Chemical Engineering Science 174 (2017) 189–202

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Optimization of axial catalyst loading in transient-operated zone-structured monoliths: Reduction of cumulative emissions in automotive oxidation catalysts

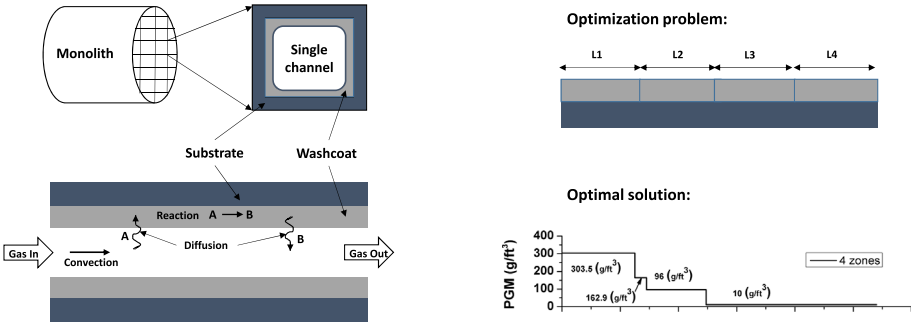
Sivaram Kannepalli [a], Andreas Gremminger [a], Steffen Tischer [b,*], Olaf Deutschmann [a,b]

[a] Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany
[b] Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany

HIGHLIGHTS

- A new model for the optimization of axial precious metal loading in zone-structured catalysts for automotive applications was developed.
- A methodology to incorporate derivative based optimization scheme to transient models is demonstrated.
- For a Diesel Oxidation Catalyst it was found that an axially decreasing loading profile improves the cold-start behavior and increases the steady-state conversion of CO.
- Deactivation effects by ageing of palladium catalysts for methane oxidation can be minimized by an axially decreasing loading profile.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 May 2017
Received in revised form 17 August 2017
Accepted 1 September 2017
Available online 8 September 2017

Keywords:
Zone-structured monolith
Loading profile
Transient simulation
Optimization

ABSTRACT

A model based mathematical optimization methodology to optimize the precious metal loading profile (PGM loading) in zone-structured catalytic converters is developed. To carry out this task, a multi zone-structured optimization formulation, where the catalyst is divided into N zones axially to obtain a non uniform optimal PGM loading profile, which can be tested experimentally, is used. The effects of the PGM loading on washcoat diffusion limitations is also considered. The objective is to optimize the spatial distribution of loading for a fixed amount of precious metal to maximize the chemical conversion efficiency under transient operation. To achieve this, the transient 1D + 1D model is solved with the help of implicit solver DASPKADJOINT and translated into a non-linear optimization problem that can be solved with any derivative based nonlinear programming (NLP) solvers. The model is applied to two example cases: CO oxidation on a Pt/Al_2O_3 based Diesel Oxidation Catalyst catalyst (minimizing cold-start emissions) and CH_4 oxidation on Pd/Al_2O_3 (minimizing deactivation effects). In both the cases it was observed that the optimal solution with maximum PGM loading in the channel entrance region improved the performance of the catalysts. The methodology presented is generic and can be transferred to different systems with different chemistries, which may result in significantly different optimization results and loading patterns.

* Corresponding author.
E-mail address: steffen.tischer@kit.edu (S. Tischer).

http://dx.doi.org/10.1016/j.ces.2017.09.013
0009-2509/

Nomenclature

a	activity, [–]
a_s	steady state activity, [–]
Area_{geo}	geometric surface area, [m^2]
Area_{cat}	catalytic surface area, [m^2]
c_p	specific heat capacity of the mixture, [J/kg K]
c_s	specific heat capacity of the solid phase, [J/kg K]
D	dispersion, [–]
D_{ch}	channel diameter, [m]
$D_{eff,i}$	effective diffusivity coefficient, [m^2/s]
D_{i,N_2}	binary diffusivity coefficient, [m^2/s]
$D_{knud,i}$	Knudsen diffusivity coefficient, [m^2/s]
d_p	particle diameter, [m]
E_{ads}	activation energy, [J/mol]
E_{deac}	deactivation activation energy, [J/mol]
E_{oxi}	activation energy, [J/mol]
$F_{cat/geo}$	catalytic activity factor, [–]
h	heat transfer coefficient, [W/m^2 K]
H_j	molar enthalpy of a species, [J/mol]
k_{ads}	adsorption pre-exponential, [–]
k_{deac}	deactivation pre-exponential, [–]
$\boldsymbol{k_{me}}$	vector of external mass transfer coefficient of species, [m/s]
k_{oxi}	kinetic pre-exponential, [mol/m^2 s]
L	channel length, [m]
L_{PGM}	precious metal loading, [g/ft^3]
L_w	washcoat loading, [g/ft^3]
m_{cat}	mass of PGM, [g]
M_{cat}	molecular weight of the precious metal, [g/mol]
Nu	Nusselt number, [–]
P	pressure, [Pa]
$\boldsymbol{P}$	control parameters
PGM_{total}	total PGM loading, [g/ft^3]
R	reaction rates, [mol/m^2 s]
$\boldsymbol{S}$	vector of the rate of production of the species, [mol/m^2 s]
S_{cat}	specific catalytic surface area, [m^{-1}]
Sh	Sherwood number, [–]
T_f	gas phase temperature, [K]
T_{ref}	reference temperature, [K]
T_s	solid phase temperature, [K]
X	conversion, [–]
$\boldsymbol{X_f}$	Vector of species mole fraction in gas phase, [–]
$\boldsymbol{X_s}$	vector of species mole fraction in solid phase, [–]
Γ_{cat}	surface site density, [mol/m^2]
δ_w	washcoat thickness, [m]
ε_g	volume fraction of the channel, [–]
ε_{wc}	washcoat porosity, [–]
λ	Solid heat conductivity, [W/m K]
ρ_g	gas mixture density, [kg/m^3]
ρ_s	solid density, [kg/m^3]
ρ_{wc}	washcoat density, [kg/m^3]
τ	Tortuosity factor, [–]

