Washcoating of catalytic particulate filters studied by time-resolved X-ray tomography

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1. Introduction

Emissions produced during the operation of combustion engines contain traces of harmful substances such as CO, NOx, unburned hydrocarbons and particulate matter (soot and ash). A catalytic converter is used to clean up gaseous emissions while the soot is trapped in a filter. The fundamental part of catalysts and filters is a monolith with honeycomb structure formed by a number of parallel channels. While all the channels in a standard catalytic converter are open at both ends, the channels in a filter are plugged alternately at the inlet and outlet in a chessboard manner so that the gas is forced to flow through the porous wall into the adjacent channel and the soot is trapped [1]. Diesel particulate filters (DPF) and recently introduced gasoline particulate filters (GPF) share similar principles, however, the material requirements are different for the two types of engines because of specific operating conditions and soot combustion strategies associated with exotherms and temperature shocks [2,3]. The DPF substrates are often made from porous SiC or aluminium titanate, while GPF substrates are based on cordierite [2].

Deposition of a catalytic material on or into the porous filter wall has become increasingly attractive in the automotive exhaust gas aftertreatment, because the resulting catalytic filter represents a compact multifunctional unit that can abate both gaseous and solid pollutants. Catalyzed filters for Diesel engines mostly utilize coatings based on PtPd/ceria/alumina for the oxidation of soot, CO, hydrocarbons and NO (CDPF, CSF) [4–8] or more recently Cu/zeolite washcoat for selective catalytic reduction of nitrogen oxides (SDPF, SCRf) [9–14]. Gasoline particulate filters are usually coated with three-way catalyst (TWC) of PdRh/ceria-zirconia/alumina type [15–21]. A wide range of catalyst deposition techniques have been reported in the literature [22–25]. The industrially relevant methods include the injection and/or suction of defined amounts of a catalyst slurry into monolith filter channels and subsequent drying of the formed washcoat [26–28].

The catalyst location on or inside the porous filter walls as well as the internal structure of the coating significantly affect the functional properties of catalytic filter, i.e., pressure loss, catalytic conversion and filtration efficiency. Recent studies on the catalyst distribution effects mostly utilize X-ray tomography (XRT), also known as computer tomography (CT), and transform the segmented 3D image into a computational domain for the simulation of flow, diffusion, reaction and filtration processes [29–35]. More detailed characterization of the catalyst location in a porous filter substrate can be achieved by the
A combination of XRT, cross-section scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP) \cite{36}. XRT also allows detection of cracks and cavities in the coated catalyst layer \cite{37} and provides visualization of ash deposited in the filter substrate \cite{33}. Information about the 3D microstructure of the filter walls can be obtained by scanning electron microscopy with focused ion beam milling (FIB-SEM) as well, though it is a destructive technique \cite{38}. However, these characterization techniques were applied only to the final structures of catalytic filters, while the processes during the monolith washcoating that lead to the structure formation remain much less explored.

An optical microscope with particle imaging velocimetry was successfully employed for the monitoring of microparticle mobility during the drying of a catalyst layer on a flat substrate \cite{39}. The overall drying process on a monolith scale was studied by magnetic resonance imaging (MRI) \cite{40,41}, however, MRI does not provide sufficient resolution for the observation of thin catalyst layers and individual pores in the filter wall. With the development of third generation synchrotron sources, sub-second time-resolved X-ray tomography has been achieved at several beamlines \cite{42}. Such a combination of 3D spatial information and temporal resolution opens the doors to study the dynamic evolution of multi-phase systems. In recent years, synchrotron time-resolved X-ray tomography has been applied to understand, for example, processes which take place during drying of water in porous structures \cite{41,43}, liquid flow through rocks \cite{44}, metal foaming \cite{45} or crack formation during casting \cite{46}.

In this paper we introduce a new application of time-resolved XRT to image the washcoating inside catalytic monolith filters with a honeycomb structure. The aim is to better understand the washcoat deposition, water transport in pores and structural changes of the coated layer during its drying, depending on the catalyst particle size distribution. The ability to monitor, understand and ultimately better control these processes represents a crucial step towards the optimization of the washcoat structure.

**Fig. 1.** Bare substrate channels, cross-section SEM image.

**Fig. 2.** Pore size distribution of the bare cordierite substrate obtained from mercury porosimetry.
2. Materials and methods

### 2.1. Filter substrate

A commercial cordierite filter substrate from NGK Ceramics was used in the experiments. The substrate possessed 300 cpsi symmetrical channels of a nearly square shape with a small additional amount of material in the corners. This channel shape is sometimes denoted as octo-square. The structure of the filter channels is shown in Fig. 1.

The SEM image analysis revealed a wall thickness of the substrate of 213 ± 5 µm. The porosity of the substrate was 66% and 64% as obtained from electron microscopy and mercury intrusion porosimetry, respectively. The mean pore diameter determined from mercury porosimetry was 19 µm, but the complete pore size distribution revealed also larger pore diameters up to ca. 70 µm, see Fig. 2.

For the purpose of lab-scale experiments, a cylindrical sample with diameter of 13 mm and length 20 mm was cut out from the full-size monolith. The channels were plugged at alternating ends using the UV welder Bluefixx MGS. The plug length was 2–3 mm from each side, leaving ca. 15 mm as an active length of the filter.

### 2.2. Catalytic washcoat

γ-Al₂O₃ Puralox SCFa140 from Sasol was used as a model catalytic material, see Table 1. γ-alumina is widely used in three-way and diesel oxidation catalysts (TWC and DOC, respectively) as a carrier of platinum group metals.

The particles were deposited on the substrate from an aqueous suspension. In the first step, the γ-Al₂O₃ particles were mixed with distilled water so that the weight fraction of the particles in the water was 38%. The alumina particles were subsequently milled in a pearl mill with recycle (Eiger Torrance M100). The desired particle size distribution was achieved by adjusting the grinding time.

After milling, the resulting volume particle size distribution was measured by laser diffraction granulometry based on static light scattering (Horriba Partica LA-950 V2). The particle size can be characterized by quantiles for which p percent of particles are smaller or equal to a diameter \(d_p\), and (100-p) percent of particles are greater than \(d_p\). In this work we will use mostly the quantile \(d_{90}\), which means that 90% of particles are smaller or equal to this diameter, considering their volume distribution.

Three different particle size distributions were obtained by milling: \(d_{90} = 6 \text{ µm}, d_{90} = 12 \text{ µm} \) and \(d_{90} = 20 \text{ µm}\), see Fig. 3. The fourth suspension denoted as \(d_{90} = 6 \text{ & 20 µm}\) was obtained as a mixture of the \(d_{90} = 6 \text{ µm} \) and \(d_{90} = 20 \text{ µm}\) suspensions in a 1:1 ratio by weight. Note that the mixture of particles \(d_{90} = 6 \text{ & 20 µm}\) exhibits a similar mean particle diameter to \(d_{90} = 12 \text{ µm}\) but its particle size distribution is wider. Prior to the coating, pH of the suspensions was adjusted close to the isoelectric point [39].

### 2.3. Coating and drying followed by time-resolved XRT

Coating and drying of the cordierite filter have been examined by X-ray tomography at the TOMCAT beamline (Swiss Light Source). The experimental setup comprises of two heat guns with diameter of 25 mm (LE MINI from Leister) blowing hot air, an in-house modified rotary union (JR 1-1-4 R40 from TDS Precision Products GmbH) and a vacuum pump.

