Pore scale modeling of cold-start emissions in foam based catalytic reactors

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HIGHLIGHTS

- Detailed washcoat diffusion model with multi-step chemistry.
- We show the effect of axial solid conduction on cumulative cold-start emissions.
- Comparison of foam based and honeycomb reactors.
- We propose a correlation that captures the essential features of cold-start.

GRAPHICAL ABSTRACT
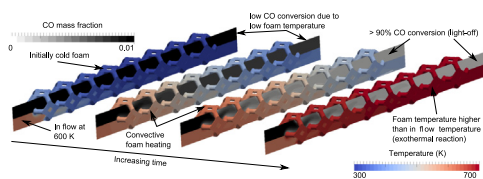
ABSTRACT

Foam based catalytic converters have the potential to decrease cold-start emissions in automotive applications due to their low thermal inertia and excellent mass and heat transfer properties. A 3D CFD model of a foam based catalytic converter is proposed and employed here to simulate cold-start transients. The modeled phenomena include conjugate heat transfer, finite rate washcoat diffusion and detailed multi-step chemistry of CO oxidation over Pt. The simulation results confirm that foam based catalytic reactors have potentially lower cold start emissions compared to honeycomb reactors. Cumulative emissions decrease with increasing foam porosity, decreasing pore diameter and decreasing effective axial solid conductivity. The effects of inflow velocity, inflow CO mass fraction and washcoat surface area (Pt loading) on cold start emissions are discussed in detail. The effects of foam properties and inflow conditions on cumulative emissions are summarized with a correlation that matches the results of the pore scale simulations.

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1. Introduction

Recently, foam based catalytic converters have been proposed as an alternative to the established extruded honeycombs for the cleaning of automotive exhaust gases (Bach and Dimopoulos Eggenschwiler, 2011). Foam based reactors provide a high surface area and efficient mass transfer combined with a low pressure drop. In catalytic converters for automotive applications a large fraction of the pollutants is emitted in the cold-start phase. In addition to their benefits at steady state operation, foam based reactors have the potential to reduce the cold-start emissions due to their high porosity (low thermal inertia). Studies of cold-start in honeycomb reactors show that the thermal inertia of the solid and solid conduction play decisive roles during the transient cold start

phase (Oh and Cavendish, 1982; Koltsakis, 1997; Ramanathan et al., 2003).

Modeling of foam based catalytic reactors is mostly concerned with heat transfer (Kopanidis et al., 2010; Krishnan et al., 2006; Bianchi et al., 2012, 2013) or mass transfer (Lucci et al., 2014). If both mass transfer (chemical reactions) and heat transfer are considered simultaneously, studies are restricted to steady state reactor operation (von Rickenbach et al., 2014; Gräf et al., 2014). Transient studies of foam based catalytic reactors are limited to one-dimensional volume averaged models (Tsinoglou et al., 2009).

To increase the surface area of the catalytic reactor the surface of the pores is typically coated with a washcoat. The chemical reactions are catalysed by precious metal particles, which are added to the washcoat using an appropriate coating procedure. Numerous studies of honeycomb reactors have shown that washcoat diffusion resistance can have a significant effect on conversion at both steady state reactor operation and transient light-off (More et al., 2006; Hayes et al., 2004; Leung et al., 1996; Santos and Costa, 2008). Washcoat diffusion resistance has not been considered in modeling studies of foam based reactors although it is potentially important (von Rickenbach et al., 2015).

In addition to the interactions of heat transfer, mass transfer and fluid dynamics, an accurate prediction of cold start emissions depends on the heterogeneous chemistry model. Here we consider the oxidation of CO over Pt both due to its practical importance and relative simplicity (Salomons et al., 2007). Multi-step reaction mechanism have been shown to yield accurate prediction of light-off (Chatterjee et al., 2001).

The goal of the present work is to devise strategies to minimize cumulative emissions during the cold-start transient in foam based reactors. We simulate the full cold-start transient on the pore scale thereby accurately modeling the interactions of fluid dynamics, chemical reactions in the washcoat layer and heat transfer. The model includes multi-step chemistry and considers washcoat diffusion resistance. Heat transfer in the solid and the fluid are directly resolved at the pore scale.

