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Reduced order multimode transient models for catalytic monoliths with micro-kinetics

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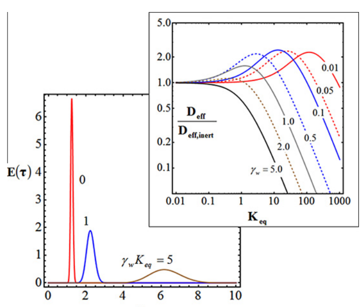
HIGHLIGHTS

- A new reduced order model is developed for monoliths with micro-kinetics.
- The multimode model is independent of the solid–fluid interfacial flux.
- The model is more accurate than two-phase models for transient reacting flows.
- Traditional flux expression has limited validity for fast transients with reaction.
- Comparisons with two-phase and 1+1 dimensional models is presented.

GRAPHICAL ABSTRACT

Response curve of adsorbing solute in monolith for a unit impulse input: effective velocity decreases and overall spreading increases with increase in adsorption–desorption equilibrium constant K_{eq}. The effective dispersion coefficient of adsorbing solute varies non-monotonically with K_{eq}.



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ABSTRACT

We present a reduced order model for describing the transient diffusion and convection in monolith channels with diffusion, adsorption, desorption and reaction in the porous washcoat layer. Unlike the traditional two-phase or the 1(axial)+1(washcoat) dimensional models whose validity may be limited for transient reacting flows, the present multi-mode model is accurate to first order in the transverse diffusion time (t_D) and hence is valid over a much wider range of operating conditions and kinetics. We provide a physical interpretation of the various effective coefficients appearing in the reduced order model. For the case of inert and non-reacting solutes, we obtain effective transport coefficients and relate them to experimental observations. For the steady-state reacting case, we present a multi-mode form of the model with intra- and interphase mass transfer coefficients. In the general transient case, we show that the traditional external mass transfer coefficient concept is not applicable as the solid–fluid interfacial flux cannot be expressed in terms of concentration differences even to leading order in t_D. We also show that for transient reacting flows, the widely used two-phase and 1+1 dimensional models may lead to errors of order unity in the solid–fluid interfacial flux and order t_D in the exit concentration or moments. Finally, we apply the reduced order model to the chromatographic method to relate the first and second moments to the effective diffusivities and kinetic parameters and compare the results with those obtained from the traditional two-phase models.