Fig. 4. Configuration of the washcoating setup at the TOMCAT beamline.
pump (KNF N828KNE), see Fig. 4. The design of the rotary union allows transport of liquids between rotating and static parts of the experimental setup. The union connects the top sample part with the rotational stage, which allows the sample to rotate. The vacuum pump is attached to the central stator part of the union which thus connects the pump with the rotating sample.

The cylindrical filter sample with a 13 mm diameter and 20 mm height was wrapped in Teflon and fixed in a holder mounted on top of the rotary union. At the start of the time-resolved experiment, alumina slurry was placed on top of the filter sample and the rotation of the stage initiated at 180 °C. First, a scan of the bare filter without washcoat was acquired. Then a defined pulse of vacuum (0.5 bar) was applied to the sample, pulling the alumina slurry into the filter substrate followed by an acquisition of a second scan. Subsequently, heating guns set to a constant temperature of 90 °C were moved to the sample position. The sample was thus heated simultaneously from both sides at the center of the filter while rotating continuously, and tomographic scans were taken at defined time intervals. There was no flow of gas through the sample during the drying period so that the transport of the evaporated water to the open ends of the channels was driven by diffusion. After the drying step was finished, an additional scan of the dried sample with higher quality was acquired.

Temperature inside the sample could not be measured directly during the washcoating and drying experiment because any thermocouple would disrupt the coating distribution and damage the wet washcoat in the rotating sample. However, independent drying experiments were performed afterwards with re-wetted final samples, using the same drying set-up but with an added thermocouple inserted into a selected location in the sample. These measurements showed a quick initial increase of the sample temperature to approx. 50 °C, which remained constant during the first period of drying, including water evaporation from large pores of the filter wall. The sample temperature then increased during the second period of drying (water evaporation from smaller pores inside the catalyst washcoat) and reached approx. 75 °C in steady state. The rest of heat provided by the heat guns was transferred to the surrounding air and table through the sample holder. The temperature in the channels close to the sample perimeter was slightly higher than in the sample center, and similarly the temperature at the sample top was slightly higher than at the sample bottom. The maximum measured temperature difference across the sample was ca. 5 °C. The effect of X-ray beam on the sample temperature was only minor – the measured steady state temperatures with and without the beam differed by 2 °C. More detailed data on the temperature profiles during the experiments are given in Appendix 1.

Filtered polychromatic X-ray radiation with a peak energy of about 26 keV originating from a 2.9 T bending magnet source was used for all experiments. The in-house developed GigaFReLU camera [47] was used in combination with a high-resolution white-beam microscope (Optique Peter) with 13.7 × magnification, yielding an effective pixel size of 0.8 μm. To capture the full extent of at least one or even several channels, an extended field-of-view scanning procedure was used where the rotation axis of the sample was aligned with one side of the detector’s field-of-view and the sample is rotated through 360° instead of the 180° normally required for the parallel beam geometry [48]. The resulting field of view was 3985 × 2001 pixels, meaning that the size of the scanned section was 3188 × 3188 × 1600 μm³. The exposure time per projection was 2 ms with 2500 projections per 360° scan. Consequently, the total time to acquire a single scan was 5 s. The imaging sequence consists of a 5 s scan of a bare monolith, 5 s pause to deliver the washcoat, 5 s scan of a coated structure, 10 s pause to move the heat guns to the drying position and 75 scans of drying with 5 s acquisition time and 15 s pause between to reduce the amount of the collected time-series data. The process time referenced throughout this paper uses t = 0 s for the start of drying, so that the two earlier scans are denoted with negative times: t = –25 s corresponds to the bare filter sample, and t = –15 s corresponds to the newly washed coated sample prior to drying. A fast X-ray shutter was closed between the scans to prevent unnecessary sample exposure to the beam. In total, 78 scans were obtained capturing approximately 25 min of the drying process. The higher quality scans of the dried samples were obtained with the exposure time set to 5 ms and 4000 projections resulting in an acquisition time of 20 s. The 3D volume data sets were reconstructed using the propagation-based phase contrast method [49] and the gridrec algorithm [50].

Four filter samples were coated with different catalyst particle sizes: d₉₀ = 6, 12, 20, and 60 & 20 μm. The amount of applied suspension was approximately 0.9 g so that the weight fraction of the dried coating in the substrate was 20–25%, resulting in a loading of around 1.5 g/in³, see Table 2. However, a larger amount of the suspension, 1.58 g, was necessary for the particle size of d₉₀ = 20 μm to achieve the desired loading and complete coating (more suspension remained on the external surface of the substrate).

Table 2 also shows the amount of water remaining in each sample after 1500 s of drying, measured as a difference between the sample mass at t = 1500 s and after several hours of drying at room temperature. According to these data, drying of all samples was practically completed within the 1500 s period monitored by time-resolved XRT, just the sample d₉₀ = 60 & 20 μm contained a non-negligible residual amount of water at 1500 s and its drying continued a little bit longer. Nevertheless, all important structural changes of the washcoat were captured within the 1500 s scanning period as will be demonstrated in the Results section.

### 2.4. Additional characterization of the coated samples

Cross-section scanning electron microscopy (SEM) was used to provide additional characterization of the final washcoated samples at eight different locations. Small sections were cut out of the filters and mounted in epoxy resin. In order to achieve completely flat surfaces of the specimens, they were lapped with SiC foils and polished using diamond foils and colloidal silica. The surface was then sputtered with a several nanometer thin layer of gold to prevent local charging. The specimens were scanned by a Tescan VEGA 3 SBU microscope and the backscattered electron (BSE) signal was used to achieve higher contrast between the individual phases. For single channel images, the SEM pixel size was 280 nm. Image analysis was performed using the ImageJ-Fiji software [51,52].

In addition, the samples were characterized by mercury intrusion porosimetry using a Quantachrome PoreMaster 33 device. Approximately 1–2 cm³ of the sample was placed in a measurement cell, degassed and filled with mercury. Subsequently, the pressure inside the cell was increased step-wise from 3 to 60,000 psi and the mercury intruded the pores of the sample. Pore diameters were calculated from
the applied pressure using the Washburn equation. Using this method, the porosity and pore-size distribution in the range of 3 nm–100 µm were determined for the bare substrate as well as for the washcoated samples. Combining the data from XRT, SEM and mercury porosimetry, it was possible to reliably determine the structure of the substrate and coated catalytic material.

2.5. Image processing and segmentation

In order to simplify and speed up the image processing, the acquired XRT scans with dimensions of 3188 × 3188 × 1600 µm³ were cropped to approximately 1600 × 1600 × 1300 µm³ to contain one coated channel near the center of the scanned domain, as shown in Fig. 5. It can be seen that the coating of individual walls varies slightly, which is influenced by a natural inhomogeneity of the porous substrate, however, no systematic trend between different channels was observed. The selected channel section was thus treated as a reasonable representation of the entire sample. In the sample \( d_0 = 6 \) µm, the cross-section SEM analysis of the prepared sample revealed that approx. 5% of the channels were excessively loaded with the catalyst slurry due to its leaking prior to the vacuum pulse. These channels were excluded from the XRT image analysis. No such maldistribution was observed in the other samples. The coating uniformity along the channels is further discussed in Appendix 2.

