

xD+1D Catalyst Simulation-A Numerical Study on the Impact of Pore Diffusion

Wilfried Edelbauer, Susanne Kutschi and Johann C. Wurzenberger
AVL LIST GmbH

ABSTRACT

This paper presents a numerical study on the impact of washcoat diffusion on the overall conversion performance of catalytic converters. A comprehensive transient 1D pore diffusion reaction model is embedded in state-of-the-art 1D and 3D catalytic converter models. The pore diffusion model is discussed with its model equations and the applied diffusive transport approaches are summarized. The diffusion reaction model is validated with the help of two available analytical solutions. The impact of basic washcoat characteristics such as pore diameters or thickness on overall conversion performance is investigated by selected 1D+1D calculations. This model is also used to highlight the impact of boundary layer transfer, pore diffusion and reaction on the overall converter conversion performance. The interaction of pore diffusion and flow non-uniformities is demonstrated by 3D+1D CFD simulations.

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INTRODUCTION

The worldwide trend towards more stringent emission limits is a steady driving force to search for new propulsion concepts and to optimize existing powertrains. Besides measures within the combustion engine to directly reduce its raw emissions the application of appropriate exhaust aftertreatment systems is indispensable to meet future emission limits. Comprehensive Diesel exhaust systems typically consist of a variety of dedicated components such as DOCs, DPFs and urea-SCRs. The increased number of individual components, their interaction with each other and also their control is a major challenge in developing modern exhaust aftertreatment systems. In addition, the increasing size of overall aftertreatment systems constitutes a challenge in view of packaging constraints, thermal operation and finally also cost.

One promising approach to comply with packaging constraints and the need for thermal fast responding exhaust systems is the integration of multiple catalytic functionalities within common exhaust devices. Here at least three different technologies are successfully pursued. The application (1) of catalytic coatings within DPFs (see [Figure 1c, d](#)) has been done for many years (see Konstandopoulos et al. [1] or Pfeiffer et al. [2]). Apart from oxidation functionalities to support the passive soot regeneration, special focus is put on deNOx capabilities within DPFs. They are either realized by NOx storage coatings (see Mizuno and Suzuki [3]) or by

applying SCR coatings (see He et al.[4]) where the adsorption of ammonia is an essential characteristic. The application (2) of zone-coatings as sketched in [Figure 1a, c](#) is based on different coatings distributed over the axial catalyst/DPF length and therefore integrates multiple functionalities within one common substrate in a sequential manner. An example for this is the catalytic support of the hydrolysis reaction at the inlet of the SCR converter. Another zone coating application targets to optimize the NO/NO₂ ratio entering SCR catalysts. It is well known that the SCR conversion performance deteriorates when the inlet NO₂ fractions exceed the NO fractions (see Chandler et al. [5]). Thus, the oxidation of NO to NO₂ can be optimized with the help of e.g. zone coated DPF outlet channels of the right zone length. The application (3) of layered coatings as sketched in [Figure 1b, d](#) is based on different coatings lying upon each other. This allows the combination of multiple catalytic functions at the same spatial position within a substrate. Here the ammonia slip catalyst (see Votsmeier [6]) is an example where an oxidation catalyst layer is positioned underneath an SCR catalyst layer. With this technique, NOx produced by the oxidation of ammonia is further catalytically reduced in the SCR layer during its diffusive way back to the gas bulk.

