Low-dimensional Models for Real Time Simulations of Catalytic After-treatment Systems

Saurabh Y. Joshi,
Divesh Bhatia
Jin Xu
Michael P. Harold
Vemuri Balakotaiah

Department of Chemical and Biomolecular Engineering
University of Houston, Houston, Texas 77204

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LNT/SCR, TWC/DOC & DPF Research at UH

Experiments
- Lean NOx Storage
  - Steady-state lean NOx reduction
- NOx storage & reduction (cycling)

Modeling & Simulation

Kinetic Modeling
- Microkinetics (from TAP)
- Global kinetics

Reactor Modeling
- Isothermal / short monoliths
- Non-isothermal effects

Analysis & Simulation
- Bifurcation analysis
- Parametric studies
- Simulation and Comparison to Expts

Implementation / Optimization of LNTs
- Software development
- Integration of engine & emission controls

Bench-scale reactor studies

Transient kinetics studies (TAP)

Full-Scale Testing

Engines & Controls (ME.)
Ford
BASF
City of Houston

Low-dimensional Models for Control and Optimization
Overview

Part A: Low-dimensional Models for Real Time Simulations of Catalytic After-treatment Systems (TWCs, DOCs, LNTs, SCRs and DPFs)  
[Ref: Joshi, Harold and Balakotaiah, AIChE J., May 2009]  
• low-d models for diffusion-convection-reaction  
• simulation of TWC cold start behavior in real time  
• extensions of low-d models

Part B: Analysis of monolith reactors using low-d models  
(i) Controlling regimes  
(ii) External Mass transfer controlled regime  
(iii) Light-off Behavior  
(iv) Multiple steady-states and periodic states  
(v) Fronts in monoliths  
(vi) Bifurcation analysis  
(vii) Microkinetic models vs. global kinetic models
Catalytic Monoliths—Multiple Length/Time Scales

Catalytic Converter

Monolith
Radius ~10 cm
Length ~10 cm

Channel Diameter ≈ 1 mm

Washcoat Thickness ≈ 20 µm

Precious Metals (Pt, Rh, Pt/Ba)
Pore Diameter: 10-50 Å
Models of Homogeneous & Catalytic Reactors

**Packed-Bed Catalytic Reactor**

**Homogeneous Tank Reactor**

**Detailed Model:**
\[
C \frac{\partial u}{\partial t} = F(x, u, \nabla u, \nabla^2 u, p); \quad x \text{ in } \Omega, \ t > 0
\]

I.C.: \( \Gamma(x, u, \nabla u, p) = 0 \) in \( \Omega \), \( t = 0 \)

B.C.: \( B(x, u, \nabla u, p) = 0 \) in \( \partial \Omega \), \( t > 0 \)

**Ideal CSTR Model:**
*(Bodenstein & Wolgast, 1908)*
\[
\frac{d\overline{C}}{dt} = \frac{1}{\tau}(C_{in} - \overline{C}) - R(\overline{C}); \quad t > 0
\]

I.C.: \( \overline{C}(t = 0) = \overline{C}_0 \)

**Objective:** Develop accurate low-dimensional models (in terms of average/measurable quantities) *without losing any important physics at small length/time scales.*
Detailed Diffusion-Convection-Reaction Models for Monoliths

Shape Normalized Diffusion Lengths

\[ R_\Omega = \frac{A_{\Omega_1}}{P_\Omega} \]

\[ \delta_w = \frac{A_{\Omega_2}}{P_\Omega} \]

**Steady State Balance Equations**

Convection

\[ \frac{\partial C_f}{\partial t} + u(x', y') \frac{\partial C_f}{\partial z'} = D_m \left( \nabla^2 C_f + \frac{\partial^2 C_f}{\partial z'^2} \right), \quad (x', y') \in \Omega_1 \]

Diffusion

\[ \frac{\partial C_f}{\partial t} = \frac{\partial C_s}{\partial t} + R(C_s) = D_m \left( \nabla^2 C_f + \frac{\partial^2 C_s}{\partial z'^2} \right), \quad (x', y') \in \Omega_2 \]

Reaction

\[ \varepsilon_p \frac{\partial C_s}{\partial t} + R(C_s) = D_m \left( \nabla^2 C_s + \frac{\partial^2 C_s}{\partial z'^2} \right), \quad (x', y') \in \Omega_2 \]

