MULTI-SCALE REDUCED ORDER MODELS FOR COUPLED HOMOGENEOUS-CATALYTIC REACTIONS IN MULTILAYERED MONOLITHS

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Abstract

We use the Lyapunov Schmidt (L-S) reduction technique of bifurcation theory to develop reduced order models for catalytic monolith reactors with multiple washcoat layers for multicomponent systems including homogeneous reactions in the flow channel and thermal effects. The reduced order models are expressed in the multi concentration/temperature modes and interfacial fluxes which are related through various transfer/cross-transfer coefficients. We consider some special cases to compare the reduced order models with detailed models and discuss their utility for real time simulations and optimization, solving inverse problems and parametric/bifurcation studies.

Keywords

Multicomponent diffusion, Homogeneous and heterogeneous reactions, Low dimensional models, Transfer coefficients, Real time optimization, Inverse problems, Parametric studies.

Introduction

Monolith reactors are widely used in catalytic after-treatment, catalytic combustion and partial oxidations. In most applications, the washcoat containing precious group metals is deposited as a single layer on the channel walls. In recent years, multi-functional monolith reactors consisting of two or more washcoat layers with different functionalities are also used. Examples include dual layered selective catalytic reduction (SCR) units, hydrocarbon (HC) trap and an oxidation layer, and diesel oxidation catalysts (DOCs) with two different oxidation layers. In these systems, the exhaust gases including the reactant, product and carrier gases flow through the channel in axial direction and diffuse into the washcoats where they are trapped/adsorbed or react. In the automobile exhaust treatment applications, the monolith reactors operate under highly transient conditions. Therefore, the development of coarse-grained (reduced order) models for these systems is important for various control and optimization algorithms related to fuel efficiency and real time implementation of emissions constraints. These reduced order models have also other advantages such as speed-up of the transient reactor calculations by several orders of magnitude, parametric studies and bifurcation analysis, and estimation of kinetic and transport parameters from a limited number of macroscopic experimental observations (or the solution of the so called inverse problem). In addition, they facilitate the incorporation of the model in larger scale process and optimization schemes.

Because of their significant utility, several researchers have developed the reduced order models for catalytic monoliths (Joshi et al. 2009, Ratnakar et al. 2012, Mozaffari at al. 2016). More recently, Ratnakar et al. (2018) developed multi-scale models for monoliths with dual and multiple-layers for multicomponent systems. It was shown that these models are more accurate than the traditional two-phase models and lead to exact solutions when position or local property dependent transfer coefficients are utilized. In the current work, we extend the results to include thermal

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effects coupled with homogeneous reactions in the fluid phase. We provide the reduced order models for heat and mass-transfer processes in multi-mode form containing inter and intra-phase heat/mass fluxes as well as phase or velocity averaged temperatures and concentrations, which are most suitable for bifurcation analysis and solving inverse problems for estimating transport/reaction parameters. Finally, we give physical interpretations of various inter- and intra-phase transfer coefficients and discuss some limiting cases of physical importance.

Method

The detailed mathematical model describing diffusion-convection-reaction processes for a multi-component system in the i-th layer of a catalytic monolith is given by

$$\mathbf{f}_i \equiv \mathbf{D}_i \nabla_{\perp}^2 \mathbf{c}_i - t_{Di}\left[\mathbf{E}_i \frac{\partial \mathbf{c}_i}{\partial t} + u_i \frac{\partial \mathbf{c}_i}{\partial x} + \mathbf{r}_i(\mathbf{c}_i)\right] = \mathbf{0} \text{ in } \Omega_i$$

with continuity in concentration and interfacial fluxes. Here t_D is transverse diffusion time and other terms have their usual meaning. To obtain the reduced order model, we use the Lypunov-Schmidt (L-S) procedure where the vector of concentrations and temperature (**c**) and non-linear functions (**f**) are projected onto the orthogonal spaces, leading to global and local equations.

Results and Discussion

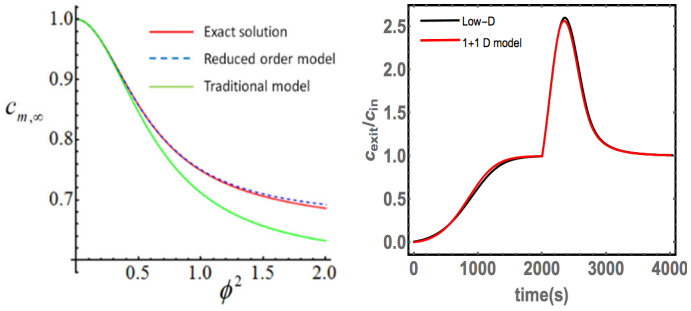
The transverse averaging of the above detailed model leads to the global equations that are equivalent to phase averaged (macroscopic) balances that contain various modes and interfacial fluxes, which are related through local equations having following form:

$$\langle \mathbf{c} \rangle_i - \mathbf{c}_{si} \equiv -\mathbf{\Lambda}_{Ti} \langle u \rangle_i \frac{\partial \langle \mathbf{c} \rangle_i}{\partial x} + \mathbf{K}_{mi}^{-1} \mathbf{J}_i + \widehat{\mathbf{K}}_{mi}^{-1} \mathbf{J}_{i+1},$$

where the dispersion and transfer coefficient matrices depend on diffusivity matrix, velocity profile and geometry in each phase. It is noted that the structure of local equations is fundamentally different from the traditional form, where the concentration gradient in any phase depends on the mass-influx from their adjacent domains caused by the transport (diffusion/flow) and reaction in other domains.

A comparison between these reduced order models and exact solution is demonstrated by plotting exit concentration (dimensionless) in Figure 1 for the two cases: (a) short monolith reactors and (b) dual-layered monolith with hydrocarbon trap in layer-2 (no reaction in layer-1), that are used in diesel/gasoline engines.

In Figure 1, x-axis is represented by dimensionless reaction rate (Theile modulus) in case-a while real time in case-b. It can be seen from Figures 1(a) and 1(b) that our reduced order model leads to accurate solution. In addition, it can be seen from Figure 1(a) that the traditional model may not be accurate for fast reactions (hence for fast transients).



(a) (b)

Figure 1. Comparison of averaged model with exact solution for (a) short monolith, (b) dual-layered monolith with hydrocarbon trap

Summary and Conclusions

In this work, reduced order models are developed to describe transport and reaction processes in a multi-layered catalytic monolith based on L-S procedure in multi-scale multi-phase form. The inter- and intra- phase fluxes are linearly related to concentration modes that have fundamentally different structure from the traditional form. The expression relating driving force to fluxes is in similar form to the Stefan-Maxwell equations for multi-component diffusion. The concentration gradient in any phase depends on the mass-influx from all adjacent domains. The reduced order models are shown to have good accuracy by comparing with exact solution for special case of a short monolith reactor and realistic case of dual-layered monolith with hydrocarbon trap used in diesel/gasoline engines. Thus, these models can be utilized in parametric studies, real time simulation, and design and performance evaluation of catalytic monolith reactor systems.

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