

Experimental Study of Thermal Aging on Catalytic Diesel Particulate Filter Performance

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ABSTRACT

In this paper, a methodology is presented to study the influence of thermal aging on catalytic DPF performance using small scale coated filter samples and side-stream reactor technology. Different mixed oxide catalytic coating families are examined under realistic engine exhaust conditions and under fresh and thermally aged state.

This methodology involves the determination of filter physical (flow resistance under clean and soot loaded conditions and filtration efficiency) and chemical properties (reactivity of catalytic coating towards direct soot oxidation). Thermal aging led to sintering of catalytic nanoparticles and to changes in the structure of the catalytic layer affecting negatively the filter wall permeability, the clean filtration efficiency and the pressure drop behavior during soot loading. It also affected negatively the catalytic soot oxidation activity of the catalyzed samples. Based on the characterization results, feedback to the catalyst synthesis process can be provided and improved aging-tolerant catalytic formulations can be developed that exhibit minimal degradation after thermal aging. A set of relevant physicochemical properties of the fresh and aged DPFs is derived by analyzing mathematically the results permitting the extrapolation of this study to larger filter systems.

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INTRODUCTION

Diesel Particulate Filters (DPFs) constitute the most frequently selected technology for the abatement of particle emissions from Diesel engines. Furthermore Catalytic DPFs (CDPFs), which promote soot oxidation at lower temperatures [1, 2] are widely used nowadays. Therefore, the automotive industry is ever more interested towards the development of CDPFs that can be applied for the collection of soot particles and their direct oxidation at the conditions that are prevalent at the exhaust. Some of the most popular candidates for direct catalytic soot oxidation on CDPFs are metal oxide catalysts. Direct catalytic oxidation of soot in CDPFs is a complex process which can be described by a set of oxidation mechanisms mentioned in the past [1, 3, 4]. The oxidation of soot in CDPFs is affected by two main aspects, the catalyst chemistry and the structural distribution of the catalyst on the substrate. Direct catalytic soot oxidation requires soot-catalyst proximity, a fact that has been known for almost half a century [5]. The spatial distribution of the

catalyst along the filter wall affects the deep-bed filtration characteristics of the catalyzed filter which determine the degree of the contact between soot and catalytic active sites. Two other very important factors that can improve contact probability between soot and catalyst are also the filtration area of the DPF and the amount of catalyst located at the surface of the filter [6].

An important issue that affects the performance of a CDPF is its deterioration rate through time. Catalyst performance decreases over the CDPF lifetime but still compliance with emission regulations has to be ensured. The overall aging of a CDPF is a combination of deactivation mechanisms such as chemical, mechanical and thermal aging. Chemical aging occurs when inorganic ash particles, deriving mostly from lubrication oil consumption and engine wear, poison the catalyst or accumulate in the CDPF deactivating its catalytic sites and plugging its channels. Mechanical aging occurs due to engine exhaust vibration and catalyst abrasion [7, 8]. The ash aging effect on CDPFs has been extensively studied by the authors in [9] and a fast ash aging technique

has been developed that highly resembles field aging. According to the authors' experience, mechanical aging is of lesser importance in modern systems with high quality insulation and exhaust support systems.

In the case of thermal aging, the majority of published work has been conducted on precious metal catalysts [10,11,12,13,14,15]. Few studies exist on base metal catalyst CDPFs, such as in [16] where the focus is on non-road applications. Moreover, most thermal aging studies concern field or engine bench testing (with or without auxiliary exhaust heaters) of full-scale systems, a fact that can add significant delays and cost in catalyzed filters development. The application of base metal catalysts requires considerable effort in the optimisation of the catalyst formulation with the employment of the appropriate dopants as well as the proper tuning of the coating technique. To overcome this, in the present paper, a methodology for the evaluation of the aging effect is presented which builds on previous experience [17] in screening catalyzed DPFs based on small-scale (core samples) CDPF evaluation. Such core samples based evaluation has been used in a limited number of cases in the literature, as in [8], but for CDPFs with noble metal catalysts.

Thermal aging of the CDPFs, i.e. the exposure of the filters to high temperatures which may appear in the exhaust, has as a result the deterioration of CDPF performance mainly due to sintering of catalyst particles, and due to changes in the structure of the catalytic layer, including possible interactions of the catalyst particles with the porous substrate.

Current DPF substrate materials such as SiC do not demonstrate material or structural changes under realistic exhaust conditions up to 800 °C [18, 19, 20] unless high temperature gradients occur. Therefore exposure of such systems in thermal aging temperatures of about 800 °C does not result in any significant changes in the uncoated DPF performance (pressure drop, filtration efficiency).

