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Structure characterisation of catalytic particulate filters for automotive exhaust gas aftertreatment

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ABSTRACT

Modern automobiles with internal combustion engine are equipped with several different converters of exhaust gas and a particulate filter. The size and cost of exhaust aftertreatment system can be reduced by coating the catalytically active material on or into the porous filter walls. The characterisation of filter morphology including the distribution of catalytic material inside the filter wall is a key prerequisite for the development of porous structures with optimum performance with respect to pressure loss, filtration efficiency and catalytic activity.

Three SiC filter samples with different amount of SCR catalyst were characterised by X-ray tomography (XRT), scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP). Combination of the techniques provides detailed and consistent information on filter and coating hierarchical pore structure. The segmented XRT image revealed 3D distribution of catalytic material and larger macropores inside filter wall. The 3D XRT images were further used as the input for mathematical models evaluating porosity, pore size distribution (PSD), effective diffusivity and tortuosity. Maximum sphere inscription method applied to XRT data gave PSD shifted to larger pore sizes in comparison with the MIP results, in line with the bottleneck limitation of MIP. On the other hand, MIP was able to determine also smaller internal pores in the catalyst layer. Pressure loss of the filters measured in lab reactor increased non-linearly with the amount of catalytic coating. The PSD and XRT suggest that a large number of substrate pores is filled up completely by catalytic material.

1. Introduction

Particulate matter (soot) produced by internal combustion engines is known to have adverse health effects [1] – the particles (10^1 nm–10^1 μm in size) can penetrate deep into lungs which can result in pulmonary diseases [1]. Moreover, a variety of noxious substances can be adsorbed to particle surface, such as sulfates and unburnt hydrocarbons [2]. In addition to the health outcomes, eco- and genotoxicity of particulates has been reported [3], as well as their effect on climate change [4]. To meet strict emission limits, automobiles with Diesel engines and newly some gasoline powered ones must be equipped with particulate filters (DPF for Diesel engines, and GPF in the case of gasoline engines). In addition to particulate filter, catalytic converters are needed for abatement of gaseous pollutants (CO, hydrocarbons and NO_x).

Both catalyst and filter are in the form of a cylindrical monolith with a large number of parallel channels in a honeycomb arrangement – however, catalytic converters are flow-through while the filter channels are plugged at one end so the exhaust gas is forced to permeate through the porous monolith walls, filtering out the soot (Fig. 1). Multiple catalytic converters often need to be combined (one for oxidation of CO and hydrocarbons, other for NO_x reduction) [5] which makes the whole aftertreatment system space-demanding. A promising approach to make the system more compact is to apply the catalytically active material (washcoat) either in several layers on a single substrate [6–7] or directly into the porous structure of particulate filter [8]. There are advantages beyond space, weight and cost savings, for example reduction of overall heat-losses [7–8]. Additionally, catalysed filters can be regenerated at lower temperatures when a layer of oxidation catalyst is applied [2,9]. However, several parameters of such multi-functional devices have to be optimized at once – activity of the catalyst, filtration efficiency and pressure loss [8].

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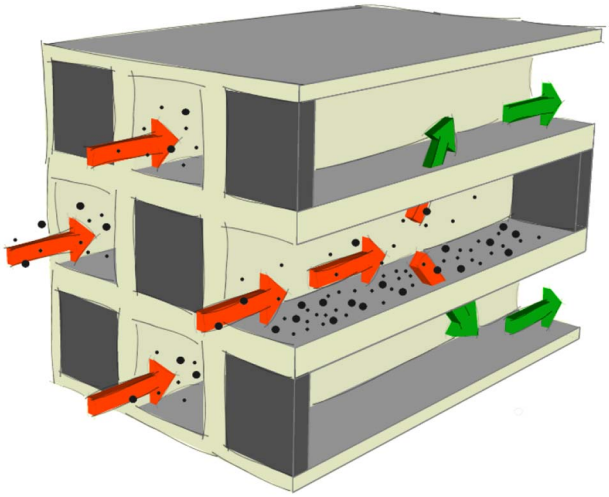

Fig. 1. Scheme of a wall-flow particulate filter.

The coated catalytic material activity may be lowered by diffusion of gaseous reactants in small macro-, meso- and micropores in the washcoat – the transport might become the rate determining step, limiting the overall conversion of pollutants [10–11]. Filtration efficiency and pressure loss in the filter depend on size and interconnectivity of large macropores in the filter substrate and spatial distribution of washcoat domains – the gas tends to follow the path of smallest resistance and the flow thus may by-pass some coated zones. The main focus of this work is characterisation of the macroporous network in the filter and its effect on the pressure loss.