Boundary Conditions

\[ n.D_m \nabla . C_f = n.D_e \nabla . C_s \]

\[ C_f = C_s \]

\[ n.D_e \nabla . C_s = 0, \quad (x', y') \in \partial \Omega_2 \]

Coupled PDEs in \((x', y', z')\)
Traditional Low-dimensional Models for Catalytic Reactor Models

**Pseudo-homogeneous PFR model**

\[
\frac{\partial c}{\partial t} + \bar{u} \frac{\partial c}{\partial x} + R(c) = 0; \quad 0 < x < L, \quad t > 0 \quad \text{B.C.} \quad c(0,t) = c_{in}(t), \quad \text{I.C.} \quad c(x,0) = c_o(x)
\]

Two-phase model for a packed-bed reactor \( (\text{Wicke, 1960; Liu & Amundson, 1963}) \)

\[
\varepsilon_f \frac{\partial c_f}{\partial t} + \bar{u} \frac{\partial c_f}{\partial x} = -k_c a_v (c_f - c_s); \quad 0 < x < L, \quad t > 0 \quad \text{B.C.} \quad c_f(0,t) = c_{f,in}(t)
\]

\[
(I - \varepsilon_f) \frac{\partial c_s}{\partial t} = k_c a_v (c_f - c_s) - R(c_s); \quad t > 0 \quad \text{I.C.} \quad c_s(x,0) = c_{so}(x)
\]

Catalytic Reactor Model with Dispersion and Mass Transfer Coefficients

\[
\varepsilon_f \frac{\partial c_f}{\partial t} + \bar{u} \frac{\partial c_f}{\partial x} = D_{ef} \frac{\partial^2 c_f}{\partial x^2} - k_c a_v (c_f - c_s); \quad 0 < x < L, \quad t > 0 \quad \text{B.C. 1} \quad D_{ef} \frac{\partial c_f}{\partial x} = \bar{u} [c_f(0,t) - c_{f,in}(t)]
\]

\[
(I - \varepsilon_f) \frac{\partial c_s}{\partial t} = k_c a_v (c_f - c_s) - R(c_s); \quad t > 0 \quad \text{B.C. 2} \quad \frac{\partial c_f}{\partial x} = 0
\]

Catalytic Reactor Model with Dispersion, Mass Transfer Coefficients & Intra-particle diffusion

\[
(I - \varepsilon_f) \frac{\partial c_s}{\partial t} = k_c a_v (c_f - c_s) - R(c_s) \eta; \quad t > 0
\]

\[
\nabla (D_e \nabla c) = R(c) \quad \text{in } \Omega; \quad c = c_s \text{ on } \partial \Omega; \quad \eta = \frac{1}{V_\Omega} \int_{\Omega} R(c) d\Omega / R(c_s)
\]
Detailed Diffusion-Convection-Reaction Models for Monoliths

\[ \Omega \]

\[ \partial \Omega \]

\[ \Omega_1 \]

\[ \Omega_2 \]

\[ \partial \Omega_1 \]

Shape Normalized Diffusion Lengths

\[ R_\Omega = \frac{A_{\Omega_1}}{P_\Omega} \]

\[ \delta_w = \frac{A_{\Omega_2}}{P_\Omega} \]

fluid

washcoaevt

interfacial coupling

Steady State Balance Equations

\[ \frac{\partial C_f}{\partial t} + u(x', y') \frac{\partial C_f}{\partial z'} = D_m \left( \nabla_z^2 C_f + \frac{\partial^2 C_f}{\partial z'^2} \right), (x', y') \in \Omega_1 \]

\[ \text{convection} \]

\[ \text{diffusion} \]

\[ \varepsilon_p \frac{\partial C_s}{\partial t} + R(C_s) = D_e \left( \nabla_z^2 C_s + \frac{\partial^2 C_s}{\partial z'^2} \right), (x', y') \in \Omega_2 \]

\[ \text{reaction} \]

\[ \text{diffusion} \]

Coupled PDEs in \((x', y', z')\)

Boundary Conditions

\[ n.D_m \nabla.C_f = n.D_e \nabla.C_s \]

\[ C_f = C_s \]

\[ (x', y') \in \partial \Omega_1 \]

\[ n.D_e \nabla.C_s = 0, (x', y') \in \partial \Omega_2 \]

\[ D_m \frac{\partial C_f}{\partial z'} = u(x', y')(C_f - C_{in}(t)) & \frac{\partial C_s}{\partial z'} = 0, z' = 0 \]

\[ \frac{\partial C_f}{\partial z'} = \frac{\partial C_s}{\partial z'} = 0, z' = L \]
Diffusion is dominant at small length scales

Local Diffusion operator of the CDR equation (with a periodic/Neumann & Robin BCs) has a zero eigenvalue with a constant eigenfunction.