Sintering effects on the catalyst particles increase exponentially with higher temperature and exposure time [21, 22] resulting in the loss of surface area and, eventually, loss of catalytic activity. Large scale morphological changes in the catalyst layer affect CDPF filtration efficiency and pressure drop behavior under normal operation as well as catalytic soot oxidation activity.

In the current paper, to simulate the thermal aging of the CDPF the filters tested were placed in an oven at 800°C for 16 hours. Purely thermal oven aging procedures have similar results as vehicle and test bench aging as demonstrated in [7] where many full-scale catalyzed systems have been tested. Of course, purely thermal aging cannot account for catalyst poisoning from ash particles coming from oil and fuel constituents and engine wear. In this case ash aging techniques have to be employed in addition.

The specific evaluation methodology employs small-scale samples differentiating from full-scale sample testing which is time and cost intensive and does not allow the straightforward extraction of factors such as the filter permeability, filtration efficiency and soot oxidation kinetic

parameters. The specific methodology was employed to evaluate the thermal aging effect on filters coated with different catalyst amounts and formulations. The same methodology can be applied for the evaluation of every kind of aging effect for example ash aging and/or hydrothermal aging. Small scale monolithic SiC wall-flow filters were coated with mixed metal oxides and were tested with respect to their permeability, filtration efficiency, soot loading, and regeneration as fresh and aged filters. The geometric configuration and the characteristics of the filters were kept constant in order to study the effects of different catalyst loadings and catalyst formulations on the filter, as well as the effect of thermal aging. Finally, an analysis of the soot oxidation rates in CDPFs was conducted for the investigation of the kinetic parameters for the case of the fresh and aged filters, by employing an extension of the Two-Layer model, a mathematical model of incomplete soot-catalyst contact [23, 24].

EXPERIMENTAL

Materials and Methods

In the current work the samples that were employed were 300 cpsi wall-flow rectangular SiC monoliths with dimensions 34×34×50mm (total volume: 57.8 cm³), nominal pore size of 11 μm, a nominal porosity of 42% and ca 0.06 m² available filtration area. The catalysts that were deposited on the monoliths were Cerium based Mixed Metal Oxides and Cerium-Zirconium based Mixed Metal Oxides that will hereafter be named MOC1 and MOC2 respectively. The addition of Zr was based on the fact that in many cases Zr enhances the thermal stability of the catalytic structures. The technique employed for the deposition of the catalysts on the filters is referred to as Aerosol Based Deposition (ABD). In the ABD method, the synthesis and deposition of the catalyst particles on the filter is achieved in one step where a solution of the appropriate precursors is atomized into micron sized droplets that pass through a heated tubular reactor. The particles thus formed are in situ deposited on the filter substrate placed inside the heated zone of the reactor [2]. The method allows for the precise control of the catalyst amount.

Table 1. Summary of the catalyst coated filters

Catalyst type	Amount of catalyst coating (g/m ²)
MOC1	<i>x</i>
	2 <i>x</i>
	3 <i>x</i>
MOC2	<i>x</i>

The table summarizes all the samples that were evaluated and provides information on the catalytic coating, as well as the amount of catalyst deposited on the filter (determined by weighing the clean and loaded filters). The coated small-scale filters were subjected to a series of experiments evaluating

their physicochemical properties before and after the aging process.

Flow resistance measurements

For the evaluation of flow resistance, the coated filters were placed in a special pilot scale testing unit consisting of a mass flow controller, a specially manufactured filter holder a high precision pressure transducer and a thermocouple. The gas used was air at ambient temperature. Gas flow was varied corresponding to a varying filtration velocity of 0-4 cm/s. For each set of permeability measurement twenty experimental points (pressure drop versus flow) were collected. The small scale filter pressure drop measurements can be used for direct comparison as well as for evaluation of filter wall flow resistance via the use of linear regression model-based data reduction described in [25]. Identical procedures were applied to the fresh and thermally aged samples.

Filtration efficiency

The fresh and aged coated monoliths were evaluated with respect to their size specific clean filtration efficiency via an experimental setup employing side-stream Diesel engine exhaust. Particle size distributions were measured upstream and downstream of the filter with a TSI Scanning Mobility Particle Sizing (SMPS) system (consisting of a Differential Mobility Analyzer and a Condensation Particle Counter) connected to a multi-stage mini diluter. A part of the exhaust was drawn with the help of an injector to a two-stage mini dilution system. The exhaust of the second stage entered the sample and particles, which were not collected by the filter, were measured with the SMPS. The tests were performed at a filtration velocity of 1.5 cm/s.

