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Modelling transport phenomena and chemical reactions in automotive three-way catalytic converters

H. Santos [a], M. Costa [b,*]

[a] Mechanical Engineering Department, School of Technology and Management, Polytechnic Institute of Leiria, Morro do Lena – Alto Vieiro Apt. 4163, 2411-901 Leiria, Portugal
[b] Mechanical Engineering Department, Instituto Superior Técnico, Technical University of Lisbon, Avenida Rovisco Pais, 1049-001 Lisbon, Portugal

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ABSTRACT

This study concentrates on the external and internal mass transfer with multiple reactions in the catalytic layer of a three-way catalyst (TWC). A single channel model accounting for the species diffusion inside the washcoat using the effectiveness factor was developed. Validation and calibration of the model was achieved by comparing predictions against experimental data obtained previously by the same authors. The model was then applied to study the importance of both turbulent monolith structures and controlled washcoat structures on TWC conversions. The numerical results show that: (i) increasing the transport coefficients using turbulent monolith structures can produce either positive or negative effects on the TWC conversions; (ii) overall, the net effect of increasing the transport coefficients on the TWC conversions is positive; (iii) at high inlet gas temperatures and high space velocities the turbulent monolith structures present important improvements in the TWC conversions; (iv) the TWC conversions can be significantly improved enhancing the transport properties of the porous washcoat structure; (v) enhancements in the transport properties of the washcoat structure have deeper impacts on the TWC conversions than improvements in the monolith channel structure.

1. Introduction

Automotive emission standards are becoming increasingly stringent which requires continuous improvements in the exhaust after treatment systems. Since the cold start emissions may represent more than 50% of the total emissions, most studies available in the literature have concentrated on improving the light-off behavior. As a consequence of this intense research and development, today the three-way catalyst (TWC) reach the light-off temperature very rapidly and, thus, the relative importance of the emissions above light-off is becoming gradually more important. In order to achieve future emission standards (*e.g.*, US 2010 and EURO VI), conversions very close to 100% have to be achieved under warmed up conditions.

Several authors (*e.g.*, [1–4]) have demonstrated that both internal and external mass transfer resistances limit the TWC conversions above light-off temperature. Thus, the diffusion resistances in the boundary layer (external mass transfer) and in the washcoat (internal mass transfer) have to be as low as possible to achieve high conversions.

The diffusion and reaction within the washcoat can be accounted for using: (a) a detailed three-dimensional (3D) model of the porous washcoat [4], (b) a model of the pseudo-homogeneous washcoat layer with explicit solution of one dimensional (1D) internal diffusion in the transverse direction [5], and (c) a model of the washcoat layer with diffusion effects lumped into the effectiveness factor. Zygourakis and Aris [5] and Wanker et al. [6] showed that the use of the effectiveness factor model is adequate for temperatures above the light-off temperature and for low concentrations of reactants, as those encountered in exhaust aftertreatment systems such as TWC. A detailed discussion on the validity of the effectiveness factor model is presented in Appendix A.

Massing et al. [3] used the 1D plug-flow model (PFM) with the effectiveness factor and provided a comparison between measurements and predictions. To promote simplicity, they studied TWC conversions under steady-state conditions solely for propene oxidation. In the present study, TWC conversions were also studied under steady-state conditions, but the model has been extended to account for the conversion of the three main chemical species (CO, unburnt hydrocarbons – HC – and NO_x). Here we have also used the 1D PFM with the effectiveness factor implemented. The model was calibrated and validated through comparisons against our previous measurements [7]. Subsequently, the model was applied to study the importance of both turbulent monolith structures and controlled washcoat structures on TWC conversions.

In the last few years the improvements of the TWC conversions above light-off temperature were achieved through advances on

* Corresponding author. Tel.: +351 218417378; fax: +351 218475545.
E-mail address: mcosta@ist.utl.pt (M. Costa).

