

Micro-Simulation of NO-NO₂ Transport and Reaction in the Wall of a Catalyzed Diesel Particulate Filter

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ABSTRACT

Catalyzed Diesel Particulate Filters (CDPFs) continue to be an important emission control solution and are now also expanding to include additional functionalities such as gas species oxidation (such as CO, hydrocarbons and NO) and even storage phenomena (such as NO_x and NH₃ storage). Therefore an in depth understanding of the coupled transport – reaction phenomena occurring inside a CDPF wall can provide useful guidance for catalyst placement and improved accuracy over idealized effective medium 1-D and 0-D models for CDPF operation. In the present work a previously developed 3-D simulation framework for porous materials is applied to the case of NO-NO₂ turnover in a granular silicon carbide CDPF. The detailed geometry of the CDPF wall is digitally reconstructed and micro-simulation methods are used to obtain detailed descriptions of the concentration and transport of the NO and NO₂ species in the reacting environment of the soot cake and the catalyst coated pores of the CDPF wall. From these results NO-NO₂ turnover is quantified and a comparison is made with the turnover predicted by an approximate 0-D analytical model. Good agreement is found between the two models, justifying the use of the approximate but fast analytical model in large scale simulations of CDPFs.

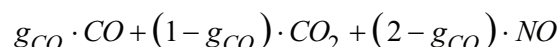
INTRODUCTION

Three-dimensional simulations at the pore scale of Diesel Particulate Filter (DPF) materials, as for example described in [1,2,3,4,5], can enhance our understanding of the transport and reaction phenomena that occur in

the minute environment of DPF wall and that are otherwise not visible by direct observation. In particular, such detailed simulations can be used to tune and validate simpler 1-D and 0-D models of the same transport and reaction phenomena. In the present paper the simulation framework previously developed and described in [1,2] will be used to study NO-NO₂ turnover in a catalyzed DPF (CDPF) in detail and to facilitate a comparison with an approximate 0-D analytical model. The detailed simulations that will be performed will involve the digital reconstruction of the geometry of a SiC-based granular CDPF wall and the simulation of NO and NO₂ transport and reaction in the soot cake and catalyst coated wall in order to quantify the NO-NO₂ turnover.

SIMULATION FRAMEWORK

The simulation framework consists of a Navier-Stokes solver for computing the flow field, a finite volume method for computing the advective-diffusive transport of gas species and a chemical reaction model. The computational domain contains the filter wall and the soot deposits in the wall and on the surface of the wall, as shown in Figure 1. The finite volume method computes gas species transport given the velocity field from the Navier-Stokes flow solver. Two reaction paths are considered, the NO₂ assisted oxidation of soot in the soot deposits,



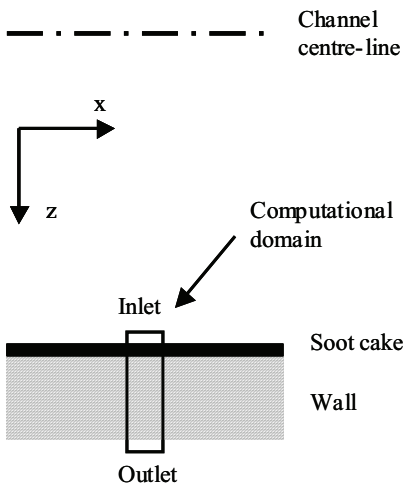
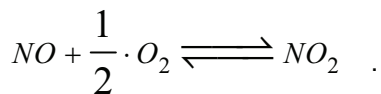


Figure 1. The computational domain

and the catalytic oxidation of NO on the catalyst coated solid surfaces in the filter wall,



The reaction rates are described by modified Arrhenius equations that depend on the local concentrations of the O_2 , NO and NO_2 species [6]. Since oxygen is usually in excess it is only necessary to consider the transport of the NO and NO_2 species. Furthermore, on account of the small exotherm of these reactions, isothermal conditions can be assumed and therefore it is not necessary to consider heat transport within the filter wall. The transport of the NO and NO_2 species is solved for using the finite volume method. A modified Danckwerts boundary condition is applied at the inlet of the computational domain,

$$\omega_i^+ = \omega_i^- + \frac{D_i}{(u + h_i)} \frac{\partial \omega_i^+}{\partial z},$$

where ω_i^+ is the inlet concentration, ω_i^- is the average concentration across the channel above the inlet, D_i is the species diffusivity, u is the filtration velocity and h_i is the species mass transport coefficient in the channel. This applies the condition that the advective and diffusive flux just inside the inlet of the computational domain must be equal to the sum of the advective flux to the wall due to the filtration velocity and the diffusive flux to the wall due to the concentration profile across the channel. A zero gradient boundary condition is applied at the exit of the domain. Since the soot deposits are permeable to the gas, species transport is also solved for within these regions. Boundary conditions are applied to the species fields within the soot deposits and on the catalyst coated solid surfaces in the form of volumetric source terms determined from the local reaction rates. Since the local reaction rates themselves depend on the local species concentrations, an iterative relaxation of the source terms is performed in order to arrive at a

steady state solution for the species transport and reaction through the filter wall.