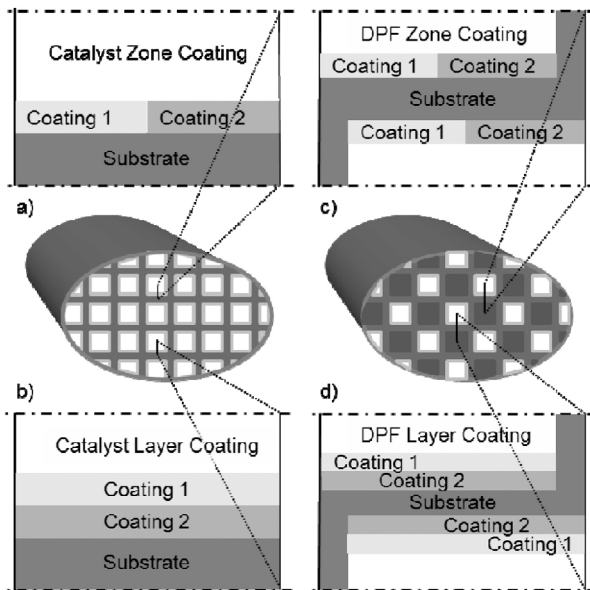


Figure 1. Variants of layered and zoned coatings in catalyst and DPFs

The application of zoned or layered catalyst washcoat technologies opens significant room for optimization taking into account all operating conditions of IC engines. Here numerical modeling as a complementary tool to experimental investigations, helps to take basic design decisions, and consequently to shorten the development process. It is also well known that numerical simulation itself can be expensive and time consuming. Therefore it is the more important to apply the appropriate modeling depth, depending on the simulation goal. 3D CFD models (see Ottaviani et al. [7]) are typically used to study real-live aftertreatment geometries. 3D models are applied to investigate the impact of radially non uniform flow patterns in catalytic converters regarding the spatial distribution of temperature, species, urea droplet transport, evaporation, etc. Once the flow uniformities are optimized, 1D models are an appropriate choice to investigate different exhaust line component configurations, sizes and operating strategies, e.g. urea dosing, HC dosing, etc., during transient driving conditions typically given by various legislation cycles. 1D models of e.g. Diesel exhaust lines, from single DOCs up to comprehensive systems of DOC-Pipe-DPF-Pipe-Injector-Pipe-SCR-Pipe, typically can be simulated with real-time factors of 0.05 up to 0.9 (see Henrichsen [8]). This does not only allow performing hundreds/thousands of single simulations within reasonable overall times as it might be required for kinetic parameter optimization, the computational speed of 1D approaches also enables the integration of aftertreatment models in full engine and vehicle simulations (see Wurzenberger et al. [9]). Such system engineering models are mandatory e.g. to investigate aftertreatment performance during cold starts induced by start-stop control strategies of modern HEV configurations. The gap between 1D and 3D simulation models can be

bridged by establishing workflows, where e.g. kinetic parameters gained from numerical efficient 1D calibration simulations are reused in detailed 3D CFD simulations. The necessary precondition allowing such workflows is a thorough implementation of identical physical and chemical models in both the 1D and 3D code. Following this essential requirement, this work emphasizes comparison simulations proving a seamless parameter transfer from 1D to 3D without introducing systematic errors.

In literature the modeling approaches used to describe catalytic converters, as discussed later in this work, have reached a common point in the trade-off between required modeling depth and reasonable corresponding computational effort. According to the comprehensive overview of Depcik and Assanis [10] transient 1D models are most commonly used to capture all relevant effects taking place within one single channel of a honeycomb type catalytic converter. Nevertheless the area of reaction diffusion modeling describing the washcoat shows the broadest diversification of modeling approaches. Models reach from simplifying effectiveness considerations to transient fully 3D resolved simulations. Strictly considered, the application of effectiveness factors, as derived by Thiele (see Froment and Bishoff [11]), only applies for one single reaction of first order in an isothermal system. Nevertheless the simplicity of the effectiveness concept inspired several research groups to extend the base idea to catalysts operated under real conditions. Tavera [12] presented an analytical study to consider non-isothermal n^{th} order reactions. Dadvar and Sahimi [13] performed a theoretical analysis considering a reaction rate with inhibition terms (Michaelis-Menten rate). A numerical approach to calculate the effectiveness of slab geometries was published by Kim and Lee [14]. Considering the typical washcoat shape in squared channels Hayes and Kolaczowski [15] applied a 3D resolved washcoat model as a part of a 3D single channel model. Non-uniformities of the spatial washcoat distribution and their impact on overall effectiveness were investigated by Padadias et al. [16] and Hayes et al. [17] using numerical 3D studies. The computational times of such comprehensive 3D studies can be significantly shortened by reducing the modeling dimensions considered in the washcoat. Dieterich [18] presented a "1D+1D model". Assuming that in the washcoat the gradients of the species concentration in axial direction are small compared to the gradients in perpendicular direction, a series of 1D models can be applied along the axial discretization. The same approach is applied by Massing et al. [19] for a steady-state regime. One key feature of this approach lies in the similarity of the different dimensions. Thus, for single catalyst channels as well as for the porous washcoat the same type of conservation equation (transient, 1D, gaseous and solid phases) is applied. Wurzenberger et al. [20] e.g. uses this concept to model spherical porous 1D pellets in a 1D reactor model.