The 3D scans of final structures were processed using ImageJ-Fiji [52]. Brightness and contrast were adjusted and images were segmented so that each voxel in the image was assigned to one of the three phases: filter substrate, alumina coating, or free pore [29]. A machine-learning-based segmentation was performed by Trainable Weka Segmentation [53]. Regions of air, catalyst and substrate were chosen in one slice in the center location of each sample stack to train the algorithm. Training features chosen to obtain a visually accurate representation of the segmented coating in and on the wall include Gaussian blur, maximum, edges, mean and variance in combination with fast random forest. The training process generated one classifier, which was then used to segment all scanned samples.

The acquired tomographic time series of the washcoat drying were also processed in ImageJ-Fiji [52]. Due to low contrast of the washcoat in the ceramic filter, so called “subtracted” images were constructed by subtracting a 3D image at time \( t \) from another 3D image at time \( 0 \) s. Such an image aims to depict changes initiated by the movement of liquid–air interfaces. Prior the subtraction, the tomographic time series was registered by using 3D correct drift plugin integrated in ImageJ-Fiji [54] to minimize any movement of a sample during drying. Thus, a contrast variation in a subtracted image indicates a change of washcoat occupation. Increase of the contrast corresponds to a washcoat shrinking. On the other hand, contrast reduction shows an empty pore filling with washcoat. Segmentation was done again by Trainable Weka [53], which was trained to capture the contrast changes. Training features chosen to obtain a visually accurate representation of the segmented contrast variation included Gaussian blur, maximum, edges, mean and variance in combination with fast random forest. The resulting volume fraction of the substrate was compared with the data of bare substrate to check that the thresholding was done consistently.

Comparison of the results obtained with Weka segmentation and the simple thresholding of XRT and cross-section SEM images is given in Appendix 3.

2.6. Pressure drop measurement

The pressure drop across the catalytic particulate filter is one of the most important functional parameters. To compare the performance of individual samples, their pressure loss was measured at room temperature in a flow of nitrogen, using a Bronkhorst F-201CV-20 K-AAD-11-K mass flow controller with a maximum flow rate of 50 dm³/min. The sample was placed in two plastic holders that contract around the sample at the inlet and outlet. Differential pressure sensors (Cresto SHD 411 QSU D) were placed in front of and behind the sample. Nitrogen was blown through the sample at room temperature and the pressure drop was measured as a function of the flow rate.

3. Results

Selected snapshots of the washcoat drying recorded by X-ray tomography are shown for particle size \( d_0 = 12 \) µm in Fig. 6. A video showing the evolution of the \( d_0 = 12 \) µm sample structure during drying is available in Supplementary material (video_12um.avi). During the washcoating, the substrate wall is partially filled with the wet suspension and an on-wall wet layer is formed. No cracks or large pores can be detected in the washcoat shortly after deposition (Fig. 6a). During the drying, the water is first evaporated from large pores inside the filter wall. The smaller pores, including those between the individual catalyst particles in the coated layer, remain filled with water (Fig. 6b). Once the large pores inside the substrate wall are dried, water starts to be removed also from the smaller pores inside the wet coating. This is accompanied by a shrinking of the on-wall layer [22], which in this case leads to the formation of small cracks, preferentially in the channel corners (Fig. 6c). As the layer shrinks further, the existing cracks extend and a few more new cracks are formed. The cracks appear in a relatively short period (compare Fig. 6b to Fig. 6c).

The continued drying of the on-wall layer finishes with emptying the internal mesopores of alumina. The alumina mesopores with the diameter of 8 nm are far smaller than the spatial resolution of the XRT data, however, the change of water content within the pores affects the X-ray absorption. Therefore, drying of internal pores in the alumina layer can be seen as a contrast variation – compare the brightness of the coated layer in Fig. 6c and d. After drying is completed, a higher quality scan of the sample was taken (Fig. 6e). The comparison of Fig. 6d and Fig. 6e reveals that the structure obtained after 1500 s of drying is identical to the final structure (sample left 29 h at room temperature). It confirms that the sample was already completely dried during the 25 min drying period.

Selected snapshots of the \( d_0 = 6 \) µm washcoat drying observed by XRT are shown in Fig. 7. A video showing the evolution of the \( d_0 = 6 \) µm sample structure during drying is available in Supplementary material (video_6um.avi). The sequence of drying steps remains the same as with...
the sample $d_{90} = 12 \mu m$, however, several differences can be seen. Larger part of the catalyst particles gets inside the wall pores, the coated layer cracking starts earlier (1000 s for $d_{90} = 6 \mu m$ vs. 1260 s for $d_{90} = 12 \mu m$), and the number and size of the cracks is higher despite the fact that the on-wall layer is thinner.

No cracking is observed during the drying of the sample with the largest catalyst particles ($d_{90} = 20 \mu m$), see Fig. 8. A video showing the evolution of the $d_{90} = 20 \mu m$ sample structure during drying is available in Supplementary material (video_20um.avi). Fig. 8a shows that at the start of drying the pores inside the wall as well as the surface of the outlet channels are almost completely wet. However, these locations do not contain the catalyst slurry, but just plain water separated from the suspension. This is confirmed by Fig. 8b showing the dried sample where no coating can be observed in the initially wet locations. Practically all catalyst particles remain trapped on the inlet channel wall.

Evolution of the mixed $d_{90} = 6$ & $20 \mu m$ sample structure during drying is visually similar to the $d_{90} = 12 \mu m$, with initial crack formation at $t = 1140$ s as can be seen in the video available in Supplementary material (video_6 + 20um.avi). Further differences between the $d_{90} = 6$ & $20 \mu m$ and $d_{90} = 12 \mu m$ structures evolution are revealed only after more detailed analysis of the acquired data that will be discussed in the following text.

Temporal evolution of the filter wall filling with the catalyst slurry during the coating and drying is shown in Fig. 9. For each sample, the first point at $t = 25$ s corresponds to the structure before coating. No initial wall filling was observed for the samples $d_{90} = 12 \mu m$ and $d_{90} = 6$ & $20 \mu m$. In contrast, sample $d_{90} = 20 \mu m$ shows majority of the wall porosity filled already prior to the coating process. This is caused by a relatively low viscosity of the $d_{90} = 20 \mu m$ slurry and a separation of water from the catalyst particles so that the sample is spontaneously wetted before the vacuum pulse. The sample $d_{90} = 6 \mu m$ exhibits much lower but still noticeable initial wall filling (approx. 12%).

The second time point in Fig. 9 shows a fraction of the wall filled by washcoat after the coating process. As expected, the filled fraction
increases in all samples as the alumina slurry is distributed across the wall; the only exception is sample $d_{90} = 20 \, \mu \text{m}$ as its walls were already filled before the coating. The filling fraction just after the coating is higher for $d_{90} = 6 \, \mu \text{m}$ compared to $d_{90} = 12 \, \mu \text{m}$ indicating that the washcoat with smaller particles can more easily travel into the wall. Similar applies to the sample $d_{90} = 6 \& 20 \, \mu \text{m}$, which shows higher wall filling than $d_{90} = 12 \, \mu \text{m}$.