Within this simulation framework the degree to which NO_2 assisted soot oxidation is enhanced by catalytic NO to NO_2 conversion is quantified by the NO- NO_2 turnover or recycling factor, defined here as

$$R_{simulation} = \frac{\dot{s}_{NO_2}''}{\rho u \omega_{NO_2}^-},$$

where $\dot{s}_{NO_2}''$ is the total NO_2 sink due to the NO_2 assisted soot oxidation reaction in the soot deposits and $\rho u \omega_{NO_2}^-$ is the nominal rate at which NO_2 is supplied to the filter wall.

APPROXIMATE ANALYTICAL SOLUTION

The homogenized mass balances of the reacting species in the porous wall and soot cake are elliptical convection-diffusion-reaction equations coupled to the mass transfer problem in the channel. Additional difficulties arise from the shrinking domain (due to soot cake oxidation) in which these equations must be solved. A direct numerical attack to the problem requires a fine discretization of the soot cake and the porous wall [7,8,9]. According to [10] a detailed approach of this type is superfluous since in any case the exact distribution of the soot, the catalyst and the contact between them are not known in any realistic or practical situation. In addition, the computational burden imposed by the discretization of the filter wall and soot cake prohibits routine applications of this framework to large scale simulators that need to rapidly produce many parametric runs. Devoting excessive detail on only some aspects of the problem while adopting a less detailed treatment for the microstructural details is therefore not only computationally expensive but also of limited utility. Based on this reasoning it has been our standard practice [10] to ignore the diffusion terms in order to keep the simplicity and the mathematical structure of the convection dominated approach, already used extensively in the DPF simulation literature. The effect of diffusion was replaced in [10] by the *ansatz* of a mixed state between soot and catalyst. Of course, such an approximation is meaningless in the absence of catalyst in which case diffusion significantly increases the local soot- NO_2 reaction rate and therefore it cannot be ignored. On the other hand, in the presence of catalyst the reverse (NO_2 to NO) reaction leads to an almost uniform concentration profile of the reactants having more or less the same effect with diffusion. This is why diffusion can be replaced by the *ansatz* of a mixed soot-catalyst layer. The major advantage of this approach is that it can lead to an analytical solution for the distribution of species in the wall and for the NO_2 turnover factor that is given in [10] as:

$$R = \frac{C_1 C_2 C_3}{1 + C_3 + C_4} + \frac{1}{1 + C_3 + C_4} \times \left(1 - \frac{C_2 C_3}{1 + C_3 + C_4}\right) (1 - e^{-(1+C_3+C_4)C_1})$$

where $C_1 = k_1 w/u$, $C_2 = Z_o/X_i$, $C_3 = k_A/k_1$, $C_4 = k_B/k_1$ and w is the thickness of the mixed layer, X_i the inlet molar NO_2 concentration, Z_o the inlet molar total NO_x concentration and k_1 , k_A , k_B are the effective reaction constants (on a volume basis) for soot oxidation by NO_2 , forward NO oxidation and reverse NO oxidation, respectively. The pseudo-first order reaction constant k_B includes the oxygen concentration term $[\text{O}_2]^{0.5}$. The surface reaction constants used in simulations of reconstructed CDPF wall geometries can be transformed to volumetric based reaction constants employing the appropriate specific surface area value. Also, attention must be paid when rescaling the reaction constants referring to soot layer and porous wall thicknesses to the reaction constant referring to the mixed layer thickness.

The analytical turnover factor as given above cannot be compared directly to a turnover factor computed from the 3-D simulation results in the present work because the expression for the analytical turnover factor has been derived ignoring channel to wall mass transfer limitations that are automatically included in the 3-D simulations. To allow a direct comparison the analytical solution must be extended in a simple way in order to incorporate the mass transfer effect. Approximating the mass transfer process and the chemical reaction as two resistances in series leads to a new, mass transfer-corrected turnover factor. The NO_x concentration is taken to be the driving force for mass transfer since, effectively, both NO_2 and soon-to-be-oxidized NO react with soot,

$$R_{\text{cor}} = \frac{-1 + \sqrt{1 + 4c}}{2c} R \quad c = \frac{RuX_i}{h_i Z_o}$$

where h_i is the channel to wall mass transfer coefficient. It is noted that the analytical turnover factors will be compared to the 3-D simulated turnover factors under the most stringent case of a completely separated (non-overlapping) soot and catalyst layer. In practice the two layers are partially overlapping and the analytical solution is likely to perform even better.