With the goal to investigate the impact of pore diffusion on catalyst conversion performance, this study presents a comprehensive 1D pore diffusion reaction model. The model is used within two different catalyst simulation environments. First, the model is embedded in the 1D single channel model of the simulation package AVL BOOST [21] representing the 1D+1D tool. Second, it is combined with the available aftertreatment simulation capabilities of the 3D CFD framework AVL FIRE [22] representing the 3D+1D simulation tool.

MODEL

From the modeling point of view the comprehensive catalyst model used in this study can be divided into two main areas. The first area deals with the applied single channel model (SCM), and its key characteristics are discussed. In the second area the applied 1D pore diffusion reaction model as complement to the SCM is presented by its governing equations and the chosen pore transport models.

SINGLE CHANNEL MODEL IN 1D AND 3D

Honeycomb type catalytic converters are typically made of ceramic or metal substrates and consist of a huge number of individual parallel channels with the goal to provide the greatest possible exchange surface between exhaust gas and solid surface. This surface is supposed to support heterogeneous catalytic reactions taking place at active sites, e.g. noble metals, dispersed within the wall washcoat layers. Figure 2 sketches the base effects of a heterogeneous catalytically driven reaction in a catalytic converter. As discussed by Froment and Bischoff [11], Hayes and Kolaczkowski [23] and others the following steps can be distinguished:

- Transport of the reactants from the bulk gas phase to the solid surface across the boundary layer (1)→(2), and from the surface back to the bulk gas (6)→(7)
- Diffusion of the reactants from the surface into the washcoat material (2)→(3) and vice versa (5)→(6)
- Adsorption of the reactants at the active site (3)→(4), catalytic reaction and desorption of the products (4)→(5)

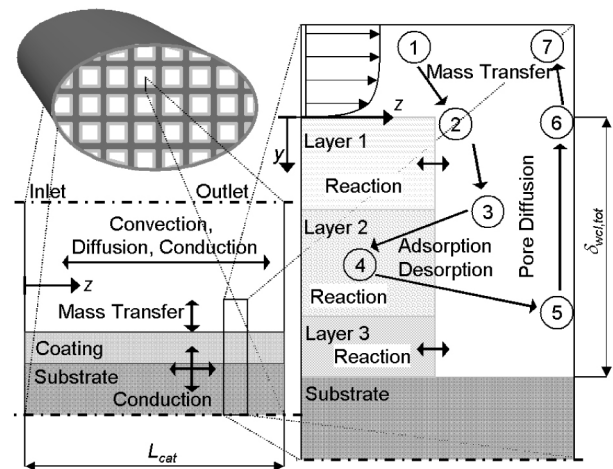


Figure 2. Transport effects in a square cell catalyst with washcoat layers

Simulation models for honeycomb type catalytic converters have been developed for many years. Single channel models feature a broad variety modeling depths. They reach from simplifying isothermal steady-state 1D models with constant convection dominated flow (see Wendland [24]) to transient 3D models fully resolving the channel flow including the washcoat (see Wanker et al. [25]). The SCM used in the present study (see Wurzenberger et al. [26]) covers the following base effects:

- The bulk flow of mass, energy and species is described by transient 1D balances covering convective and diffusive transport for laminar and turbulent flow conditions.
- Heat and mass transfer through the boundary layer are described by empirical Nusselt and Sherwood number correlations.
- Washcoat diffusion is described either by effectiveness factors or by a detailed 1D diffusion model, as it is described in the next section.
- Chemical conversion or surface storage reactions take place within the washcoat.
- Depending on the operating temperatures, homogeneous gas phase reactions are considered.
- Axial heat condition in the substrate is covered by transient 1D heat balance equations.
- Radial heat losses or sources from electro-heating are modeled by a transient 2D conduction/radiation/convection model.
- Gas properties depend on pressure, temperature and composition. Solid properties depend on temperature.

