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DOC modeling combining kinetics and mass transfer using inert washcoat layers

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ABSTRACT

The aim of this study was to develop a kinetic and transport model for diesel oxidation catalysts (DOC) with a satisfactory compromise between accuracy and computational demands for robust simulation of transient full-scale operation. Specifically the model accounts for surface concentrations of key species needed to capture transient features for typical lean exhaust conditions. In addition, the model accounts for transport limitations and distinguish them from reaction kinetics as well as apparent NO oxidation inhibition effects due to reactions. To achieve this, lab scale experiments were performed with DOCs with different platinum loadings and three different washcoat configurations of which two had an inert top layer. Both kinetic parameters for a detailed kinetic model and effective diffusivities were optimized for the experimental data using a single channel catalyst model. The experiments showed a clear effect of increased transport resistance for propene and CO and also that NO_2 plays an important role as an oxidizing agent for preferentially CO at low temperature (<120 °C). The resulting model showed good agreement with measurement data using O, CO and NO_2 as the only surface species. The use of different thicknesses of an inert washcoat layer closest to the gas bulk aided the resolution of kinetics from transport phenomena.

1. Introduction

The diesel oxidation catalyst (DOC) is an indispensable part of the aftertreatment system of heavy duty diesel engines that has been in use since the 1990s. The role of the DOC is to utilize the oxygen excess of the lean burn engine to oxidize CO and hydrocarbons (HC) to CO_2 and to oxidize NO to NO_2. Generally the DOC is placed first in the aftertreatment system which means that its performance also is of utmost importance for downstream components such as the selective catalytic reduction (SCR) catalyst and the diesel particulate filter (DPF). Strengthened emission standards are continuously increasing the demands on aftertreatment performance and to meet these demands mathematical models of the DOC can be an important tool in system design, optimization and providing increased insight in component operation.

When a mathematical model of a catalytic converter is derived it is important to consider the effects of both reaction kinetics and transport phenomena. The kinetics determine the rate at which the components are consumed or produced as a function of temperature, concentration, and surface coverages. Transport phenomena control the transport of heat, mass and momentum. The desired level of detail of both kinetic and transport phenomena models depend largely on the purpose of the model and a wide range is available in the literature.

The kinetic models can generally be labeled as either global or detailed. The detailed kinetic models do not only describe the reaction rate as a function of temperature and gas phase concentrations but at least one surface species coverage is also included. A number of these kinds of models for the DOC have been investigated with a large span in the numbers of modeled reactions and species, e.g. [1–3]. In global kinetic models the surface species have been eliminated from the reaction rates and instead inhibition terms are used. This simplification is based on an assumption of a rate limiting step [4] and will make the models more robust and computationally less demanding. Many of the successful global kinetic models for DOC [5–8] are based on the classical work of Voltz [9] performed in the 70s. Historically the global kinetic models have been the preferred type for describing DOC kinetics but for simulation of transients the

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Nomenclature

Roman symbols Description (Units)

A	Mass transfer area (m^2)
A	Preexponential factor (mol (kg Pt)$^{-1}$ s^{-1} or m^3 (kg Pt)$^{-1}$ s^{-1})
C	Concentration (mol m^{-3})
d	Channel diameter (m)
d_p	Pore diameter (m)
D	Bulk gas diffusivity (m^2 s^{-1})
$Deff$	Effective diffusivity (m^2 s^{-1})
DK	Knudsen diffusivity (m^2 s^{-1})
Ea	Activation energy (J mol^{-1})
f_D	Ratio of void fraction and tortuosity (–)
F_{tot}	Molar flow rate (mol s^{-1})
ΔH_{net}	Enthalpy change for NO oxidation reaction (J mol^{-1})
k	Rate constant (mol (kg Pt)$^{-1}$ s^{-1} or m^3 (kg Pt)$^{-1}$ s^{-1})
kc	Mass transport coefficient (m s^{-1})
m_{Pt}	Mass of Pt in washcoat segment (kg)
M	Molecular weight (kg mol^{-1})
N_s	Sites in washcoat segment (mol)
P	Total pressure (Pa)
r	Reaction rate (mol (kg Pt)$^{-1}$ s^{-1})
res	Residual (–)
Re	Reynolds number (–)
Sc	Schmidt number (–)
Sh_∞	Asymptotic Sherwood number (–)
ΔS_{net}	Entropy change for NO oxidation reaction (–)
t	Time (s)
T	Temperature (K)
w	Weighting factor (–)
X	Mean fractional conversion (–)
y	Molar fraction (–)
Δz	Length of segmental tanks (m)