Spatial degrees of freedom (small length scales) can be eliminated near the zero eigenvalue (small parameter).

Procedure:

- Write the detailed (microscopic) model
- Identify the smallest length/time scale (expressed in terms of a small parameter, say p)
- Express all other parameters ($\lambda_i$) as $\lambda_i = \alpha_i p^n$, where $\alpha_i$ is $O(1)$ & $n = 1, 0, -1, \ldots$
- Apply the L-S reduction (eliminate spatial degrees of freedom)
Concentration Modes

\[ C_{fm} = \frac{\int_{\Omega_1} u(x, y) C_f(x, y) \, d\Omega}{\int_{\Omega_1} u(x, y) \, d\Omega} = \text{cup-mixing concentration} \]

\[ < C_f > = \frac{\int_{\Omega_1} C_f(x, y) \, d\Omega}{\int_{\Omega_1} d\Omega} = \text{average concentration in fluid} \]

\[ C_s = \frac{\int_{\partial\Omega_1} C_1(x, y) \, d\Gamma}{\int_{\partial\Omega_1} d\Gamma} = \frac{\int_{\partial\Omega_1} C_2(x, y) \, d\Gamma}{\int_{\partial\Omega_1} d\Gamma} \]

\[ \langle C_{wc} \rangle = \frac{\int_{\Omega_2} C_2(x, y) \, d\Omega}{\int_{\Omega_2} d\Omega} = \frac{1}{A_{\Omega_2}} \int_{\Omega_2} C_2(x, y) \, d\Omega \]
On the Relationship Between Aris and Sherwood Numbers and Friction and Effectiveness Factors

(i) Concept of an internal mass transfer coefficient:

\[ k_{ci} = \frac{1}{A_{\Omega'}} \int_{A_{\Omega'}} D_e \nabla C \cdot n \, dS }{(C_s - \langle C \rangle)} \]

Flux, \( j = k_{ci} (C_s - \langle C \rangle) \)

Sherwood number, \( Sh_{\Omega} = k_{ci} R_{\Omega} \frac{D_e}{D_e} \)

(ii) Effectiveness factor:

\[ \eta = \frac{\langle r(C) \rangle}{r(C_s)} = \frac{\langle C \rangle}{C_s} \text{ (for linear kinetics)} \]

(iii) Aris numbers:

\[ \eta = 1 - A_{r_1} \Phi^2 + A_{r_2} \Phi^4 - ... \]

\[ \eta = \frac{1}{1 + \frac{\Phi^2}{Sh_{\Omega}}} \]

(iv) Friction factors for viscous flow in a duct (2-D):

\[ \frac{f \, Re}{8} = Sh_{\Omega_{\infty}} = \frac{1}{A_{r_1}} ; \quad Re = \frac{4 R_{\Omega} \langle u \rangle}{\nu} \]

(i) Low-dimensional Model for Multicomponent Nonlinear Diffusion-Reaction Problems
(ii) Low-dimensional Models for Diffusion-Convection-Reaction Problems

Low-Dimensional Models for Diffusion-Reaction Problems

The Internal Diffusion-Reaction Problem in a Porous Catalyst

\[ \varepsilon_p \frac{\partial C}{\partial t'} = \nabla \cdot (D_c \nabla C) - R(C); \quad (x', y', z') \in \Omega', t' > 0 \]

\[ C = C_s(t'); \quad \text{on } \partial \Omega'. \]

\[ C = C_i(x', y', z') \quad \text{at } t' = 0 \]

Volume averaged concentration in particle

\[ \langle C \rangle(t') = \frac{1}{V_{\Omega'}} \int_{\Omega'} C(x', y', z', t') d\Omega' \]

\[ C = \langle C \rangle + C' \]

\[ \langle C' \rangle = 0 \]

\[ \langle R(\langle C \rangle + C') \rangle = R(\langle C \rangle) + O(C')^2 \]