The consideration of the above listed phenomena for one single channel can be summarized as transient 1D model. Assuming that radial gradients over an entire catalytic

converter are negligible, the SCM is sufficient to represent the entire converter. For configurations where at the catalyst inlet circumferential and radial non-uniformities of mass, temperature or species composition cannot be ignored the SCM is embedded into a 3D CFD package. The radial distribution and overall number of SCMs follows the resolution of the 3D mesh in the specifically assigned catalyst domain. This highly resolved approach is enabled by the numerically efficient SCM solver. The integration of the SCM into CFD simulations additionally facilitates the investigation of the interaction of pressure drops induced by catalytic converters on the flow distribution at its upstream/inlet side. One essential characteristic of sub-sonic (elliptic) flows-as it is resolved by CFD-is that flow disturbances located downstream have influence on the upstream flow field. This fact is contrary to the often applied practice of assuming a fixed spatial flow distribution at the catalyst inlet independent of the downstream the flow field.

PORE DIFFUSION IN 1D

Model Description/Assumptions

In many catalytic converter models the effects of pore diffusion are neglected. Theoretically, this simplification is only valid for unlimited diffusion meaning that pore diffusion is so fast (or all other reaction steps of Figure 2 are so slow) that every reactant and every product is uniformly distributed over the whole washcoat layer. For real catalyst configurations and operating conditions errors produced by neglecting pore diffusion have to be compensated. In general this is done either by introducing scaling factors on the boundary layer mass transfer model or by applying correction/effectiveness factors on the kinetic parameters of the chemical reactions. Both correction approaches fail for multi-layer coating configurations. Here, the products of the upper layer(s) influence reactants of the lower layer and vice versa. For describing such effects the transport of the species through the washcoat layers must be modeled by adequate pore diffusion approaches. The model presented in this study can be seen as a complement to the SCM and follows the concept of Dieterich [18]. It can be summarized as an xD+1D approach where an existing xD (1D or 3D) catalyst converter model is extended by a transient 1D model resolving all phenomena taking place locally within the washcoat.

In order to model pore diffusion an additional model dimension in direction perpendicular to the channel axis is necessary. As shown in Figure 2 this direction is called *y*-direction. The model considers an arbitrary number of washcoat layers. Every washcoat layer can be assigned an own transport and reaction model. In addition to the SCM characterization discussed above, the pore diffusion models feature the following effects and assumptions:

- The gas temperature T_g throughout the washcoat in *y*-direction is uniform, and it is identical to the calculated substrate temperature T_s .
- Pressure gradients in *y*-direction are neglected.

- Species diffusion through the washcoat layers is the only transport mechanism in *y*-direction and convective transport is neglected.

- Diffusive transport in axial channel direction (*z*-direction) is not accounted for, and thus a 1D model is applied.

- Species diffusion in the blank substrate of the monolith is ignored since the ceramic substrate is assumed to be catalytic inert.

- Transport of the species from the bulk gas to the solid surface ($y=0$) across the boundary layer is modeled via a Sherwood number based mass transfer correlation.

The main benefit of the xD+1D approach compared to complete 3D modeling of the washcoat is the significantly reduced computational effort. The effect of circumferential washcoat thickness variation can be considered in lumped manner by a mean washcoat layer thickness.