The onset of drying is at $0 \, \text{s}$, which coincides with the third time point in Fig. 9. As it is seen for the samples $d_{90} = 6 \, \& \, 20 \, \mu \text{m}$ and $d_{90} = 12 \, \mu \text{m}$, the fraction of wall filling can temporarily increase during the first minute of drying due to water transport from the on-wall coating into the wall, which is driven by capillary forces. As long as the pores between the catalyst particles in the on-wall coating are bigger than the accessible pores of the cordierite wall, then water is transported from the on-wall washcoat into the wall. The sample $d_{90} = 20 \, \mu \text{m}$ cannot increase its high initial wall filling any more but it shows constant wall filling during a long period of drying (until $t = 420 \, \text{s}$), which again suggests that any water evaporated from the wall during this period is compensated by the water transport from the on-wall layer into the wall. On the contrary, the sample $d_{90} = 6 \, \mu \text{m}$ with the smallest interparticle pores in the coated layer does not show any increasing or constant trend and its wall filling fraction clearly decreases already from the beginning.

Fig. 7. Washcoat drying observed by XRT, sample $d_{90} = 6 \, \mu \text{m}$: a) substrate after washcoating with the catalyst slurry ($t = 0 \, \text{s}$); b) water is removed from the large pores inside the filter walls, the coated catalyst layer remain wet but already shrank a bit ($t = 980 \, \text{s}$); c) catalyst layer further shrinks due to de-wetting, first cracks appear ($t = 1020 \, \text{s}$); d) coating is dry, cracks propagated ($t = 1500 \, \text{s}$). White = substrate, grey = washcoat (brightness increases with water content), black = void.

Fig. 8. Washcoat drying observed by XRT, sample $d_{90} = 20 \, \mu \text{m}$: a) substrate after washcoating with the catalyst slurry, large pores inside the filter filled with the separated water ($t = 0 \, \text{s}$); b) dried sample without any cracks ($t = 1500 \, \text{s}$). White = substrate, grey = washcoat (brightness increases with water content), black = void. Separated water appears as dark grey. The lower quality of the top left corner reconstruction is caused by fewer available projections as the sample went out of the field of view during scanning.
In the later stage of drying, all samples in Fig. 9 show a gradual decrease of the wall filling until reaching a limit value at the end of drying. The sample $d_{90} = 6 \mu m$ shows significantly higher fraction of the terminal in-wall coating compared to the other samples. The sample $d_{90} = 20 \mu m$ shows only minimum filling of the wall pores after drying despite its almost complete initial wall filling. This confirms that the majority of wall porosity was occupied just by water separated from the catalyst slurry.

As observed in Fig. 6, also the washcoat layer on the channel wall contracted during the drying. Its thickness was measured in each corner as schematically depicted in Fig. 10 together with the relative volume obtained from XRT segmentation. All samples except $d_{90} = 20 \mu m$ exhibit a sudden initial decrease of the on-wall layer thickness between $t = -15$ s (immediately after the coating) and $t = 0$ s (start of drying). We can see simultaneous minor decrease also in the in-wall filling (Fig. 9), therefore this shrinking cannot be attributed to the water transport between the on-wall layer and wall pores. This initial shrinking of the layer in the scanned zone could be caused by the slurry redistribution along the channel.

Subsequent data in Fig. 11 reveal that the on-wall washcoat layer is shrinking steadily after the drying begins. This corresponds to the first period of drying. At a certain point, the layer shrinking accelerates, which is associated with the transient to the second period of drying. The first cracks appear at approx. $t = 1020$ s for $d_{90} = 6 \mu m$, $t = 1140$ s for $d_{90} = 6$ & $20 \mu m$, and $t = 1260$ s for $d_{90} = 12 \mu m$. From the moment of crack formation, the curves for relative thickness (Fig. 11b) and relative volume (Fig. 11c) of the on-wall layer stop to correspond to each other – the layer thickness remains nearly the same, while its volume continues to decrease due to the growing cracks. The shape of curves in Fig. 11c suggest that the washcoat volume approaches a steady value at the end of 1500 s scanning period, just the coating $d_{90} = 6$ & $20 \mu m$ would need a little bit more time to achieve constant volume. This is in line with the residual water mass obtained by weighing the individual samples (Table 2). The layers containing larger particles ($d_{90} = 20 \mu m$ and $d_{90} = 6$ & $20 \mu m$) exhibit the lowest relative volume change in the layer thickness, ca 5–10%. The smaller is the $d_{90}$, the higher relative volume change in the layer thickness is observed (up to 30% for the washcoat with $d_{90} = 6 \mu m$). This trend correlates well with the number and size of

![Fig. 9. Fraction of wall filling by washcoat during coating and drying as observed by XRT. Fraction of one denotes complete saturation of the filter wall.](image)

![Fig. 10. On-wall washcoat layer thickness measurement in the channel corners.](image)

![Fig. 11. Shrinking of the on-wall layer during the washcoat drying process: a) absolute thickness in the channel corner, b) relative thickness, c) relative volume.](image)
formed cracks, the highest number of cracks being detected in the sample with \(d_{90} = 6 \, \mu m\).

Fig. 12 shows higher-quality scans of the final structures obtained after several hours of subsequent drying at room temperature. It can be seen that the final coating structures are identical to those observed at 1500 s in the time-resolved XRT scanning sequence but the higher quality scan enables more accurate image analysis. A large portion of the \(d_{90} = 6 \, \mu m\) slurry penetrated into the pores inside the substrate wall, leaving only a thin on-wall layer that accumulated mostly near the channel corners. The middle part of the channel wall remained uncovered, Fig. 12a. Furthermore, a relatively high number of cracks were formed in the thin on-wall layer. On the contrary, the sample coated with the particle size distribution \(d_{90} = 20 \, \mu m\) showed only a minor penetration of catalyst particles into the substrate wall and majority of the applied slurry formed a thick on-wall layer, see Fig. 12d. Despite the considerable thickness of the on-wall layer, the \(d_{90} = 20 \, \mu m\) sample contained no cracks at all. The relationship between the alumina particle size and crack formation is in agreement with the observations made in another filter washcoating study [55] that used SEM for the characterization of final coated layers. The crack formation tendency can be related to different cohesive strength and mobility of the alumina particles depending on their size [39]. In order to check the possible impact of drying rate on the crack formation, we prepared additional samples and dried them completely at room temperature. The obtained coatings contain cracks in a similar extent as those dried with heating guns, suggesting that the observed crack formation is not enforced by too high drying rate but it is inherent to the given catalyst particle size distribution.