Soot loading

The evaluation of the performance of the catalyst coated filters with respect to soot loading was performed in an in-house built, pilot scale filter testing unit that has been described in detail in previous works [1, 23, 24]. The monolithic filters were exposed to a side stream of the exhaust flow from a passenger car Diesel engine with a 1.9 L displacement operated at a steady state conditions (1500rpm, 3.1bar BMEP), coupled to a hydraulic bolt-on dynamometer. The testing unit sits on a bench that incorporates sampling pumps and ancillary controllers and transducers to maintain constant volume flow through the filter. The samples were enclosed in a cartridge with an oven around the cartridge allowing the precise control of its temperature. The filters were loaded with soot up to 2 g/m² (i.e. g of soot per m² of available filtration area, equivalent to 2.08 g/L) at 250 °C and at a filtration velocity of 1.4 cm/s.

Regeneration

The evaluation of the catalyst coated filters with respect to their soot oxidation activity, was performed by exposing the soot loaded filter samples to a constant flow synthetic exhaust (10% O₂ in N₂) and applying a temperature ramp from 200 to

700°C at a rate of 3 °C/min. Outflow CO and CO₂ concentrations were monitored during the temperature ramp to determine the soot oxidation rate and overall soot conversion.

Thermal aging

All of the aforementioned testing was employed for the evaluation of both the fresh catalyst coated filters as well as of the filters that were subjected to a thermal aging process. The thermal aging of the catalyst coated filters was conducted by placing them in an oven at 800°C for 16 hours under an atmosphere of 21% O₂ in N₂. It should be pointed out that initially, selected samples have been also subjected to hydrothermal aging. These samples have been placed in cartridges inside a furnace and exposed to air flow (2.2 NL/min) containing water (10 % v/v) at 800 °C for 16 hours. These samples demonstrated comparable results to the results from the purely thermally aged samples with respect to catalyst deactivation. Therefore, for simplicity, it was decided to assess only the effect of the pure thermal aging and the results presented below refer only to purely thermally aged samples. Nevertheless, the described assessment methodology can also be applied without modification for hydrothermally aged samples. Results for the fresh and aged samples are compared to results from an uncoated filter sample of the same material and structural characteristics. The reason for using the uncoated filter as reference and not a commercially available catalyzed DPF is that the latter is usually a noble metal coated DPF exhibiting mostly indirect (NO₂-assisted) catalytic soot oxidation activity and not direct soot oxidation activity as the base metal catalytic materials presented in this work. Comparison of noble metal catalyzed filters aging effects to the aging effects of the presented catalyzed systems would thus be confusing. Nevertheless, it is obvious that the proposed methodology could also be applied to systems demonstrating indirect soot oxidation activity. In such case, the regeneration performance assessment should also account for the NO presence in the exhaust gas.

RESULTS

Catalyst Amount Effect

The ABD synthesis/coating process generally produces a nanoparticle layer on the filter wall surface. After the aging process, the morphology of the catalyst layer on the channels of the filters may be altered and lead to changes in filter performance. These changes are studied in the present section.

Flow resistance

The normalized wall permeability of the catalyst coated filters is illustrated in [Figure 1](#). It can be observed that increase of the amount of catalyst leads, as expected, to the decrease of the clean wall permeability of the filter, while implementation of the aging process on the filters had as a



result further increase of the resistance to the flow. These results are consistent with a thermally-induced change of the catalytic layer microstructure. However, the coated samples exhibited different degrees of permeability reduction. The most heavily catalyst loaded filter exhibits the lowest impact on the permeability from the thermal aging. Apparently different competing phenomena take place affecting the evolution of the catalytic coating microstructure i.e. the loss of the micro-porosity in the catalytic layer due to sintering may compete with the increasing of the gap enlargement and flow channeling which also are due to the sintering of catalytic particles. A detailed microscopic study of such phenomena is beyond the scope of the present paper and it will be undertaken in the future.

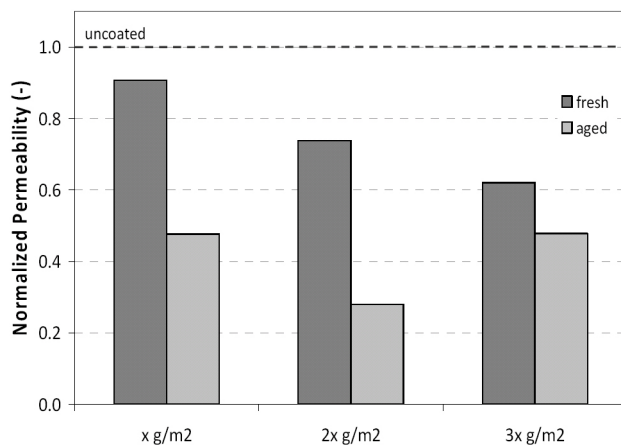


Figure 1. Normalized to the uncoated filter permeability of the fresh and aged filters coated with different amounts of the first catalyst formulation

