Applied Catalysis B: Environmental 144 (2014) 203–215

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

# An experimental and simulation study on the cold start behaviour of particulate filters with wall integrated three way catalyst

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ARTICLE INFO

*Article history:*
Received 18 March 2013
Received in revised form 24 June 2013
Accepted 27 June 2013
Available online 10 July 2013

*Keywords:*
Exhaust
GPF
Chemical reactors
Simulation
Light-off
Wall-flow

ABSTRACT

Upcoming legislation will most likely require the introduction of particulate filters for gasoline engines. One attractive technical solution combines the three way catalytic functionality and the filter in one device, the so called 'catalysed Gasoline Particulate Filter'.

The current study uses temperature step experiments and CO oxidation as a test reaction to compare the catalysed particulate filter and the conventional flow-through monolith with respect to their dynamic cold-start behaviour. Despite the fact that the two reactor configurations are tested with identical washcoat formulation, precious metal loading and thermal mass, experiments show a significantly delayed cold-start for the particulate filter. The resulting cumulated CO emissions of the catalysed filter exceed those of the open monolith by 190–300% in the temperature range between 250 °C and 325 °C.

The experimental results are analysed by means of numerical simulation. In a first step a kinetic model of the CO oxidation is parameterised using only experimental data obtained for the conventional flow-through catalyst. The resulting kinetics are implemented in a model of the wall-flow filter. Without further modification of the kinetic parameters, this model quantitatively predicts the cold-start behaviour of the catalysed filter.

Finally, the numerical model is used in a sensitivity analysis to identify and quantify the individual physical effects contributing to the experimentally observed difference in the light-off behaviour. It is shown that a part of the observed difference in the cold-start performance can be traced back to differences in cell density and the heat capacity of the plugs. Even at identical cell density and without the plug effect the filter shows significantly higher CO emissions. It is shown that this intrinsic difference between the filter and the conventional monolith can be quantitatively explained by differences in heat transfer, internal mass transfer and external mass transfer.



## 1. Introduction

Gasoline particulate filters Today, Diesel Particulate Filters (DPFs) are standard emission control devices for diesel engines. Recently particulate filters are also considered for gasoline engines. Although the soot mass emitted by gasoline engines is orders of magnitude lower, particulate numbers can be high due to a lower average particle size [1]. Small particles are known to be more hazardous since they have a higher potential to penetrate the fine capillaries in the lung [2,3]. For this reason, upcoming legislation will also impose limits for the particulate number emissions of gasoline vehicles. Most likely this EURO 6 legislation will require the implementation of filter devices for gasoline engines [4]. This is especially evident for fuel efficient gasoline direct injection (GDI) engines. These engines emit particle numbers that are an order of magnitude higher than those of conventional port fuel injected engines and can even exceed the particulate number emissions of diesel engines without DPF [5].

Probably the most economical way to remove soot from gasoline exhaust is to combine a conventional three way catalyst (TWC) and a particulate filter in one single device, the so called 'catalysed Gasoline Particulate Filter' (cGPF). This device consists of a ceramic filter with a three way washcoat finely dispersed inside the wall pore system. The cGPF is also referred to as a 'Four-Way Catalyst' since it simultaneously removes the four pollutants CO, hydrocarbons (HC), NO and soot.

The feasibility of the cGPF concept has recently been demonstrated in a number of studies [6–8]. Thereby it has been shown that the filtration efficiency of such systems is sufficient to fulfil the currently discussed particulate number limits, despite the small size of gasoline soot particles. Furthermore, the backpressure of the cGPF can be reduced to a level where the impact on fuel efficiency and $CO_2$ emissions becomes negligible [7,8].

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http://dx.doi.org/10.1016/j.apcatb.2013.06.035

Besides filtration efficiency and backpressure, the development criteria for a cGPF are the same as for a conventional three way catalyst:

- CO and HC emissions, which are mainly influenced by the cold-start performance of the catalyst.
- NO emissions that are mainly caused by the interaction of the catalyst and a non-perfect lambda control system.

This paper focuses on the cold-start behaviour of the cGPF. Despite the fact that modern engines reach exhaust temperatures of several hundred degrees Celsius within a few seconds, cold-start is responsible for a significant part of total CO and hydrocarbon emissions. Due to the fast heat-up of the exhaust gas, the cold-start of the three way catalyst can be described as a dynamic light-off which is also called 'fast light-off'. This means that the temperature increase of the exhaust gas is fast compared to the characteristic time of the catalyst heat-up. Therefore, during cold-start a temperature front is moving through the catalyst from the inlet towards the outlet. This 'fast light-off' scenario is significantly different from the conventional stationary laboratory light-off test with a slow heating ramp, which leads to a more or less uniform temperature distribution within the entire catalyst.