The other two samples (\(d_{90} = 12 \, \mu m\) and \(d_{90} = 6 \, & 20 \, \mu m\), see Fig. 12b and Fig. 12c, respectively) fit into the trend – their on-wall layer

| Sample | Coating volume fraction \(V_{coating}/V_{section}\) (%) | Coating volume fraction \(V_{coating}/V_{monolith}\) (%) | Relative amount of in-wall coating \(V_{in-wall coating}/V_{coating}\) (%) |
|--------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| \(d_{90} = 6 \, \mu m\) | 9.10 | 6.49 | 57.8 |
| \(d_{90} = 12 \, \mu m\) | 9.81 | 7.20 | 20.2 |
| \(d_{90} = 6 \, & 20 \, \mu m\) | 10.13 | 7.28 | 23.2 |
| \(d_{90} = 20 \, \mu m\) | 15.16 | 10.85 | 15.9 |

Table 3 summarizes the coating volume fraction and relative amount of the in-wall coating in the final structures as determined from the cropped higher quality XRT scans by Weka segmentation. thickness as well as the number of cracks lie in between the previously discussed samples. When we compare the structures obtained with \(d_{90} = 12 \, \mu m\) (Fig. 12b) and \(d_{90} = 6 \, & 20 \, \mu m\) (Fig. 12c) slurries, it can be concluded that the wider alumina particle size distribution in the sample \(d_{90} = 6 \, & 20 \, \mu m\) decreased the number of cracks. Let us remember that the \(d_{90} = 12 \, \mu m\) and \(d_{90} = 6 \, & 20 \, \mu m\) slurries possess similar mean particle diameters, but the particle size distribution in the \(d_{90} = 6 \, & 20 \, \mu m\) slurry is significantly wider (Fig. 3), which improves the particle packing capability [56].
monolith volume. The coating volume fraction in individual samples correlates with the coated catalyst mass in Table 2. In the sample \( d_{90} = 6 \) \( \mu m \), more than half of the coated catalyst is located inside the filter wall. In all other samples majority of the coating remains on the wall and only 15–23% of the catalyst went to the wall, mainly to larger pores open to the external surface. These results are consistent with the trend in terminal values of the wall pore filling in Fig. 9. It must be considered that \( d_{90} = 20 \) \( \mu m \) sample possesses thicker on-wall layer than the other samples so that with the similar terminal wall pore filling as \( d_{90} = 12 \) \( \mu m \) and \( d_{90} = 6 \) & 20 \( \mu m \) (Fig. 9) it reaches the lowest ratio of in-wall coating (Table 3).

The impact of coating on filter pressure drop was measured for a range of different gas flow rates (expressed in terms of space velocity related to the sample volume), see Fig. 13. The overall pressure loss in the filter is co-determined by the gas contraction and expansion at the inlet and outlet of the channels, friction along the channels, and wall pressure drop (including the coating) [57]. The inlet and outlet pressure drop generally depends on the fraction of open frontal area so that it increases with the coated layer thickness. Similarly, the friction along channels increases for the thicker coatings because the velocity in channels increases at a constant overall flow rate. However, for short channels increases for the thicker coatings because the velocity in the channel seems similarly thick as \( \mu m \). Therefore we can expect that an average \( \mu m \) layer contains a thicker washcoat layer, its on-wall layer in the scanned channel seems similarly thick than \( d_{90} = 12 \) \( \mu m \) (Fig. 12), however, the observed overall pressure drop of the short samples. Nevertheless, the contribution of friction along the channels becomes quite important in full-size filters with the length on the order of 10 cm [57].

The pressure drop in all samples increases nearly linearly with space velocity, but the individual coating structures add to the overall pressure drop with respect to the bare filter to a different extent. The lowest pressure drop is observed for the sample \( d_{90} = 6 \) \( \mu m \), thanks to a thin, non-compact on-wall layer with numerous cracks. The cracks significantly increase both effective diffusivity and permeability of the coated layer [29,37]. A significantly higher pressure drop arises when \( d_{90} = 12 \) \( \mu m \) particles are used, because a thicker and more compact on-wall layer is formed. Except through the few cracks, the gas cannot bypass the coating and it is forced to flow through its small internal pores that have an order of magnitude lower permeability than the large pores in bare substrate [29]. A similar pressure drop is observed for \( d_{90} = 20 \) \( \mu m \) where no cracks have been formed at all but, on the other hand, the larger catalyst particles created larger internal pores inside the coating. Note that according to the Carman-Kozeny equation for the layer of spherical particles

\[
\kappa_c = \frac{d_c^2 \varepsilon c,M}{180(1-\varepsilon c,M)^2}
\]

the permeability of the coated layer \( \kappa_c \) is proportional to the square of the mean catalyst particle diameter \( d_p \) (corresponding to \( d_{90} \) in Fig. 3) and depends non-linearly on the coating macroporosity \( \varepsilon c,M \) [58]. For example, an increase of the macroporosity from 20% to 30% increases the coating permeability by a factor of 4.4. The highest pressure loss is observed in the \( d_{90} = 6 \) & 20 \( \mu m \) sample. Its on-wall layer in the scanned channel seems similarly thick than \( d_{90} = 12 \) \( \mu m \) (Fig. 12), however, the amount of coating in Table 2 obtained by weighing the samples shows ca. 20% higher catalyst loading in the sample \( d_{90} = 6 \) & 20 \( \mu m \) compared to the sample \( d_{90} = 12 \) \( \mu m \). Therefore we can expect that an average channel of the sample \( d_{90} = 6 \) & 20 \( \mu m \) contains a thicker washcoat layer than detected in the studied channel during the local XRT scan, and/or the internal porosity of \( d_{90} = 6 \) & 20 \( \mu m \) layer is lower. Smaller particles can fill the pores in between the larger ones, leading to somewhat decreased internal porosity and pore-size of the coating, which then limits its permeability. Furthermore, in comparison to \( d_{90} = 12 \mu m \) layer, the coating of \( d_{90} = 6 \) & 20 \( \mu m \) contains smaller cracks.

To verify the presumed internal structure of the coated layer, the samples were further analyzed by mercury intrusion porosimetry (MIP), see Fig. 14. Three main peaks can be detected in the complete range of pore sizes: (i) large pores of the filter substrate with a maximum around 20 \( \mu m \), (ii) washcoat macropores with a maximum around 1–2 \( \mu m \), and (iii) washcoat mesopores with a maximum around 10 \( nm \), see Fig. 14a. In the presence of the washcoat, the porosity of the substrate decreases as certain parts of its large pores become filled by the in-wall washcoat. The range of macropores inside the washcoat is shown in detail in Fig. 14b. The results confirm that the internal macroporosity (corresponding to the integral under the curve) and mean pore size are by far the highest for the washcoat \( d_{90} = 20 \) \( \mu m \). Both macroporosity and mean

![Fig. 13. Pressure loss in the coated filter samples depending on gas space velocity.](image-url)

![Fig. 14. Pore size distribution of bare and coated filter samples obtained by MIP: a) complete range, b) detail of washcoat macropore range.](image-url)

| Sample | Coating macroporosity \( \varepsilon c,M \) (%) | Mean macropore size (nm) |
|--------|-----------------------------------------|--------------------------|
| 6 \( \mu m \) | 19.4 | 1274 |
| 12 \( \mu m \) | 26.7 | 1399 |
| 6 & 20 \( \mu m \) | 26.0 | 1347 |
| 20 \( \mu m \) | 37.6 | 1856 |
Macropore size are noticeably lower for $d_{90} = 6$ & $20 \, \mu m$. Generally, the washcoat porosity and pore size decrease with the particle size in the slurry, the lowest being observed for $d_{90} = 6 \, \mu m$, Fig. 14b.

The corresponding values of internal macroporosity and mean macropore size are given in Table 4. The values were obtained by integration of the MIP curves [36], considering the pores in the range from $d_{pore} = 50\, \text{nm}$ to $d_{pore} = 5 \, \mu m$ and the actual substrate and coating weight. The pore size limit of $5 \, \mu m$ was selected as a boundary between the internal macropores in the coating and large pores present in the bare substrate, see Fig. 14. The numbers in Table 4 confirm a superior internal macroporosity and mean pore size of the washcoat $d_{90} = 20 \, \mu m$. The coating $d_{90} = 6 \, \mu m$ possesses clearly the lowest internal macroporosity but the calculated mean macropore size differs from the sample $d_{90} = 12 \, \mu m$ only by a relatively small amount. This is explained by the shape of the pore size distribution curve for the sample $d_{90} = 6 \, \mu m$ in Fig. 14b: it shows a maximum around $d_{pore} = 500 \, \text{nm}$, corresponding to macropores between the closely packed catalyst particles in compact domains, and then a wide range of larger pore sizes that include microcracks as well as partially filled substrate pores, which increases the evaluated mean macropore size.