Such detailed modeling provides insight for the involved processes at the local level, and serves as an accurate benchmark to extract simplified yet reliable predictive tools for cold-start emissions.

By comparing the results of the pore scale simulations with a one-dimensional model, we correlate the cumulative emissions based on three non-dimensional parameters that describe foam geometry, foam thermal properties, surface chemistry and boundary conditions. This correlation can be used to estimate cumulative emissions in various foam geometries and it allows us to identify optimal foam parameters that lead to fast light-off for given operating conditions. Finally, cold-start emissions of foam based reactors and honeycombs are compared.

2. Methods

2.1. Simulation methodology

To model the cold-start of foam reactors we solve the momentum, mass and energy transport equations at the pore scale. Due to the large thermal inertia of the solid, the time scale of solid heating is on the order of seconds whereas the flow and the chemical timescales are on the order of 10 ms. A detailed estimate of characteristic time scales can be found in Appendix A. A quasi-steady state is assumed to make the simulation of the full cold-start transient computationally tractable. This assumption is accurate if the fast phenomena (flow, chemical reactions) reach a quasi-steady state in a time scale that is much shorter than the timescale of the slow phenomena (heating of the foam). A quasi-

steady state assumption has been successfully used before in modeling start-up of honeycomb reactors (Karagiannidis and Mantzaras, 2010).

In addition to the large variety of timescales a foam based catalytic reactor entails a large range of characteristic length scales. The reactor size is typically of the order of cm, the thickness of the catalytically active coating (washcoat) is of the order of 10 μm whereas the diameter of the smallest pores in the washcoat is of the order of 10 nm. In this work it is assumed that the catalytic coating is thin compared to the pore diameter and we compute the effective reaction rate in the washcoat layer by solving a one-dimensional reaction diffusion equation. Since the solution of the washcoat equations is expensive due to stiff kinetics and has to be repeated for each surface cell of the pore scale simulation, the effective reaction rate is tabulated with respect to temperature and the surface mass fraction of the limiting reactant (CO). The surface reaction rate in the pore scale simulations is then obtained by interpolating the effective reaction rate from the table. Using a multi-scale approach in space and time allows us to simulate a complete cold-start phase with detailed chemistry taking into account the effect of washcoat diffusion.

A one-dimensional model of the foam heating phase is employed, in addition to the above, valid as long as the reaction rates are low. This model is used to obtain a correlation for cumulative emissions during the cold-start transient.

2.2. Pore scale simulations

2.2.1. Governing equations

The Navier–Stokes equations together with the energy conservation equation and the species conservation equation are used to model the flow in the pores of the foam-based reactor. We consider a mixture of N components with the mass fractions Y_i. For a reacting mixture at Ma << 1 the conservation equations are the following:

Conservation of total mass:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{1}$$

Conservation of momentum:

$$\frac{\partial (\rho \mathbf{u})}{\partial t} + \rho (\mathbf{u} \cdot \nabla \mathbf{u}) = \nabla \cdot \mathbf{T} \tag{2}$$

with the stress tensor

$$\mathbf{T} = -p\mathbf{I} + \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}\mu (\nabla \cdot \mathbf{u})\mathbf{I} \tag{3}$$

Conservation of species mass:

$$\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho \mathbf{u} Y_i) = -\nabla \cdot \mathbf{j}_i \tag{4}$$

We assume that the diffusive flux can be closed with Fick's law

$$\mathbf{j}_i = -\rho D_i \nabla Y_i, \tag{5}$$

where D_i is the mixture diffusion coefficient for species i (Kee et al., 2005). Using mixture diffusion coefficients has been shown to yield accurate predictions at a lower computational cost compared to the more rigorous Stefan–Maxwell diffusion models in similar applications (Kumar and Mazumder, 2008).

Conservation of energy in the fluid:

$$\rho c_p \frac{\partial T}{\partial t} + \rho c_p \mathbf{u} \cdot \nabla T = \nabla \cdot \lambda_f \nabla T + \left(\rho \sum_{i=1}^{N} c_{p,i} D_i \nabla Y_i \right) \cdot \nabla T \tag{6}$$

In the energy equation we neglect viscous dissipation and assume that the total derivative of the pressure is small due to the low Ma number.