Low-Dimensional Model

\[ \varepsilon_p V_{\Omega'} \frac{d\langle C \rangle}{dt'} = A_{\Omega'} k_{ci} (\overline{C_s(t')} - \langle C \rangle) - V_{\Omega'} R(\langle C \rangle) \]

\[ \langle C \rangle = \langle C_i \rangle \quad \text{at } t' = 0, \]
Three-mode Model for an Isothermal Monolith ($L/d_h >> 1$)

\[
\frac{\partial C_{fm}}{\partial t} + \langle u \rangle \frac{\partial C_{fm}}{\partial x} = -\frac{k_{ce}}{R_\Omega} (C_{fm} - C_s)
\]

\[
\varepsilon_p \delta_w \frac{\partial \langle C_w \rangle}{\partial t} = k_{ci} (C_s - \langle C_w \rangle) + \delta_w R(\langle C_w \rangle)
\]

\[
k_{ce} (C_{fm} - C_s) = k_{ci} (C_s - \langle C_w \rangle)
\]

Two-Mode form:

\[
\frac{\partial C_{fm}}{\partial t} + \langle u \rangle \frac{\partial C_{fm}}{\partial x} = -\frac{k_{mo}}{R_\Omega} (C_{fm} - \langle C_w \rangle)
\]

\[
\varepsilon_p \delta_w \frac{\partial \langle C_w \rangle}{\partial t} = k_{mo} (C_{fm} - \langle C_w \rangle) - \delta_w R(\langle C_w \rangle)
\]

\text{IC1: } C_{fm}(x,t=0) = C_{m0}(x)

\text{IC2: } \langle C_w \rangle(x,t=0) = \langle C_{w0} \rangle(x)

\text{BC: } C_{fm} = C_{in}(t) @ x = 0

\[
k_{ci} = \frac{Sh_i \Omega D_e}{\delta_w} \quad k_{ce} = \frac{Sh_e \Omega D_m}{R_\Omega}
\]

\[
\frac{1}{k_{mo}} = \frac{1}{k_{ci}} + \frac{1}{k_{ce}}
\]

\[
= \frac{\delta_w}{Sh_i \Omega D_e} + \frac{R_\Omega}{Sh_e \Omega D_m}
\]

\[
\approx \frac{\delta_w}{Sh_i \Omega \infty D_e} + \frac{R_\Omega}{Sh_e \Omega \infty D_m}
\]
Analogy between internal and external mass transfer coefficients
\[ \nabla^2 c = g(x', y' )\phi^2 c \quad (x', y') \in \Omega_2 \quad n_{\Omega_2} \cdot \nabla c = 0 \quad \text{on} \ \partial \Omega_2 \quad c = 1 \quad \text{on} \ \partial \Omega_1 \]

\[
k_{mi} = \frac{\int_{A_{\Omega_2}} R(C) \, dA}{P_{\Omega} \left( C_s - \langle C \rangle \right)} \quad Sh_i = \frac{k_{mi} R_{\Omega}}{D_e} \quad Sh_i = Sh_{i,\infty} + \frac{\Lambda \phi^2}{1+\Lambda \phi}
\]


$Sh_i$ for some common geometries

<table>
<thead>
<tr>
<th>Channel Shape</th>
<th>$Sh_{i\infty}$ and $\Lambda$</th>
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</thead>
<tbody>
<tr>
<td>Figure a</td>
<td>$Sh_{i\infty} = 3$ and $\Lambda = 0.32$</td>
</tr>
<tr>
<td>$R_2/R_1$</td>
<td>$Sh_{i\infty}$</td>
</tr>
<tr>
<td>1.01</td>
<td>3.0125</td>
</tr>
<tr>
<td>1.1</td>
<td>3.153</td>
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<tr>
<td>1.2</td>
<td>3.311</td>
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<td>Figure b</td>
<td>$a/R$</td>
</tr>
<tr>
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<td>0.826</td>
</tr>
<tr>
<td>1.1</td>
<td>1.836</td>
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<tr>
<td>1.2</td>
<td>2.533</td>
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<tr>
<td>Figure c</td>
<td>$a/R$</td>
</tr>
<tr>
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<td>0.84</td>
</tr>
<tr>
<td>1.9245</td>
<td>1.45</td>
</tr>
<tr>
<td>2.4744</td>
<td>2.92</td>
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<tr>
<td>Figure d</td>
<td>$b/a$</td>
</tr>
<tr>
<td>1.11</td>
<td>5</td>
</tr>
<tr>
<td>1.25</td>
<td>10</td>
</tr>
<tr>
<td>Figure f</td>
<td>$a/R$</td>
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<tr>
<td>1.155</td>
<td>0.814</td>
</tr>
<tr>
<td>1.17</td>
<td>1.16</td>
</tr>
<tr>
<td>1.2</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Joshi SY, Harold MP and Balakotaiah V. On the use of internal mass transfer coefficients in modeling of diffusion and reaction in catalytic monoliths. Chemical Engineering Science (in review)
Three-mode Model for an Isothermal Monolith \((L/d_h \gg 1)\)