Macroporosity and mean macropore sizes detected by MIP in the coatings $d_{90} = 12 \, \mu m$ and $d_{90} = 6$ & $20 \, \mu m$ seem close to each other, with only slightly higher values for the sample $d_{90} = 12 \, \mu m$. However, according to the Carman-Kozeny equation (1), even such a small difference in the macroporosity ($\varepsilon_{\text{M}}$ in Table 4) and mean particle size ($d_{p}$ in Fig. 3) results in ca. 20% higher permeability of the coating $d_{90} = 12 \, \mu m$ compared to that of $d_{90} = 6$ & $20 \, \mu m$, see Table 5. Considering the possible experimental error of the coating porosity evaluated from the MIP analysis, even larger variation of the coating permeability between the samples $d_{90} = 6$ & $20 \, \mu m$ and $d_{90} = 12 \, \mu m$ cannot be excluded. A significantly lower permeability of $d_{90} = 6$ & $20 \, \mu m$ would be also in line with the slow drying of this sample in the second period (compare the slopes of the coating volume curves in Fig. 11c and the residual mass of water in Table 2). The sample $d_{90} = 6$ & $20 \, \mu m$ also possesses 20% higher catalyst loading and less cracks that noticeably affect the effective permeability [29]. All these effects contribute to the significantly higher pressure loss of the sample $d_{90} = 6$ & $20 \, \mu m$ compared to $d_{90} = 12 \, \mu m$ as observed in Fig. 13. The predictions in Table 5 further confirm very high permeability of the coating $d_{90} = 20 \, \mu m$ that leads to a relatively low pressure drop despite its considerable thickness. A very low permeability is predicted for the coating $d_{90} = 6 \, \mu m$, but this sample exhibits a non-compact on-wall layer with numerous cracks and open wall pores that allow gas to by-pass the coating, which enables the low pressure drop.

### Table 5

| Sample | Coating permeability $\varepsilon$ (m$^2$) |
|--------|------------------------------------------|
| 6 \, \mu m | $7.61 \times 10^{-16}$ |
| 12 \, \mu m | $1.14 \times 10^{-14}$ |
| 6 & 20 \, \mu m | $9.40 \times 10^{-15}$ |
| 20 \, \mu m | $9.46 \times 10^{-14}$ |

Theoretical permeability of the coating without cracks calculated from Carman-Kozeny equation (1), using internal macroporosity of the coating $\varepsilon_{\text{M}}$ from MIP (Table 4) and mean catalyst particle size from laser diffraction granulometry ($d_p = d_{90}$ in Fig. 3).

### Conclusion

In this paper we studied the washcoating of monolith filters with honeycomb structures by time-resolved XRT. The results were supplemented by cross-section SEM images and MIP analysis of the final structures. Several alumina washcoats with different particle size distributions from $d_{90} = 6 \, \mu m$ to $d_{90} = 20 \, \mu m$ were examined. The observed evolution of in-wall pore filling and on-wall layer thickness revealed reversible transport of water between these two regions driven by capillary forces as well as separation of water from the catalyst particles. The layer formed from the smallest particles ($d_{90} = 6 \, \mu m$) showed the highest relative change of its volume during drying, the highest tendency to crack, and the lowest final macroporosity. On the other hand, the in-wall coating fraction was the highest (approx. 60% of the catalyst inside the wall) and the absence of a compact on-wall layer enabled the lowest pressure drop of this sample. When the slurries of $d_{90} = 12 \, \mu m$ and larger were employed, the coating was not able to penetrate that much into the wall and a compact on-wall layer was formed. In this case, the pressure drop was controlled mainly by the on-wall layer thickness, its internal macroporosity and macropore size. The highest internal macroporosity and the largest macropores (beneficial for permeability) were achieved with the $d_{90} = 20 \, \mu m$ coating, however, the thickest layer was formed on the wall. Still, the pressure drop of the $d_{90} = 20 \, \mu m$ coating was similar to the $d_{90} = 12 \, \mu m$ coating with a thinner on-wall layer.

The minimum pressure loss was achieved after coating the small particles with $d_{90} = 6 \, \mu m$. However, when we consider the filtration efficiency and possible reactant slip at higher flow rates, the coating $d_{90} = 6 \, \mu m$ would be most probably the worst one [29,30]. The coating structure must balance these opposing demands and the preference depends on the configuration of the entire exhaust gas aftertreatment system as well as the engine calibration.

The presented reconstructed XRT datasets have been published open access at https://doi.psi.ch/detail/10.16907/2c501d81-99a4-4bce-a6de-765b86ede4ab and may be used in subsequent studies of coating and drying processes. The processed XRT images can be further exploited for the generation of computational meshes and subsequent pore-scale simulations of permeation, diffusion, reaction and filtration in the reconstructed catalytic filter [29,30,57]. This combination of advanced experimental and simulation techniques provides a useful feedback for further optimization of the washcoat structure and distribution in catalytic filters.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix 1. Temperature profiles

The evolution of temperature during the drying of re-wetted bare and coated ($d_{90} = 6 \, \mu m$) filter samples is shown in Fig. 15. Note that the length of the entire drying process, and particularly its first period is longer for the re-wetted sample due to the higher initial amount of water so that the time axis origin for the measured temperatures in Fig. 15 cannot be exactly compared to that of washcoating and drying experiment. Nevertheless, the results show several characteristics relevant to both cases. The initial heating from room temperature to the steady temperature of the first period takes approx. 2 min. The steady temperature during the first period of drying is ca. 50 °C, independent of the presence or absence of the washcoat in the filter. The bare filter then exhibits a relatively fast increase of temperature up to ca. 72 °C. The coated sample shows again different length of the first period due to different initial amount of water and, more importantly, much slower increase of temperature in the second period of drying. This indicates that the drying rate of water from internal washcoat pores is slowed down by diffusion limitations. The length of this period (approximately 900 s from $t = 1800 \, s$ to $t = 2700 \, s$ in Fig. 15) corresponds well to the period of the $d_{90} = 6 \, \mu m$ washcoat shrinking (approximately 900 s from $t = 500 \, s$ to $t = 1400 \, s$ in Fig. 11c). On the contrary, transport of water through the large pores of the filter wall does not limit the drying rate in our set-up, and practically all pores in the substrate wall are emptied during the first period of drying. The terminal temperature of the coated sample (approx. 75 °C) is slightly higher than that of the bare filter, which could be explained by an increased radial heat conductivity of the monolith due to the added coating.

Appendix 2. Coating uniformity along the channels

Additional SEM cross-section images covering a larger area of ca. 12 coated channels with a spatial resolution of 2.4 \mu m were acquired at different locations along the sample to check the coating uniformity. These SEM images were segmented by the simple thresholding into two phases: (i) solid phase, including substrate and coating, and (ii) void, including empty channel space and large uncoated pores inside the wall. The evaluated volume fraction of the solid phase revealed only a slight decrease of the coating amount along the channels, see Fig. 16. The
higher detected volume fraction of the coating in the sample \( d_0 = 20 \ \mu m \) is in line with its higher loading (Table 2) as well as the increased internal macroporosity of this washcoat (Table 4).