Filtration efficiency

The clean filtration efficiency of the catalyst coated filters is illustrated in Figure 2. It is observed that the increase of the amount of catalyst on the filter has as a result the increase in the filtration efficiency of the coated filters. After the aging process this trend is maintained. The total filtration efficiency of the fresh and the aged catalyst coated filters is presented in Table 2. In terms of total number filtration efficiency, the aged samples are somewhat worse than the fresh samples in the lightly and the heavily loaded cases. The 2x MOC1 sample demonstrates approximately the same total filtration efficiency after the aging process.

Table 2. Total clean filtration efficiency of the fresh and aged coated filters (particle number basis)

	fresh	Aged
x g/m ²	0.682±0.009	0.659±0.012
2x g/m ²	0.787±0.014	0.790±0.016
3x g/m ²	0.845±0.016	0.797±0.008

An important observation in the results of Figure 2 is that, in all cases, the size-specific filtration efficiency minimum is

shifted to lower particle sizes for the aged samples. This shift suggests that the diffusion filtration mechanism becomes weaker with thermal aging of the catalyst layer and the resulting changes in its structure that are induced.

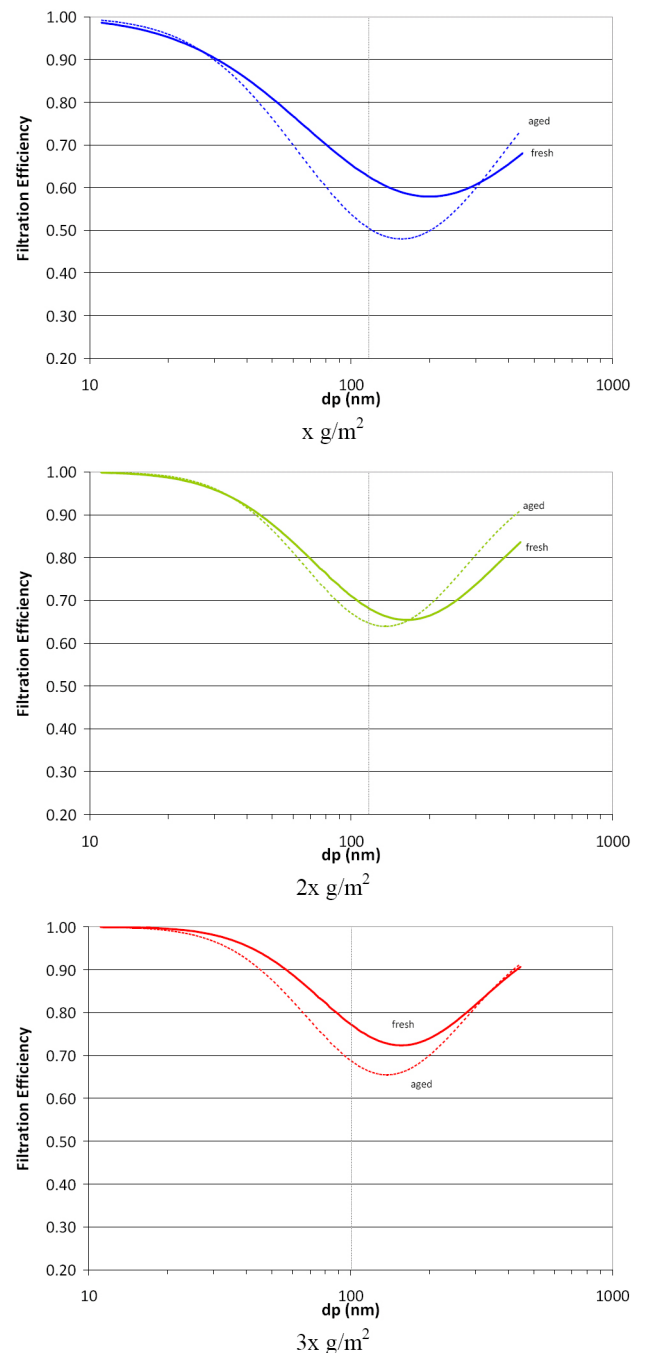


Figure 2. Size specific clean filtration efficiency of the fresh and aged catalyst coated filters

Soot loading

The effect of catalyst amount on the development of the pressure drop during soot loading can be seen in Figure 3 (a) and (b) for the fresh and the aged catalytic filters. In the case of the fresh catalyst coated filters, all sample monoliths start