Balance Equations

The balance equation for species *k* within the washcoat layer is described by

$$\varepsilon_{wcl} \cdot \frac{\partial (\rho^L \cdot w_k^L)}{\partial t} = \frac{\partial}{\partial y} \left(D_{eff,k} \cdot \rho^L \cdot \frac{\partial (w_k^L)}{\partial y} \right) + M_k \cdot \sum_i v_{i,k} \cdot \bar{r}_i(c_k^L, T_s) \quad (1)$$

where ε_{wcl} is the porosity (gas void fraction) of the considered washcoat layer. ρ^L is the density of the gas mixture in the washcoat layer, and w_k^L is the mass fraction of species *k*. The left hand side describes the transient change of mass of species *k* in the washcoat layer. The first term on the right hand side represents diffusive species transport according to Fick's law. In general, in a porous medium the molecular movement is hindered by the solid walls resulting in a higher diffusion resistance and longer diffusion paths. This is covered in the model by applying an effective species diffusion coefficient $D_{eff,k}$. As discussed later, effective diffusion is described in literature by a broad variety of different diffusion models. The second term on the right hand side represents species sources/sinks due to chemical reactions. M_k is the molecular weight of species *k*, $v_{i,k}$ is the stoichiometric coefficient of species *k* in reaction *i* and $\bar{r}_i$ is the reaction rate per unit volume washcoat typically depending on species concentration c_k^L and substrate temperature T_s .

The boundary condition at the solid surface ($y=0$) is determined by the balance of diffusive flux and mass transfer through the boundary layer from the bulk gas to the solid surface and vice versa. This is described by the equation following steady-state mass balance equation, which yields

$$D_{\text{eff},k} \cdot \rho^L \cdot \frac{\partial (w_k^L)}{\partial y} = k_{m,k} \cdot (\rho^L \cdot w_k^L - \rho^B \cdot w_k^B) \quad @ \quad y = 0 \quad (2)$$

$k_{m,k}$ is the mass transfer coefficient of the individual species k , ρ^B is the bulk gas density, and w_k^B is the mass fraction of the species in the bulk gas. The second boundary condition at the total washcoat layer thickness ($y = \delta_{\text{wcl,tot}}$) is simply described by

$$\frac{\partial w_k^L}{\partial y} = 0 \quad @ \quad y = \delta_{\text{wcl,tot}}, \quad (3)$$

leading to no diffusive flux out of the last washcoat layer.

Reaction Rate Formulation

Special attention has to be paid on the reaction term used in Equation (1). It is common practice in literature (see Dubien et al. [27] or Koltsakis and Stamatelos [28]) to specify kinetic parameters and consequently reaction rates related to geometrical surface area of the catalyst surface in the unit (kmol/(s·m²_cat)). An absolute reaction rate in (kmol/s) is simply obtained by multiplying the surface specific rate with the geometrical surface area a_{trans} and the discretized catalyst volume V_{cat} . This is given by

$$\dot{\bar{r}}_i = \tilde{\bar{r}}_i \cdot \underbrace{a_{\text{trans}}}_{(\text{m}_{\text{cat}}^2/\text{m}_{\text{cat}}^3)} \cdot \underbrace{V_{\text{cat}}}_{(\text{m}_{\text{cat}}^3)} \quad (4)$$

Surface specific rates do not directly apply in pore diffusion reaction models. Here volume specific rates are favored simply because of the lacking information on reaction surfaces within the washcoat. This correlation is described by

$$\dot{\bar{r}}_i = \tilde{\bar{r}}_i \cdot \underbrace{V_{\text{wcl}}}_{(\text{m}_{\text{wcl}}^3)} \quad (5)$$

where V_{wcl} represents the volume of the washcoat layer. In the literature often surface specific kinetic parameters are published. With the goal to keep and apply these parameters in the volume based pore diffusion model a simple transformation can be introduced. This avoids recalculating kinetic parameters and allows a more efficient comparison of different catalyst models. By equalizing Equations (4) and (5) a correlation between the volume and surface specific rate formulations can be obtained. This is given by the equation

$$\tilde{\bar{r}}_i = \tilde{\bar{r}}_i \cdot a_{\text{trans}} \cdot \left(\frac{V_{\text{cat}}}{V_{\text{wcl}}} \right) = \tilde{\bar{r}}_i \cdot a_{\text{trans}} \cdot \left(\frac{1}{\chi_{\text{ref}}} \right), \quad (6)$$