### Appendix 3. Segmentation

For comparison, the coating volume fraction in the final structures was evaluated by three different image processing methods: (i) trainable Weka segmentation [53] of the cropped XRT 3D images (as used in the main part of paper), (ii) simple thresholding of the cropped XRT 3D images, and (iii) simple thresholding of 2D SEM images, see Fig. 17. The resulting coating volume fractions and relative amounts of in-wall coating are summarized in Table 6 and Table 7, respectively. The simple thresholding of XRT images provides quick basic information about the coating amount and proportion of coating on or inside the filter wall, however, it can suffer from relatively low resolution of the XRT image, limited contrast between the coating and substrate (particularly inside the wall) and reconstruction artifacts. For example, the transient from bright substrate to dark pore may transform into a thin artificial layer of the wall) and reconstruction artifacts. For example, the transient from bright substrate to dark pore may transform into a thin artificial layer of the wall.

### Appendix 4. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/jcej.2020.128057 (videos). The reconstructed XRT datasets can be found at https://doi.org/10.16907/2c501d8-1-99a4-4bce-a6de-765b86ede4ab.

### References

[1] B. Guan, R. Zhan, H.e. Lin, Z. Huang, Review of the state-of-the-art of exhaust particulate filter technology in internal combustion engines, J. Environ. Manage. 154 (2015) 225–258.

[2] A. Joshi, T.V. Johnson, Gasoline Particulate Filters—a Review, Emis. Control Sci. Technol. 4 (4) (2018) 219–239.

[3] K. Yang, J.T. Fox, B. Hunmicker, Characterizing diesel particulate filter failure during commercial fleet use due to pinholes, melting, cracking, and fouling, Emis. Control Sci. Technol. 2 (3) (2016) 145–155.

[4] R. Allansson, P.G. Blakeman, B.J. Cooper, H. Hens, P.J. Silзcock, A.P. Walker, A. Walker, “Optimising the low temperature performance and regeneration efficiency of the continuously regenerating diesel particulate filter (CR-DPF) system,” SAE Technical Papers, pp. 2002-01-0428, 2002.

[5] M. Schebjal, J. Stepanek, M. Marek, P. Koci, M. Kubicek, Modelling of soot oxidation by NO2 in various types of diesel particulate filters, Fuel 89 (2010) 2365–2375.

[6] D. Fino, Diesel emission control: Catalytic filters for particulate removal, Sci. Technol. Adv. Mater. 8 (1-2) (2007) 93–100.

[7] G. Koltsakis, O. Haralampos, C. Depick, J. Rageone, “Catalyzed diesel particulate filter modeling,” Rev. Chem. Eng., vol. 29, pp. 1-61, 2013.

[8] V. Di Sarli, G. Landi, L. Lisi, A. Salvia, A. Di Benedetto, Catalytic diesel particulate filters with highly dispersed ceria: Effect of the soot-catalyst contact on the regeneration performance, Appl. Catal. B 197 (2016) 116–124.

[9] K. Rappe, Integrated selective catalytic reduction-diesel particulate filter aftertreatment: Insights into pressure drop, NOx conversion, and passive soot oxidation behavior, Ind. Eng. Chem. Res. 53 (2014) 7547–17557.

[10] T.C. Watling, M.R. Ravencroft, G. Avery, Development, validation and application of a model for an SCR catalyst coated diesel particulate filter, Catal. Today 188 (1) (2012) 32–41.

[11] M. Nasiri, C. Aydin, S. Molla, R. Conway, S. Chatterjee, Development of emission control systems to high NOx emissions on heavy duty diesel engines, SAE Int. J. Engines 8 (2015) 1144–1151.

[12] L. Cumsaranutunge, A. Chifley, J. Stetina, K. Mcgonigle, G. Repley, A. Lee, S. Chatterjee, A study of the soot combustion efficiency of an SCRF® Catalyst vs a CSF during active regeneration, Emis. Control Sci. Technol. 3 (3) (2017) 93–104.

[13] A. Beale, F. Gao, I. Leccano-Gonzalez, C. Peden, J. Scanyi, Recent advances in automotive catalysis for NOx emission control by small-pore microporous materials, Chem. Soc. Rev. 44 (2015) 7371–7405.

[14] E. Tronconi, I. Nova, F. Marchetti, G. Koltsakis, D. Karamitros, B. Maletic, N. Markert, D. Chatterjee, M. Hehe, Coating, interaction of NOx reduction and soot oxidation in a DPF with Cu-Zeolite SCR, Emis. Control Sci. Technol. 1 (2015) 154–151.

[15] J. Richter, R. Klinking, S. Spies, K-F. Wong, Application of catalyzed gasoline particulate filters to GDI vehicles, SAE Int. J. Engines 5 (2012) 1361–1370.

[16] Y. Ito, T. Shimoda, T. Aoki, Y. Kuyuki, H. Sakamoto, K. Kato, D. Thier, P. Kattouah, E. Ohara, C. Vogt, “Next Generation of Ceramic Wall Flow Gasoline Particulate Filter with Integrated Three Way Catalyst,” SAE Technical Papers, pp. 2015-01-1073, 2015.

[17] C. Lambert, T. Chanko, D. Dobson, X. Liu, J. Palako, Gasoline particle filter development, Emis. Control Sci. Technol. 3 (1) (2017) 105–111.

[18] H. Seong, S. Choi, S. Lee, N.J. Zaluzec, T.J. Toops, M.J. Lance, D. Kim, K. Nguyen, Origin of the continuously regenerating diesel particulate filter (CR-DPF) system, Ind. Eng. Chem. Res. 57 (2018) 7840–7846.

[19] P.S. Lambrou, C.N. Costa, C.Y. Christou, A.M. Efratiadhas, Dynamics of oxygen storage and release on commercial aged Pel-Rh three-way catalysts and their characterization by transient experiments, Appl. Catal. B 54 (4) (2004) 237–250.

[20] N.R. Collins, M.V. Twigg, Three-way catalyst emission control technologies for spark-ignition engines—recent trends and future developments, Top. Catal. 42-43 (1-4) (2014) 323–332.

[21] J. Wang, H. Chen, Z. Hu, M. Yao, Y. Li, A review on the Pel-based three-way catalyst, Catal. Rev. 57 (2015) 79–144.

[22] T. Nijhuis, A. Beers, T. Vergunft, I. Hoek, F. Kaptanj, J. Moulijn, Preparation of monolithical catalysts, Catal. Rev. 43 (2001) 345–380.

[23] P. Avila, M. Montes, E. Miro, Monolithic reactors for environmental applications: A review on preparation technologies, Chem. Eng. J. 109 (2005) 11–36.

[24] V. Meille, Review on methods to deposit catalysts on structured surfaces, Appl. Catal. A 315 (2006) 1–17.

[25] C. Cristiani, C. Vicconti, E. Finocchio, P. Stampino, P. Forzatti, Towards the rationalization of the washcoating processing conditions, Catal. Today 147 (2009) S24–S29.

[26] D. Aderhold, A.G. Haynes, M.L.W. Spencer, D.J.W. Winterborn, “Monolith coating apparatus and method therefor,” Patent US 6595570, 2003.