\[
\frac{\partial C_{fm}}{\partial t} + \langle u \rangle \frac{\partial C_{fm}}{\partial x} = - \frac{k_{ce}}{R_\Omega} (C_{fm} - C_s)
\]

\[
\varepsilon_p \delta_w \frac{\partial \langle C_w \rangle}{\partial t} = k_{ci} (C_s - \langle C_w \rangle) + \delta_w R(\langle C_w \rangle)
\]

\[
k_{ce} (C_{fm} - C_s) = k_{ci} (C_s - \langle C_w \rangle)
\]

**Two-Mode form:**

\[
\frac{\partial C_{fm}}{\partial t} + \langle u \rangle \frac{\partial C_{fm}}{\partial x} = - \frac{k_{mo}}{R_\Omega} (C_{fm} - \langle C_w \rangle)
\]

\[
\varepsilon_p \delta_w \frac{\partial \langle C_w \rangle}{\partial t} = k_{mo} (C_{fm} - \langle C_w \rangle) - \delta_w R(\langle C_w \rangle)
\]

**IC1:** \(C_{fm}(x,t=0) = C_{m0}(x)\)

**IC2:** \(\langle C_w \rangle(x,t=0) = \langle C_{w0} \rangle(x)\)

**BC:** \(C_{fm} = C_{in}(t) \at x=0\)

\[
k_{ci} = \frac{Sh_i \Omega D_e}{\delta_w} \quad k_{ce} = \frac{Sh_e \Omega D_m}{R_\Omega}
\]

\[
\frac{1}{k_{mo}} = \frac{1}{k_{ci}} + \frac{1}{k_{ce}}
\]

\[
= \frac{\delta_w}{Sh_i \Omega D_e} + \frac{R_\Omega}{Sh_e \Omega D_m}
\]

\[
\approx \frac{\delta_w}{Sh_i \Omega \infty D_e} + \frac{R_\Omega}{Sh_e \Omega \infty D_m}
\]
Comparison of Accuracy of Low-D Model for Linear Kinetics, Single Reaction and Isothermal Case:

Circular channel with uniform washcoat thickness

Low-Dimensional Model for Multi-component DCR Problem:

Species conservation:

\[
\frac{\partial C_{fmj}}{\partial t} + \langle u \rangle \frac{\partial C_{fmj}}{\partial x} = - \frac{k_{ce,j}}{R_\Omega} \left( C_{fmj} - C_{sj} \right)
\]

\[
\varepsilon_p \delta_w \frac{\partial \langle C_w \rangle_j}{\partial t} = \sum_{m=1}^{s} k_{ci,jm} \left( C_{ms} - \langle C_w \rangle_m \right) + \delta_w \sum_{i=1}^{N} v_i R_i \left( \langle C_w \rangle_1, \langle C_w \rangle_2, \ldots, \langle C_w \rangle_S, T_s \right)
\]

\[
k_{ce,j} \left( C_{fmj} - C_{sj} \right) = k_{ci,j} \left( C_{sj} - \langle C_{wc} \rangle_j \right)
\]

\[
k_{ce,j} = \frac{S_h \Omega \infty D_{m,j}}{R_\Omega}, \quad k_{ci,j} = \frac{S_h \Omega \infty D_{ej}}{\delta_w}
\]

\[j=1,2 \ldots, S \text{ (species)}; \quad N \text{ reactions}\]

