estate 96 kW (131 HP). The cDPF in the modern test car is a part of an exhaust system schematically built in the following way:

Engine(HC_{inj})→DOC→cDPF→exhaust out

where (HC_{inj}) symbolizes optional post injection of diesel fuel for temperature increase over the DOC for forced soot regeneration. The cDPF is placed underfloor in this model, which facilitated mounting and dismounting of filter samples (weighing) for the test program; the same DOC is still kept for all comparative experiments.

ACTIVE SOOT REGENERATION

The filter was weighed and loaded with soot at constant engine regime of 3000 RPM in second gear with the accelerator locked in position and weighed again after cooling. The soot mass loading was correlated to pressure drop. Typically nine hours were needed to fill the filter with 32 to 35 g of soot.

The forced regeneration was performed with the car in the chassis dynamometer site. When the desired filter soot load of approximately 8 g/l was confirmed by weighing, the filter was remounted. The engine is warmed up at 3000 RPM. A portable computer with Ford Mondeo maintenance software was connected to the diagnostic socket of the car. The software option “forced regeneration with zero car velocity” was selected. The software starts a sequence lasting 1012 seconds, where the engine is running at 2900 RPM and the filter inlet temperature is raised to minimum 650°C. During forced regeneration, temperature at filter inlet and filter outlet, exhaust temperatures and pressure drop were measured as a function of time. Furthermore, secondary emissions together with O₂ and CO₂ were measured online.

NO₂ AND REGULATED NEDC EMISSIONS

For standard NEDC tests, a chassis dynamometer emission setup with constant volume sampling system at the Department of Mechanical Engineering, the Technical University of Denmark, was used.

Before the NEDC tests, the filter was first cleaned by a forced regeneration as described above and then filled to 3 - 4 g soot/l according to the standard filling procedure.

Regulated gaseous emissions were measured using a Cussons Analysis Bench consisting of a Model 3000 HC analyzer (HFID), a Series 4000 (LumiNOX) NO_x analyzer (CLA), CO and CO₂ analyzers (NDIR) and an oxygen analyzer. Particulate Matter was determined gravimetrically on Palflex quartz fibre filter.

Only NO_x, calculated as NO₂ (molecular weight 46), is determined according to the regulation. In order to determine the NO₂ emission, the NO content in the sample bags was also determined and NO emission in g/km was calculated (as NO, molecular weight 30). The NO₂ emission [g/km] was determined as the difference between NO_x and NO*46/30.

The gas composition in the sample bags was not at equilibrium. Thus, over relatively short time (<30 min) the ratio NO to NO₂ changed because of the high O₂ content (19-20% in the diluted exhaust gas). Increasing concentrations of NO₂ and simultaneous decreasing NO were observed in more than one test, stressing the importance of measuring the gas composition immediately after the end of the NEDC test. The time-resolved NO and NO₂ analysis was checked by direct FTIR analysis in some cases.

SECONDARY EMISSIONS

Modal online gas analyses were performed for forced regeneration and NEDC tests. During forced regenerations,