Greek symbols

β	Adsorbed species index (–)
Γ	Lumped mass transfer coefficient (m^3 s^{-1})
θ	Fractional surface coverage (–)
ν	Stoichiometric coefficient of gas phase species (–)
χ	Stoichiometric coefficient of adsorbed species (–)

Subscripts

i	Gas component index
j	Reaction index
k	Tank index
n	Layer index

inclusion of surface species may be needed to obtain a satisfactory compromise between model accuracy and computational demands [3]. Inhibition terms for hydrocarbons and CO in global kinetic rate expressions account for competitive adsorption of these species on sites. However, it has also been found that hydrocarbons can have an apparent inhibition effect on NO oxidation resulting from NO_2 acting as an oxidant in the reaction with hydrocarbons [10]. In addition it has been reported that for simulation of DOC performance under actual vehicle operating conditions, these common global kinetic models lack such reactions to account for an observed negative efficiency behavior of NO oxidation at low exhaust gas temperatures [11].

Two types of heat and mass transfer are of high importance for the catalyst model. Firstly the external transport from the gas bulk to the washcoat surface and secondly the internal transport inside the washcoat itself. The external transport is often modeled with a film model using flow properties, geometry and a gradient between the gas bulk and the washcoat surface to determine the transport rate. Several models for external heat and mass transfer parameters have been developed for catalytic monolith converters [12–14]. The internal mass transfer of different components is usually described by the effective diffusivity which is a function of the structure of the washcoat, gas composition and temperature. Effective diffusivity may either be measured by for example chromatographic [15] techniques or with a Wicke Kallenbach diffusion cell [16], or it may be calculated from models requiring detailed knowledge of the washcoat pore structure [17–19]. Regardless if the effective diffusivity is calculated or measured, specialized equipment and measurements are needed in addition to the experimental setup used for the kinetic experiments.

The conversion in a monolith catalytic converter can be either reaction rate limited or mass transport limited depending on inlet conditions and catalyst configurations such as noble metal loading and washcoat thickness [20]. If kinetic parameter estimation is to be performed mass transport limited conditions should either be carefully avoided or the catalyst model must be able to give a good description of both external and internal mass transport. Otherwise the kinetic parameters may be influenced by transport limitations and thereby not intrinsic. Internal mass transfer limitations have been shown to be of importance for operation of SCR [21–23], NO_X storage catalysts [22], ammonia slip catalysts [24] and dual layer catalysts [25,26] but for DOC the area is less studied. To highlight the effect of internal transport limitations, studies have also been made where an extra layer of inert washcoat layer was placed on top of the active washcoat layer [18].

The current study aims to develop a kinetic and transport model for DOCs with a satisfactory compromise between accuracy, computational demands and robustness for simulation of transient full-scale operation. Specifically the model shall account for surface concentrations of key species needed to capture transient kinetic features for typical lean exhaust engine conditions. The need for reactions in the kinetic model accounting for apparent inhibition effects of hydrocarbons and CO due to their reactions with NO_2 will be investigated. In addition, the model should properly account for transport limitations and distinguish them from reaction kinetics. To achieve this, lab scale experiments were performed with DOCs with different platinum loadings and three different washcoat configurations of which two had an inert top layer. Both kinetic parameters for a detailed kinetic model and effective diffusivities will be optimized for the experimental data using a single channel catalyst model.

2. Modeling method

This section includes a description of the reactor model, an of outline the adjustable parameters and the definition of the objective function of the parameter estimation algorithm.

2.1. Reactor model

Transient experiments have been shown to be significantly more rich in information than experiments at steady state [27]. The experiments in this study will therefore be of transient nature which also means that the reactor model used will need to be able to describe the dynamic behavior of a monolith catalyst reactor. In the present model the accumulation of surface species will serve to capture this dynamic phenomenon. A single channel model previously presented by the authors [28] was used. The monolith channel was discretized as tanks in series where the catalyst washcoat was discretized both radially (as layers) and axially while the gas phase was only discretized axially, see Fig. 1. This 1D/2D (gas