1. Introduction

Design and optimization of catalytic converters is crucial for the automotive catalyst industry to meet the ever increasing stringent emission standards and efficient use of precious metals to reduce costs. Cold-start emissions constitute a large fraction of the total tailpipe emissions over a driving cycle and has been a topic of investigation for a long time (Kim et al., 2009; Kirchner and Eigenberger, 1996; Tronci et al., 1999). The exhaust gas systems are not completely effective for the first few minutes during the cold start, where the catalyst is inactive due to low temperatures, resulting in pollutants passing unconverted till the catalyst heats up. Many methods have been investigated in the literature to control this problem. Preheating the catalytic converter electrically is a possible solution to this problem which is extensively studied (Bissett and Oh, 1999; Kirchner and Eigenberger, 1996; Oh et al., 1993; Oh and Bissett, 1994; Ramanathan et al., 2011). The other alternative can be the utilization of high-voltage batteries which draw energy from renewable energy sources (wind, solar etc.) especially used in hybrid cars to draw enough power to heat up the converter very quickly so as to reduce cold start emissions (Ramanathan et al., 2011). Another possible solution to curb this problem is by placing the converter in close proximity to the engine manifold. But this leads to pressure drop and in turn reduces the engine efficiency due to continuous transient pulsations (Litto et al., 2016). Non-uniform catalyst distributions in the catalytic converters present an alternative viable option to tackle this problem efficiently. The problem of reducing the cost of the precious metals and improving the ignition conditions of the catalytic monolith can be addressed simultaneously by creating optimal distribution of the active component of the catalyst along the length of the monolith.

Various studies investigating the effect of non-uniform axial distribution of precious metals along the length of the reactor with simple global reaction kinetics and different operating conditions on the performance of the catalytic converter are available in the literature (Al-Adwani et al., 2012; Khanaev et al., 2005; Khanaev et al., 2004a, 2004b; Kim et al., 2009; Kim and Kim, 2007; Oh and Cavendish, 1982; Psyllos and Philippopoulos, 1993). Firstly, Oh and Cavendish (1982) examined the light-off behavior of three Pt distribution profiles along the reactor length and concluded that the light-off performance of the linear decreasing Pt distribution with more noble metal concentrated in the upstream section of the monolith is much better than the other cases. Psyllos and Philippopoulos (1993) pre-assumed a parabolic function and showed that the performance of catalysts with parabolic axial catalyst distribution for CO oxidation is better than monoliths with uniform axial catalyst distribution. Khanaev et al. (2004a) formulated an optimization problem to determine the optimal axially non-uniform catalyst activity distribution along the fixed catalyst bed under isothermal conditions and proposed that uniform distribution profile performed better than a non uniform profile. Khanaev et al. (2004b) showed that the non-uniform active component distribution is in many cases more effective than the uniform distribution for CO oxidation over a Pt-containing monolith catalyst. The aforementioned studies indicated that non-uniform catalyst distribution can improve the performance of catalytic converters. However, an optimal catalyst distribution has not been identified. Khanaev et al. (2005) also showed that in an adiabatic reactor the optimal profile is the one that monotonically decreases along the bed length in the case of an exothermic reaction and monotonically increases in the case of an endothermic reaction, while the uniform active component distribution profile is found to be optimal for a first-order reaction in an isothermal reactor. The optimization of the loading pattern for improving warm-up catalyst performance using an optimization algorithm has been performed by Tronci et al. (1999), Kim and Kim (2007) and Kim et al. (2009). A zone-structured catalyst by dividing the channel length into 2 zones is studied by Tronci et al. (1999), showing that a high noble metal surface area in the upstream section of the