SIMULATION OF NO- NO_2 TURNOVER IN A SIMPLIFIED 2-D WALL PORE

To begin with, NO- NO_2 turnover is simulated in a simplified 2-D representation of a DPF wall pore. Two parallel vertical slabs represent the pore. The slabs are 100 μm long by 5 μm thick and are separated by a distance of 15 μm . Based on this geometry the porosity of the wall is 60% and the volume specific surface area is $0.87 \times 10^5 \text{ m}^2/\text{m}^3$. A soot cake of 95% porosity and 30 μm thickness is placed on top of the pore. An exhaust gas stream containing 8% O_2 , 100 ppm NO_2 and 300

ppm NO is assumed. Five exhaust gas temperatures are considered ranging from 300 $^\circ\text{C}$ to 350 $^\circ\text{C}$ inclusive. The filtration velocity is 4 cm/s. A square channel of 1.4 mm width above the wall is assumed. A Sherwood number of 3.3 is assumed for mass transport in the channel (this is the average Sherwood number for a square duct for the cases of constant value and constant flux wall boundary conditions). The modified Danckwerts inlet boundary condition is applied at a very small distance (10 μm) above the surface of the soot cake.

It is noted that under the above exhaust conditions gas species diffusivity is of the order of $5 \times 10^{-5} \text{ m}^2/\text{s}$ and therefore the Peclet number ($Pe = uL/D_i$) based on the pore width and assuming a maximum pore velocity of 10 cm/s (based on the porosity and assuming Poiseuille flow in the pore) is of the order of 0.03, in other words species transport is diffusion dominated.

Simulation results for the simplified 2-D pore at 300 $^\circ\text{C}$ are shown in Figures 2 to 5. The NO_2 and NO molar fluxes through the soot cake and along the pore are shown in Figures 2 and 3 respectively and the laterally averaged NO_2 and NO concentrations are shown in Figures 4 and 5 respectively. Results are shown with and without precious metal catalyst coating on the solid surfaces of the pore. It is noted that the ranges on the

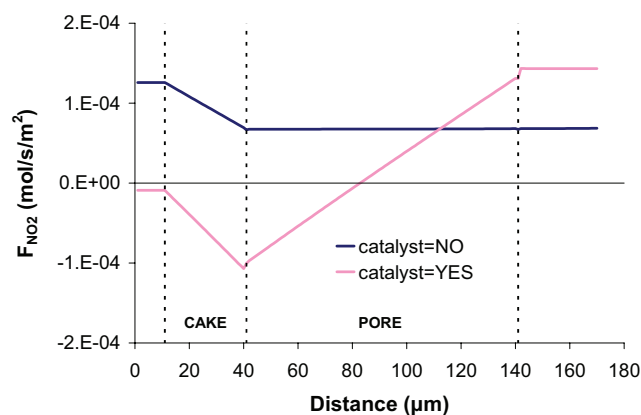


Figure 2. NO_2 molar flux along the simplified 2-D pore at 300 $^\circ\text{C}$, with and without catalyst

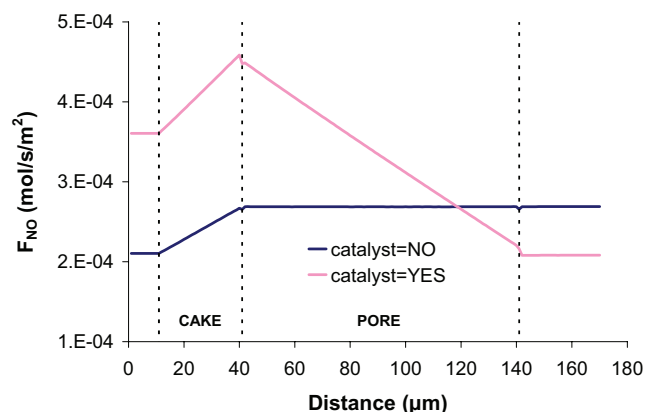


Figure 3. NO molar flux along the simplified 2-D pore at 300 $^\circ\text{C}$, with and without catalyst