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Nomenclature

$a_{j,k}$	stoichiometric coefficient of specie j in reaction k
A	pre-exponential Arrhenius factor (mol K m^{-3} s^{-1})
c_{pg}	gas specific heat capacity (J kg^{-1} K^{-1})
c_{ps}	solid specific heat capacity (J kg^{-1} K^{-1})
C_g	mean concentration in the gas phase, mole fraction
C_{ref}	reference concentration in the solid phase, $C_{\text{ref}} = C_s(\rho_g/M_g)$ (mol m^{-3})
C_s	mean concentration in the solid phase, mole fraction
d_p	mean pore diameter (m)
D	combination of bulk and Knudsen diffusion (m^2 s^{-1})
D_b	bulk diffusion (m^2 s^{-1})
D_{eff}	effective diffusion (m^2 s^{-1})
D_K	Knudsen diffusion (m^2 s^{-1})
E_a	activation energy (J mol^{-1})
ΔF	elementary exchange area (m^2)
h	heat transfer coefficient (W m^{-2} K^{-1})
ΔH	enthalpy of the reaction (J mol^{-1})
ΔHa	adsorption enthalpy of the reaction (J mol^{-1})
k_m	mass transfer coefficient from the bulk gas to the washcoat surface (m s^{-1})
k_s	solid phase conductivity (W m^{-1} K^{-1})
k_V	reaction rate constant based on washcoat volume (s^{-1})
$\dot{m}_g$	mass flow rate (kg s^{-1})
M	molecular weight (kg mol^{-1})
M_g	molecular weight of the exhaust gases (kg mol^{-1})
$\dot{n}$	molecular flux (mol m^{-3} s^{-1})
$NTUh$	number of transfer units for heat
$NTUm$	number of transfer units for mass
Nu	Nusselt number
$Nu_{T,\infty}$	asymptotic Nusselt number for constant wall temperature
Pr	Prandtl number
r_k	reaction rate (mol m^{-3} s^{-1})
R_Ω	effective transverse diffusion length (m)
R_E	external mass transfer resistance
R_G	global (total) mass transfer resistance
R_L	internal mass transfer resistance
R	species rate, expressed per channel volume (mol m^{-3} s^{-1})
R_P	particular gas constant (J kg^{-1} K^{-1})
r_k	reaction rate (mol m^{-3} s^{-1})
S	mass transfer area per unit of catalyst volume (m^{-1})
Sc	Schmidt number
Sh	Sherwood number
$Sh_{T,\infty}$	asymptotic Sherwood number for constant wall temperature
Δt	time step (s)
T_g	mean temperature in the gas phase (K)
T_s	mean temperature in the solid phase (K)
u_z	flow velocity in the longitudinal direction (m s^{-1})
V_{macro}	macro pore volume (m^3)
V_{meso}	meso pore volume (m^3)
V_{total}	total pore volume (m^3)
ΔV	elementary reactor volume (m^3)
X	fractional conversion
z	axial length (m)
ΔZ	elementary axial grid length (m)

Greek letters

α_g	gas thermal diffusivity (m^2 s^{-1})
α_s	solid thermal diffusivity (m^2 s^{-1})
δ_C	effective washcoat thickness (m)
ε	void fraction
ε_p	porosity
η_L	local effectiveness factor
μ_g	gas dynamic viscosity (N s m^{-2})
ν_g	kinematic viscosity of the exhaust gas mixture (m^2 s^{-1})
ρ_g	gas mass density (kg m^{-3})
ρ_s	solid mass density (kg m^{-3})
τ	pore tortuosity factor
ϕ_L	washcoat Thiele modulus

Sub- and superscripts

amb	ambient
E	external
g	gas
G	global
i	space node index
in	at channel inlet
j	indication of exhaust species
k	indication of reaction k
L	local (internal, within the washcoat)
m	mass
n	temporal index
N	total number of gas phase species
s	solid
z	axial coordinate

the external mass transfer of the monolith structures. To this end, for example, both metallic and ceramic straight channel monoliths with cell densities from 400 cpsi up to 1200 cpsi along with thin foils have been introduced [8]. In spite of these reactors providing larger geometrical surface areas, the TWC still operates within the laminar flow region which limits the external mass transport process.

The external mass transfer limitation of the laminar flow through monoliths can be overcome by using the so-called turbulent monoliths [9,10]. These innovative monolith structures can operate in the transition or turbulent regions because they usually have a small diameter and are constructed with protrusions in the channel walls in order to enhance the radial transport within the TWC channels. Thus, with these monolith structures, the external transport phenomenon is significantly enhanced as compared with the straight channels.

The internal mass transfer limitation on the TWC conversions can be reduced by favoring the accessibility of the reactants towards the active sites located within the washcoat structure. In this respect, an enormous progress has recently been made in the field of ordered porous structured materials. Studies concerning the synthesis of materials with controlled micro–meso–macro pore structure, zeolites type or metal oxides such as alumina, silica, titania or zirconia are now available in the literature (*e.g.*, [11,12]). Given these recent advances in the washcoat structures, it is important to study its performance when applied to TWC, as it is done in the present study.

2. Mathematical model

2.1. Model description

The most important simplification encountered in the modelling approaches available in the literature is the representation of the whole matrix (thousands of channels) by a single channel with the