Thorough characterisation of the pores provides also a very helpful input for mathematical modelling in design of catalytic particulate filters – for example, models of gas flow, pressure loss and/or filtration efficiency have been published [12–13], some including catalytic reactions as well [14–15].

A traditional technique for macropore characterisation is mercury intrusion porosimetry (MIP) [16]. The alternatives include intrusion of other liquids, liquid permeation tests or capillary condensation – while all have their merits, mercury porosimetry cannot be fully replaced yet [17]. Complementary techniques have arisen by fast development of 3D imaging techniques, such as X-ray tomography (XRT) [18] or scanning electron microscopy coupled with focused ion beam milling (FIB-SEM) [19]. A great advantage of these methods is that the porous structure can be digitally reconstructed and mathematical simulations can be applied directly to representation of real structure of the media.

The aforementioned techniques and their combinations are applied in a wide range of fields – geology [20], medicine [21–22] and tissue engineering [23], chromatography [24] or study of construction [25] and energy materials [26], i. e. fuel cells [27]. Studies of porous ceramics are available [28–29], however, to our knowledge there are no characterisation studies systematically describing the porous structure of DPFs. In this work, catalysed particulate filters were studied – the filter substrates were coated with a catalyst on which NO_x are selectively reduced by ammonia, commonly denoted as NH_3-SCR catalyst [30]. When combined with a particulate filter, the whole device is called SCRF® [31–32]. Porous structure of the SCRF® samples was studied by a combination of SEM, XRT and MIP. Furthermore, pressure losses in the samples at varying flow rate were measured in a lab reactor.

2. Material and Methods

In this section, a description of catalysed particulate filters studied in this work is provided together with the characterisation & testing techniques applied to them. Measurement results, including comparison of the techniques and calculation of morphological descriptors from the characterisation data will be summarized in Section 3.

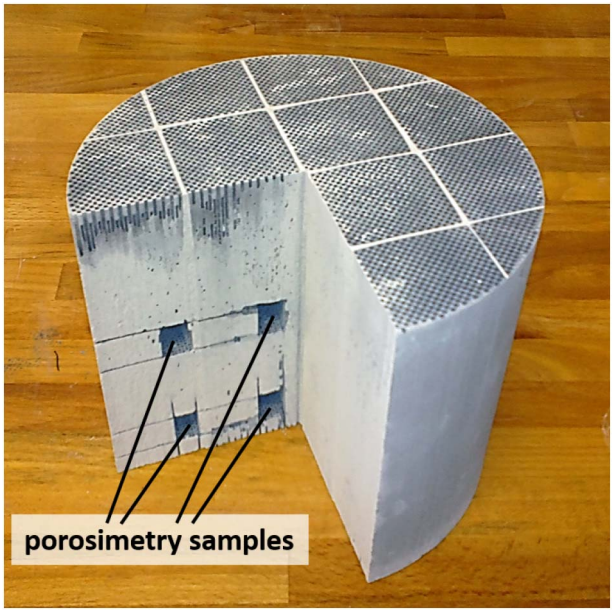

Fig. 2. Photograph of an SCR/SiC sample to indicate sections taken for mercury intrusion porosimetry.

2.1. Sample Description

The following set of samples was examined in this work – (i) bare SiC particulate filter and similar filter substrate coated with an SCR catalyst (Cu-zeolite) in two different loadings: (ii) 1.2 g/in^3 and (iii) 1.9 g/in^3 (Fig. 2).

The washcoated samples contain pores that can be subdivided into three categories: (i) large macropores in the substrate (approximately 3–50 μm), (ii) smaller macropores in the washcoat – between the catalyst microparticles (50 nm–3 μm) and (iii) meso-/micro-pores inside the catalyst particles (< 50 nm). The large macropores (i) are the most significant for the gas transport through the filter wall and, thus, the main focus was placed on their description. Smaller macropores (ii) could not be fully characterised by all techniques used in this work and therefore when they are considered in the analysis, it is specifically mentioned. The smallest pores (iii) were not in the focus of this work as they were irrelevant for the convective flow of gas through the filter structure.

2.2. Characterisation Techniques

2.2.1. SEM

Scanning electron microscopy was used to observe two-dimensional macroporous structure of the SCRF® samples. Small sections were cut out of the filters (one for each filter at the similar location as the porosimetry samples showed in Fig. 2) and mounted in epoxy resin. In order to achieve completely flat surface of the specimens, they were lapped by SiC foils and polished by diamond foils and colloid silica. Their surface was subsequently sputtered with a several nanometer thin layer of gold to prevent local charging. The specimens were scanned by Tescan VEGA 3 SBU microscope – backscattered electron (BSE) detector was used to achieve higher contrast between individual phases.

2.2.2. X-ray Microtomography

Small sections were cut out of the filters (one for each filter at the similar location as the porosimetry samples showed in Fig. 2). These