[27] M. Foerster, E. Dittrich, E. Birgith, W. Leihold, B. Bergner, M. Hoffmann, W. Hassemlmann, R. Schaefer, “Process for the coating of the flow channels of a honeycomb form catalytic converter carrier with a dispersion coating,” Patent US 6149973, 2000.

[28] T. Schmiedock, B.D. Taylor, J.M. Collins Jr., “Method of impregnating ceramic monolith structures with predetermined amounts of catalyst,” Patent US 4550034, 1985.

[29] P. Koch, M. Iroz, M. Plachà, A. Arvájova, M. Vacílová, M. Svoboda, E. Price, V. Novak, D. Thompson, 3D reconstruction and pore-scale modeling of coated
catalytic filters for automotive exhaust gas aftertreatment, Catal. Today 320 (2019) 165–174.

[30] M. Plachá, P. Koci, M. Izo, M. Svoboda, E. Price, D. Thompson, K. Kallios, A. Toslakis, Pore-scale filtration model for coated catalytic filters in automotive exhaust gas aftertreatment, Chem. Eng. Sci. 226 (2020), 115854.

[31] A. Greiner, T. Prill, O. Bieb, B. van Sefien, M. Votsmeier, Tomography based simulation of reactive flow at the micro-scale: Particulate filters with wall integrated catalyst, Chem. Eng. J. 378 (2019), 121919.

[32] I. Belot, D. Vidal, M. Votsmeier, R. Hayes, F. Bertrand, Numerical investigation of the impact of washcoat distribution on the filtration performance of gasoline particulate filters, Chem. Eng. Sci. 221 (2020), 115656.

[33] C. Kamp, S. Zhang, S. Bagi, V. Wong, G. Monahan, A. Sappok, Y. Wang, Ash permeability determination in the diesel particulate filter from ultra-high resolution 3D X-ray imaging and image-based direct numerical simulations, SAE Int. J. Fuels Lubr. 10 (2017) 608–618.

[34] K. Yamamoto, T. Sakai, Simulation of continuously regenerating trap with catalyzed DPF, Catal. Today 216 (2013) 1–142.

[35] P. Lura, Visualization of water drying in porous materials by X-ray phase contrast imaging, J. Microsc. 261 (2016) 88–104.

[36] J. Jimenez-Martinez, K. Dobson, M. Stampani, Time resolved in situ X-ray tomographic microscopy unraveling dynamic processes in geologic systems, Front. Earth Sci. 7 (2020) 346.

[37] F. Yang, M. Griffs, A. Bonnin, R. Mokso, C. Di Bella, B. Münch, R. Kaufmann, P. Lura, Visualization of water drying in porous materials by X-ray phase contrast imaging, J. Microsc. 261 (2016) 88–104.

[38] S. Berg, H. Ott, S. Klapp, A. Schwing, R. Nietieler, N. Brussee, A. Makurat, L. Leu, F. Enzmann, J.-O. Schwarz, M. Kersten, S. Irvine and M. Stampani, ‘Real-time 3D imaging of Haines jumps in porous media flow,’ Proc. Natl. Acad. Sci. USA, 2011, pp. 3755–3759, 2013.

[39] F. García-Moreno, P. Kamm, T. Neu, F. Bülk, R. Mokso, C. Schlepütz, M. Stampani, J. Banhart, Using X-ray tomoscopy to explore the dynamics of foaming metal, Nat. Commun. 10 (2019) 3762.

[40] A. Messager, A. Junet, T. Palin-Luc, J.-Y. Bulpilfer, N. Saintier, N. Ranc, M. El May, Y. Gaillard, A. King, A. Bonnin, Y. Nadot, In situ synchrotron ultrasonic fatigue testing device for 3D characterisation of internal crack initiation and growth, Fatig Fract. Eng. Mater. Struct. 43 (2020) 558–567.

[41] R. Mokso, C. Schlepütz, G. Theidel, H. Billich, E. Shmid, T. Celer, G. Mikuljan, L. Sala, F. Marone, N. Schlumpf, M. Stampani, GigaFluoST: The gigabit fast readout system for tomography, J. Synchrotron Radiat. 24 (2017) 1250–1259.

[42] D. Haberthür, C. Hintermüller, J. Marone, C. Schütt, M. Stampani, Radiation dose optimized lateral expansion of the field of view in synchrotron radiation X-ray tomographic microscopy, J. Synchrotron Radiat. 17 (2010) 590–599.

[43] D. Paganin, S.C. Mayo, T.E. Gureyev, P.R. Miller, S.W. Wilkins, Simultaneous phase and amplitude extraction from a single defocused image of a homogeneous object, J. Microsc. 206 (2002) 33–40.

[44] F. Marone, M. Stampani, Regriddng reconstruction algorithm for real time tomographic imaging, J. Synchrotron Radiat. 19 (2012) 1029–1037.

[45] C. Schneider, W. Rasband, K. Eliceiri, NIH image to ImageJ: 25 years of image analysis, Nat. Methods 9 (2012) 671–675.

[46] J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J.-Y. Tinevez, D. White, V. Hartenstein, K. Elieci, P. Tomancak, A. Cardona, Fiji: an open-source platform for biological-image analysis, Nat. Methods 9 (2012) 676–682.

[47] I. Arganda-Carreras, V. Kaynig, C. Rueden, Trinable Weka Segmentation: a machine-learning tool for microscopy pixel classification, Bioinformatics 33 (2017) 2424–2426.

[48] A. Parslow, A. Cardona, R. Bryon-Richardson, Sample drift correction following 4D confocal time-lapse imaging, J. Visual. Exp. 86 (2014) 51086.

[49] M. Gálvez, S. Arco, I. Tohmas, R. Móller, M. Lázaro, Catalytic filters for the simultaneous removal of soot and NOx: Influence of the alumina precursor on monolith washing and catalytic activity, Catal. Today 191 (2012) 96–105.

[50] G. Tarì, J. Ferreira, A. Fonseca, O. Lyckfeldt, Influence of particle size distribution on colloidal processing of alumina, J. Eur. Ceram. Soc. 18 (1998) 249–253.

[51] M. Leskovjan, J. Nincic, M. Marek, Effect of cavities on catalytic activity of monolith washcoating and catalytic activity, Catal. Today 191 (2012) 96–105.

[52] E. Price, D. Thompsett, Multi-scale modeling and analysis of pressure drop in the impact of washcoat distribution on the filtration performance of gasoline particulate filters, Catal. Today 378 (2019), 121919.

[53] A. Parslow, A. Cardona, R. Bryon-Richardson, Sample drift correction following 4D confocal time-lapse imaging, J. Visual. Exp. 86 (2014) 51086.

[54] M. Gálvez, S. Arco, I. Tohmas, R. Móller, M. Lázaro, Catalytic filters for the simultaneous removal of soot and NOx: Influence of the alumina precursor on monolith washing and catalytic activity, Catal. Today 191 (2012) 96–105.

[55] G. Tarì, J. Ferreira, A. Fonseca, O. Lyckfeldt, Influence of particle size distribution on colloidal processing of alumina, J. Eur. Ceram. Soc. 18 (1998) 249–253.

[56] M. Leskovjan, J. Nincic, M. Marek, Effect of cavities on catalytic activity of monolith washcoating and catalytic activity, Catal. Today 191 (2012) 96–105.