Energy balance:

\[
\rho_f c_{pf} \frac{\partial T_f}{\partial t} + \langle u \rangle \rho_f c_{pf} \frac{\partial T_f}{\partial x} = - \frac{h}{R_\Omega} \left( T_f - T_s \right)
\]

\[
\delta' \rho_s c_{ps} \frac{\partial T_s}{\partial t} = \delta' k_s \frac{\partial^2 T_s}{\partial x^2} + h \left( T_f - T_s \right) + \delta w \sum_{j=1}^{M} R_j \left( \langle C_w \rangle_1, \langle C_w \rangle_2, \ldots, \langle C_w \rangle_N, T_s \right) \times \left( - \Delta H \right)
\]

\[T_f = T_{fin}(t) \text{ @ } x = 0; \quad T_s(x,t=0) = T_{s0}(x); \quad T_f(x,t=0) = T_{f0}(x); \quad \frac{\partial T_s}{\partial x} = 0 \text{ @ } x = 0, L\]
Simulation of Transient Behavior of a TWC with Global Kinetics

1. \( CO + \frac{1}{2}O_2 \rightarrow CO_2 \)

2. \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \)

3. \( CH_y + \frac{4+y}{4}O_2 \rightarrow CO_2 + \frac{y}{2}H_2O \)

4. \( NO + CO \rightarrow CO_2 + N_2 \)

\[
R_{CO} = \frac{k_1 \dot{X}_{CO} \dot{X}_{O_2}}{F(X, T_s)}
\]

\[
R_{H_2} = \frac{k_1 \dot{X}_{H_2} \dot{X}_{O_2}}{F(X, T_s)}
\]

\[
R_{HC} = \frac{k_3 \dot{X}_{HC} \dot{X}_{O_2}}{F(X, T_s)}
\]

\[
R_{NO} = \frac{k_4 \dot{X}_{CO}^{1.4} \dot{X}_{O_2}^{0.3} \dot{X}_{NO}^{0.13}}{T_s^{-0.17}(T_s + k\alpha_5 \dot{X}_{CO})^2}
\]

\[
\Gamma(\dot{X}, T_s) = T_s(1 + k\alpha_1 \dot{X}_{CO} + k\alpha_2 \dot{X}_{HC})^2(1 + k\alpha_3 \dot{X}_{CO}^2 \dot{X}_{HC}^2)(1 + k\alpha_4 \dot{X}_{NO}^{0.7})
\]

\[
k_i = A_i e^{-\frac{E_i}{T_s}} \quad i = 1, 3, 4
\]

\[
k\alpha_i = A_{ii} e^{-\frac{E_{i\alpha}}{T_s}} \quad i = 1 - 5
\]
Monolith Temperature

COMSOL SOLUTION

LOW-D MODEL SOLUTION

Joshi, Harold & Balakotaiah,
AIChE J., May 2009
Transient simulation showing front end ignition (a) monolith temperature without washcoat diffusion (b) monolith temperature with washcoat diffusion.
Demonstration of Real Time Simulation of the Cold-start Behavior of a TWC

Extensions to the low-D models

• Developing flows
• Microkinetics (2 equations for each gas phase species, one eqn. for each surface species)
• Estimation of kinetic parameters from bench scale expts.
• Axial variations of PGM loading
• Transverse variations in temperature (heat losses)
• Other types of catalytic and multi-phase reactors
Overview

Models:
Low-dimensional Models for Real Time Simulations of Catalytic After-treatment Systems (TWCs, DOCs, LNTs, SCR and DPFs)
• low-d models for diffusion-convection-reaction
• simulation of TWC cold start behavior in real time
• extensions of low-d models

Analysis:
Generic features of monoliths using low-d models
(i) Controlling regimes
(ii) External Mass transfer controlled regime
(iii) Fronts in monoliths
(iv) Multiple steady-states and periodic states
(v) Light-off behavior
(vi) Bifurcation analysis
(vii) Microkinetic models vs. global kinetic models
(i) Controlling Regimes

Comparison of various resistances

$$\frac{1}{k_{\text{app}}} = \frac{1}{k_{\text{me}}} + \frac{1}{k_{\text{mi}}} + \frac{1}{kR_{\Omega_2}}$$

