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Effect of washcoat diffusion resistance in foam based catalytic reactors

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ABSTRACT

Foam based catalytic converters are a promising alternative to the established honeycomb reactors for treatment of pollutants in automotive applications. They provide excellent mass transfer properties at reasonable pressure drop and have the potential to achieve high conversion at smaller external dimensions. The goal of this work is to determine the relative importance of washcoat diffusion resistance in foam based reactors. Catalytic oxidation of CO over Pt is computationally simulated with a volume averaged model. Based on micro-kinetic modelling and the resulting resolution of the reaction-diffusion processes inside the washcoat, the simulations provide a comprehensive picture of the chemistry and transport processes. Washcoat diffusion resistances in foams – although often considered negligible – are shown to be at least as important as in honeycomb converters, due to the higher external mass transfer coefficients in foams. The computations show a reduction in conversion with respect to the limit of infinitely fast kinetics of 46% for the foam-based reactor after catalytic light-off. The impact of washcoat diffusion resistance on conversion decreases with increasing surface area of the washcoat. An increase in pore size of the washcoat leads to improved conversion.

1. Introduction

Extruded honeycombs are the established technology for catalytic exhaust gas cleaning in automotive applications [1]. Recently, foam based catalytic converters have been proposed as an alternative technology [2], since they provide a high surface area and efficient mass transfer combined with a low pressure drop. In both reactor types the support material is coated with a washcoat layer containing the precious metal catalyst particles. The washcoat provides a large surface area for the chemical reaction, however, diffusion resistances in the washcoat are often significant and have been shown to reduce the observed reaction rates in honeycomb reactors [3].

The oxidation of CO over a Pt based catalyst is often used as a prototype reaction to study catalytic pollutant conversion [4]. Based on measurements and simulations it is currently believed that catalytic oxidation of CO can be described by three regimes [5]. At low temperatures the conversion is limited by slow chemical reaction rates, which results in low conversion of CO. At high temperatures conversion is limited mainly by external mass transfer from the bulk fluid to the washcoat surface. Finally, at intermediate temperatures the above mentioned washcoat diffusion resistance can severely reduce the achievable conversion. Not all of these regimes necessarily exist in all reactor configurations [5,6]. Quantifying the importance of washcoat diffusion resistance is of significant practical importance as it will guide the efforts in the optimization of foam based catalytic reactors.

For honeycomb reactors washcoat diffusion resistance has been shown to be important for a range of temperatures above light-off and a pure external mass transfer limited regime was not observed [6]. In foams the effects of washcoat diffusion have often been ignored in the experimental [7–10] and numerical literature [11,12]. It is often assumed that conversion in foam based reactors changes from kinetically limited to external mass transfer limited directly [8–10]. In this case the mass transfer limited regime is identified as where the slope in the conversion versus temperature plot decreases [9,10]. Furthermore, external mass transfer coefficients in foams are often obtained experimentally assuming negligible washcoat diffusion resistance [8–10,13]. Even if the assumption of negligible washcoat diffusion in foams is satisfied, the question remains as to why washcoat diffusion resistance in honeycomb reactors is very important, while being negligible in foam based reactors. This is especially surprising since the

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Nomenclature

A_r	pre-expontential factor for reaction r (mol, cm, s)
a_V	geometric surface area per unit volume ($A_{sf}/\Delta V$) (1/m)
A_{sf}	solid fluid interfacial area in a REV (m^2)
c_i	concentration of species i (mol/m^3 for gas phase species and mol/m^2 for surface species)
c_p	heat capacity at constant pressure (J/(kg K))
D_i	mixture diffusion coefficient of component i (m^2/s)
d_{wc}	washcoat pore diameter (m)
$E_{a,r}$	activation energy for reaction r (kJ/mol)
$F_{cat/geo}$	ratio between catalytic active surface area and geometric surface area (–)
ΔH	heat release per mole of CO (J/mol)
H	phase indicator function (Eq. (A1) (–))
k'_m	Sh/L (1/m)
$k_{m,i}$	mass transfer coefficient of species i (m/s),
k_r	reaction rate constant of reaction r (mol, cm, s)
$L_{reactor}$	reactor length (m)
L	macro scale length scale (m)
M_i	molecular weight of component i (kg/mol)
N_g	number of gas phase species (–)
$\vec{n}_{fs}$	normal vector pointing from fluid to the solid
N_s	number of surface species (–)
n_{wc}	number of cells in the washcoat
n_x	number of cells in the x-direction
R	ideal gas constant (J/(mol K))
rr_{CO}	CO reaction rate (mol/(m^2s))
S_r^0	initial sticking coefficient of reaction r (–)
S_r	sensitivity of reaction r (–)
$\dot{s}_i$	molar production rate of species i per unit surface area (mol/(m^2 s)),
ΔT_{ad}	adiabatic temperature increase along reactor (K)
T	temperature (K)
t	time (s)
t_{wc}	washcoat thickness (m)
u_{cat}	characteristic catalyst velocity (Eq. (19)) (m/s),
u	velocity in the x-direction (m/s)
ΔV	volume of the representative elementary control volume (m^3),
w	washcoat coordinate normal to washcoat fluid interface (m)
x	coordinate (m)
Y_i	mass fraction of component i (–)