where χ_{ref} is introduced as ratio of washcoat layer volume to the total substrate volume. As discussed later it is an important input parameter when using surface specific kinetic parameters and comparing catalysts of different washcoat thicknesses. Applying some geometric consideration for squared channel geometries, it can be calculated for each washcoat layer according to the equation

$$\chi_{\text{ref,lay}} = \frac{V_{\text{wcl,lay}}}{V_{\text{cat}}} = 4 \cdot \text{CPSM} \cdot \delta_{\text{wcl,lay}} \cdot \left(d_h + 2 \cdot \sum_{i=1}^{\text{lay}-1} \delta_{\text{wcl},i} + \delta_{\text{wcl,lay}} \right), \quad (7)$$

where CPSM equals CPSI/0.0254², $\delta_{\text{wcl,lay}}$ is the thickness of the individual washcoat layer and d_h represents the channel diameter. For multi-layer simulations χ_{ref} has to be calculated for every washcoat layer separately leading to $\chi_{\text{ref,lay}}$.

However, this is only one aspect, since χ_{ref} determines also the washcoat layer volume (thickness) for which surface specific kinetic parameters are valid. If the same set of surface specific kinetic parameters is applied for changing washcoat volumes (thicknesses), only one value of χ_{ref} leads to identical overall conversion rates in the absence of pore diffusion limitations. Thus, χ_{ref} can be interpreted as a reciprocal measure of the noble metal density in the washcoat layer volume, as described in the following example.

Figure 3 shows three catalysts A, B, and C with different washcoat layer coatings. Species conversion is only considered in the “DOC” coating. Unlimited diffusion is assumed and the same set of surface specific kinetic parameters for the DOC reactions is applied for all three catalysts. It is assumed that Equation (1) is solved for all species and the conversion of species k , e.g. C₃H₆ is compared. Catalyst A has one coating of volume V_δ and catalyst B has a thicker coating of $2 \cdot V_\delta$. Catalyst C also has a DOC coating of volume V_δ whereas a further coating called INERT of volume V_δ is present. It is assumed that in the coating INERT only diffusion takes place but no chemical reactions. With the assumption made above, it can be expected that the converted C₃H₆ in catalyst B is two times larger than that in catalyst A. Catalyst C should convert the same amount of C₃H₆ as catalyst A. For all three configurations Equation (7) is applied to obtain the reference volumes $\chi_{\text{ref,DOC-A}}$, $\chi_{\text{ref,DOC-B}}$, and $\chi_{\text{ref,DOC-C}}$, respectively. Due to the geometrical configuration the specific reference volume of catalyst A and C are identical, and that of B is twice as large. With these values the conversion of C₃H₆ can be calculated.

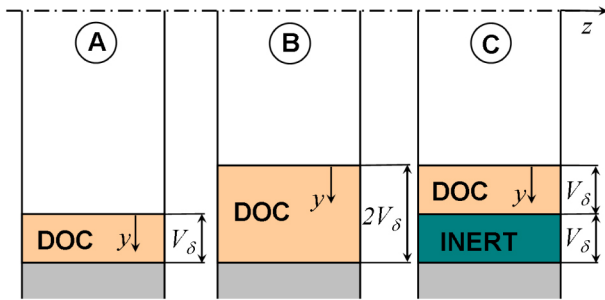


Figure 3. Example for catalytic conversion in three different washcoat layers configurations

As result, one identical overall conversion behavior is calculated for all three configurations. This is obvious when comparing the cases A and C, since $\chi_{\text{ref,DOC-A}}$ is identical to $\chi_{\text{ref,DOC-C}}$, but it may surprise that the conversion in catalyst B is also identical to that of catalyst A and C. The reason for this behavior can be found in the way how the surface specific kinetic parameters are transformed into washcoat layer volume-dependent ones. The surface specific kinetic parameters implicitly contain the information how many noble metals are located within the washcoat layer. Using the same surface specific kinetic parameters and calculating the specific reference volumes individually for the catalysts, A and B imply that the same amount of noble metals is distributed in the washcoat volume V_δ of catalyst A and also in the washcoat volume $2 \cdot V_\delta$ of catalyst B. Only the noble metal density in catalyst B is half the one of catalyst A. Thus for comparison of washcoat layer coatings with constant noble metal density but with varying thicknesses it is indispensable to use one common specific reference washcoat volume when applying surface specific kinetic parameters.