In this paper we study the dynamic light-off performance of three way catalysts and cGPFs by temperature jump laboratory experiments. These experiments reproduce the dynamic light-off conditions of real vehicle operation in an idealised form with a simplified exhaust that contains CO as the only pollutant. The objective of the study is to compare the light-off performance of the catalysed filter to the performance of a conventional open monolith. It is shown that at constant washcoat loading, precious metal loading and thermal mass, the cGPF shows significantly higher cumulated CO emissions than the conventional open channel three way catalyst. In a second step a numerical model of the cGPF is presented and it is demonstrated that the higher emissions of the cGPF are nearly quantitatively predicted by the model. Finally, the model is used in a sensitivity analysis to gain an understanding of the physical effects that are responsible for the inferior light-off performance of the catalysed filter.

## 2. Open flow-through monolith versus wall-flow filter

The ceramic filter substrate is derived from an open flow-through monolith by plugging alternating channels at the inlet and the outlet so that the gas is forced to flow through the wall. In a conventional flow-through monolith the catalyst is applied as a thin layer on the channel walls while in a cGPF the catalyst is dispersed inside the porous wall. From a reaction engineering point of view, fundamental differences exist between the two reactor configurations. The flow-through monolith relies on diffusion for the transport of reactants and products between the catalytically active washcoat and the gas phase. In the wall-flow filter the reactants are forced through the catalytically active wall by convection. This situation was analysed by numerical flow simulations in [9]. Under steady state conditions the wall-flow filter showed higher conversion rates compared to the flow-through monolith. This was explained by the absence of mass transfer limitations in the case of the wall-flow filter. A more detailed analysis of the complex interplay of diffusion, convection and reaction in the wall flow reactor has been provided in [10]. It was shown that for the wall-flow filter operation two limiting cases can be distinguished:

- At low reaction rates and low flow velocities mass transfer in radial direction is entirely dominated by diffusion. This means that radial concentration gradients between the inlet and outlet channel and inside the porous wall are negligible. The main concentration gradient is oriented in axial direction, just as in the case of the flow-through monolith.
- If reaction rates are high, radial transport is dominated by convection. In this case axial gradients along the channels become negligible and the main gradient is oriented in radial direction through the filter wall.

Under most operating conditions relevant for an automotive exhaust catalyst the filter is operated in an intermediate range where diffusion and convection both contribute to radial transport.

A model based analysis of the differences between the flow-through and wall-flow reactor concept has also been presented by Dardiotis et al. [11]. In this study the gas flow in the inlet and outlet channels is treated as one dimensional. Diffusive mass transfer is taken into account by mass transfer coefficients. The study confirms the conclusion that under steady state operation the wall-flow filter is expected to show higher conversion in those situations where the conventional flow-through monolith becomes mass transfer limited (short residence times, high reaction rates). In the context of diesel exhaust after treatment Dardiotis et al. [11] also performed a simulation study for the dynamic light-off scenario. Their simulations predicted that at comparable substrate dimensions and catalyst loading the filter is expected to show worse dynamic light-off behaviour than the flow-through monolith. In [12] this study was extended to zoned particulate filters.

More recently a number of modelling studies of the wall-flow filter have been published in the context of diesel particulate filters with wall integrated SCR catalyst functionality [13–16].

## 3. Methodology

### 3.1. Experimental

#### 3.1.1. Catalyst samples

Conventional open monoliths and wall-flow filters were coated using an identical washcoat formulation. Cordierite substrates with square channels and a typical cell density and wall thickness (filter: 300 cpsi/12 mil, open monolith: 600 cpsi/4.3 mil) were used. In case of the open monolith the washcoat was deposited on top of the monolith wall as thin layer whereas the washcoat of the catalysed filter is assumed to be completely dispersed inside the porous wall. To be comparable, monolith and filter were prepared with identical washcoat loading (100 g $L^{-1}$) and precious metal loading (46 g $ft^{-3}$ Pd; 4 g $ft^{-3}$ Rh). Both catalyst samples were aged for 4 h at 925 °C in an atmosphere of 10 vol% $H_2O$ in air.

#### 3.1.2. Fast-light-off experiments

In the temperature step experiment the initially cold catalyst is subjected to the flow of the preheated inlet gas mixture by means of a switching valve. In this way the sample is heated up by the hot exhaust gas. The axial temperature profile in the catalyst is monitored by eight thermocouples placed inside the channels. The CO outlet concentration is measured with a mass spectrometer (V&F Analyse- und Messtechnik, AirSense2000).

Temperature profiles of a typical heat-up experiment with $N_2$ are shown in Fig. 1. Starting at room temperature, it can be seen that the exhaust gas reaches 95 % of the target temperature in about 5 s.

All light-off experiments reported in this paper were carried out with an exhaust mixture containing 5000 ppm (mol $mol^{-1}$) CO, 3000 ppm (mol $mol^{-1}$) $O_2$ and $N_2$ as gas balance. The inlet gas temperature was varied in a temperature range from 250 °C to 350 °C with a step size of 25 °C. The feed gas composition and temperature was held constant during each experiment. It was made sure