Greek letters

ϵ_{wc}	washcoat porosity (–)
ϵ	macro scale porosity (–)
Γ	Pt surface coverage (mol/m^2)
$\nu'_{k,r}$	forward stoichiometric coefficient of component k in reaction r (–)
$\nu''_{k,r}$	reverse stoichiometric coefficient of component k in reaction r (–)
ρ	density (kg/m^3)
θ_i	surface coverage of species i (–)
τ_{wc}	washcoat tortuosity (–)
χ	CO conversion (Eq. (20))

Non-dimensional Groups

Pe	Peclet number
Sh	Sherwood number

Superscripts

$\langle\rangle^p$	phase averaged in phase p
^{b}	bulk value
^{f}	fluid
^{s}	surface averaged
^{wc}	value in the washcoat pore

thickness of the washcoat, its specific surface area and Pt loading in both reactor types are typically very similar.

The experimental quantification of washcoat diffusion resistance in foams is difficult because the overall conversion of CO is often the only observable quantity. However, it is impossible from the conversion alone to determine whether washcoat diffusion resistance in a reactor is important. Furthermore, the exact properties of the washcoat, such as pore size and washcoat thickness, are difficult to precisely control in an experiment. With simulations on the other hand, the external mass transfer, washcoat diffusion and the elementary reaction steps can be modeled separately and the relative impact of the different phenomena on conversion can be analyzed in great detail. It is also straight-forward to control the washcoat properties and to study the impact of the various washcoat parameters on conversion. Simulations also allow to study quantities not accessible through experiments such as concentration profiles within the washcoat layer which provide interesting insights in the small scale phenomena governing catalytic CO oxidation.

A volume averaged reactor model is used to simulate light-off curves in foams and honeycomb reactors. The honeycomb reactor serves as a validation since washcoat diffusion resistance in honeycomb reactors is easier to quantify and its impact on conversion has been shown experimentally [6]. Quantification of washcoat diffusion resistance in honeycomb reactors is significantly more accurate, since external mass transfer can be predicted with analytical methods and simulations due to their relatively simple geometry. The reactor model is used to quantify the washcoat diffusion resistance by comparing simulations assuming instantaneous washcoat diffusion with a model that resolves the reaction diffusion phenomena inside the washcoat. Since the impact of washcoat diffusion on conversion is expected to depend on temperature, ignition and extinction curves are simulated in the temperature range of 300 K to 1000 K.

2. Reactor model

The catalytic converter is modeled as a porous medium at two distinct length scales. The macro pores have a characteristic length-scale on the order of $L = 1$ mm. This corresponds to the pore diameter in a foam and the hydraulic diameter in a honeycomb channel. The honeycomb and the foam are coated with a washcoat to increase the catalyst surface area. The washcoat thickness (t_{wc}) is on the order of 100 μm. The washcoat itself is modeled also as a porous medium with a characteristic pore diameter on the order of d_{wc} = 10 nm. The relevant scales for the foam and the honeycomb are summarized in Figs. 1 and 2.

2.1. Macro pore governing equations

The governing equations for averaged quantities on the macro scale are obtained by averaging the governing equations over a representative elementary volume REV [14]. This corresponds to a cross-sectional average in a honeycomb channel and an average over a sphere with a diameter of order L in the foam. It is assumed