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Nomenclature

Roman letters

a	radius of the tube
a_{vc}	area (available for adsorption) unit volume of washcoat
A_{Ω_f}	cross-sectional area of flow channel
A_{Ω_w}	cross-sectional area of washcoat
c_a	concentration of adsorbed species (based on unit pore surface area)
c_{a0}	initial concentration of adsorbed species (based on unit pore surface area)
c_{aT}	total concentration of sites (based on unit pore surface area)
c_f	solute concentration in fluid phase
c_{mf}	cupmixing concentration
$c_{mf,in}$	inlet solute concentration in fluid phase
c_{f0}	initial solute concentration in fluid phase
c_{ref}	some reference concentration in fluid phase
c_s	solute concentration at fluid–washcoat interface
c_w	concentration in washcoat
c_{w0}	initial solute concentration in washcoat
$\langle c_a \rangle_w$	cross-sectionally averaged concentration (based on unit pore surface area) of adsorbed species in washcoat
$\widetilde{c_a}$	concentration of adsorbed species per unit volume in washcoat
$\langle \widetilde{c_a} \rangle_w$	cross-sectionally averaged concentration of adsorbed species unit volume in washcoat
$\langle c \rangle_f$	cross-sectionally averaged concentration in fluid phase
$\langle c \rangle_w$	cross-sectionally averaged concentration in washcoat
$\langle c_s \rangle$	peripheral averaged concentration at fluid–washcoat interface
D_f	molecular diffusivity of solute in fluid phase
d_h	hydraulic diameter of flow channel
D_{eff}	effective Taylor diffusivity in the monolith
D_T	Taylor diffusivity in the flow channel
D_w	molecular diffusivity of solute in washcoat
E	RTD (residence time distribution) curve
f_{sat} =	adsorption–desorption isotherm
J =	interfacial molecular flux at fluid–washcoat interface
$\langle J \rangle$=	peripheral averaged interfacial molecular flux at fluid–washcoat interface
$\langle J \rangle_{ss}$ =	Peripheral averaged interfacial molecular flux at fluid–washcoat interface at steady-state
k_a	adsorption rate constant
k_d	desorption rate constant
k_{eff}	effective reaction rate constant in monolith
k_{ext}	external mass transfer coefficient
k_w	reaction rate constant
$k_{w,eff}$	global reaction rate constant in washcoat
$k_{ff}, k_{fw}, k_{wf}, k_{ww}, k_{sf}, k_{sw}, k_{sf1}, k_{sw1}, k_{f0}$	coefficients in reduced order model
k_{int}	internal mass transfer coefficient
k_o	overall mass transfer coefficient
L	Length of the monolith
m_k	k-th moment (temporal) of exit concentration
$\mathbf{n}_{\Omega_f}$	unit normal vector to $\partial\Omega_f$
$\mathbf{n}_{\Omega_w}$	unit normal vector to $\partial\Omega_w$
$P_{\Omega f}$	perimeter of the fluid–washcoat interface
p	transverse Peclet number
r	radial coordinate
R_a	adsorption rate per unit pore surface area
R_d	desorption rate per unit pore surface area
R_w	reaction rate per unit pore surface area
$\widetilde{R_w}$	homogeneous global reaction (based on per unit volume) in washcoat
R_{Ω_f}	hydraulic radius for flow channel
R_{Ω_w}	effective (diffusion) length scale in washcoat
Sh_e	external Sherwood number
Sh_o	overall Sherwood number
$Sh_{\Omega i}$	internal Sherwood number
t	real time
t_{ads}	adsorption time constant
t_C	convection diffusion time
t_D	transverse diffusion time in flow channel
t_{des}	desorption time constant
t_{Dw}	transverse diffusion time in washcoat
t_R	reaction time constant
u_f	fluid velocity in the axial direction (dimensional)
$\langle u \rangle_f$	cross-sectional averaged velocity in fluid phase in the axial direction (dimensional)
$\langle u \rangle_{eff}$	effective velocity appearing in reduced order model at monolith scale
$\langle u \rangle_0$	effective velocity appearing in reduced order model at monolith scale to the leading order in t_D
x	coordinate along the length of the reactor (dimensional)

Greek letters

ε_{wc}	porosity of the washcoat
ϕ_d	Thiele modulus based on desorption rate
ϕ_w	Thiele modulus based on reaction rate
ϕ_{eff}	Thiele modulus based on effective reaction rate
γ	volume capacity of the washcoat
Γ	ratio of net (adsorption + volumetric) capacity of the washcoat to that of fluid phase
γ_{eq}	adsorption capacity of the washcoat
γ_w	volume ratio of washcoat to the flow channel
θ	azimuthal coordinate
θ_s	fraction of adsorbed sites occupied
χ_e	exit conversion
$\lambda =$	ratio of washcoat thickness to radius of flow channel
$\Lambda_{mf}, \Lambda_{mw}, \Lambda_a$	transverse coefficient appearing in reduced order model
Λ_{eff}	dimensionless effective dispersion coefficient
μ	ratio of solute diffusivities in fluid to washcoat
μ_2	second central moment (temporal) of exit concentration
τ	dimensionless time (non-dimensionalized by convection time t_C)
Ω	overall cross-section (flow channel + washcoat)
Ω_f	cross-section of flow channel
Ω_w	cross-section of washcoat

Operators

$\nabla_\perp^2$	transverse Laplacian operator (dimensional)
$\langle\rangle_f$	inner product (averaged) over flow channel
$\langle\rangle_w$	inner product (averaged) over washcoat

1. Introduction

Mathematical models describing the steady-state and transient behavior of chemical reactors and separation columns are obtained by combining the various conservation laws with the constitutive equations for the rate processes. When smaller scale processes such as diffusion, adsorption, desorption and reaction are included, and inlet conditions vary with time, these models are usually