Numerical Considerations

For the numerical solution of the pore diffusion model an additional 1D discretization in direction perpendicular to the channel axis across the washcoat layers needs to be introduced. Figure 4 sketches a single channel with three different washcoat layers. Assuming a 1D converter model, the total number N_{ch} of channels can be calculated according to

$$N_{\text{ch}} = A_{\text{front}} \cdot \text{CPSM} \cdot \quad (8)$$

where A_{front} represents the front surface of the converter. In the case of a 3D converter model not the total front surface is applied but a fraction given by the front face area of the individual CFD mesh cells.

For a squared cell channel, the volume ΔV_{mc} of a single washcoat cell can be calculated using

$$\Delta V_{\text{mc}} = 4 \cdot N_{\text{ch}} \cdot \Delta z \cdot \Delta y_{\text{mf}} \cdot (d_h + 2 \cdot y_{\text{mf}} + \Delta y_{\text{mf}}), \quad (9)$$

where Δz is the cell length of the axial discretization, Δy_{mf} is the cell length of the washcoat discretization and y_{mf} is the coordinate position of the considered washcoat cell. Non-squared channel geometries, e.g. sinusoidal shapes of metal substrates, can be described by modifying Equation (9) appropriately to the given geometrical configuration.

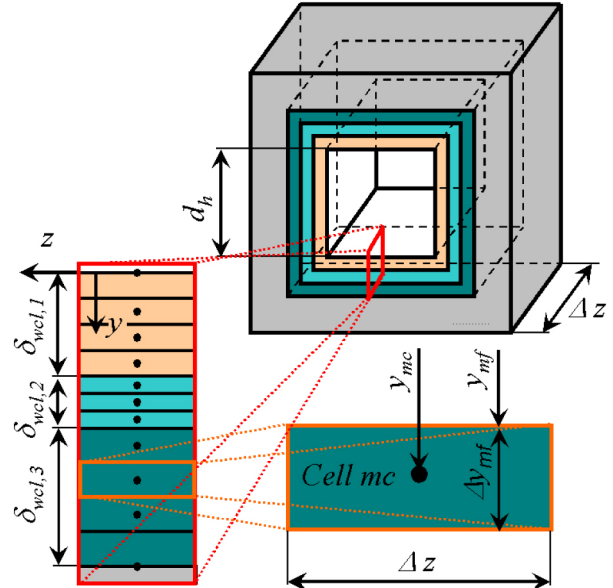


Figure 4. 1D washcoat layer discretization embedded in discretized single channel model

With the volumes of the individual washcoat cells given a numerical solution procedure can be applied to Equation (1). Following the method of lines, first the spatial derivative on the right side of Equation (1) is discretized using the finite volume approach. Assuming that $D_{\text{eff},k} \rho^L \cdot \partial w_k^L / \partial y$ and the reaction source term are constant within the finite volume ΔV_{mc} and by means of the divergence theorem of Gauss the partial differential equation can be transformed into a coupled set of ordinary different equations (ODE). The transient variation of the state within the discrete cell is determined by the diffusive fluxes through all cell faces and the reaction source terms. The solution of the typically stiff ODE system is performed using standard backward differentiating formulas. The entire solution procedure of Equation (1) is finally coupled to the solution of the SCM.

Transport Models

In a simplifying way the porous structure of a catalyst washcoat can be seen as complex network of individual channels of different diameters, lengths and shapes. Diffusive transport in such systems can be described by the general Fick's law where the applied diffusion coefficients need to be appropriately chosen. The pure gas phase diffusion coefficients do no longer apply in small pores with diameters in range of the mean free path of the diffusing molecules. Here diffusion is not dominated by fluid-fluid collisions but it changes to fluid-solid collision driven diffusion where