Total Resistance ($R_t$) = External Resistance ($R_e$) + Internal (Washcoat) Resistance ($R_w$) + Reaction Resistance ($R_r$)

Criterion for controlling regimes

- $R_r \geq 0.9R_t$ for kinetic regime or reaction controlling
- $R_e \geq 0.9R_t$ for external mass transfer controlling
- $R_w \geq 0.9R_t$ for washcoat diffusion controlling
Kinetic Regime-H$_2$ Oxidation

Kinetics and Parameters

$R_{\Omega_1} = 0.5 \text{ mm}$, $R_{\Omega_2} = 20 \mu\text{m}$, $L = 7 \text{ cm}$, $\langle u \rangle = 1 \text{ m/s}$

$$ R = \frac{1.1835 \times 10^7}{T_s} \exp\left(-\frac{1046.4}{T_s}\right) C_{H_2} $$

Washcoat Diffusion controlling

Parameters

\( R_{\Omega_1} = 0.5 \text{ mm} \), \( R_{\Omega_2} = 50 \text{ \mu m} \), \( D_e = 10^{-9} \text{ m}^2 / \text{s} \), \( L = 7 \text{ cm} \), \( \langle u \rangle = 1 \text{ m} / \text{s} \), PGM Loading = 10 g / ft³
Washcoat diffusion NOT important

\[ R_{\Omega_1} = 0.5 \, mm, \quad R_{\Omega_2} = 10 \, \mu m, \quad D_e = 10^{-6} \, m^2 / s, \quad L = 7 \, cm, \quad \langle u \rangle = 1 \, m / s, \quad PGM \, Loading = 50 \, g / ft^3 \]
(ii) External Mass Transfer Controlled Regime in Monoliths

\[ R_\Omega = \frac{A_\Omega}{P_\Omega} \]

\[ \frac{C_{Af}}{C_{A0}} = \alpha_1 \text{Exp} \left[ -\frac{\mu_1}{P} \right] \]

\[ \mu_1 = \frac{Sh_r}{4} \quad P = \frac{R_\Omega^2 \langle u \rangle}{LD_m} \]

\[ L_{\text{min}} = 4 \frac{R_\Omega^2 \langle u \rangle}{D_m} \]

Minimum lengths/front widths

At 300°C with \( R_\Omega = 0.5 \text{mm} \)

<table>
<thead>
<tr>
<th>Species</th>
<th>H2</th>
<th>NO</th>
<th>NH3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle u \rangle = 1 \text{ m/s} )</td>
<td>1.5 mm</td>
<td>6.0 mm</td>
<td>4.5 mm</td>
</tr>
<tr>
<td>( \langle u \rangle = 10 \text{ m/s} )</td>
<td>15 mm</td>
<td>60 mm</td>
<td>45 mm</td>
</tr>
</tbody>
</table>
(iii) Analysis of fronts in after-treatment systems

**Observations:**

(i) Front speeds are independent of kinetics
(ii) Front concentrations must satisfy stoichiometric relations

**Adsorption/storage/Regeneration:**

\[
u_f = \langle u \rangle \frac{R}{\delta} \left( \frac{C_{A,in}}{vN_{so}} \right)
\]

**Thermal (front end ignition):**

\[
u_f = \langle u \rangle \frac{R}{\delta} \left( \frac{\rho_{g} c_{pt}}{\rho_{s} c_{ps}} \right)
\]

**NO\textsubscript{x} Storage on Pt/Ba catalyst**

\[NO + \frac{1}{2}O_2 \leftrightarrow NO_2\]

\[BaO + 3NO_2 \leftrightarrow Ba(NO_3)_2 + NO\]

**NO\textsubscript{x} Reduction on Pt/Ba catalyst**

\[Ba(NO_3)_2 + 8H_2 \rightarrow BaO + 5H_2O + 2NH_3\]

\[Ba(NO_3)_2 + \frac{10}{3}NH_3 \rightarrow BaO + 5H_2O + \frac{8}{3}N_2\]
Summary/Conclusions

Part A: Fundamentals based
Low-dimensional Models for Real Time Simulations of Catalytic After-treatment Systems (TWCs, DOCs, LNTs, SCRs and DPFs)

Part B: Analysis of monolith features using low-d models
(i) Controlling regimes
(ii) External Mass transfer controlled regime
(iii) Fronts in monoliths
(iv) Multiple steady-states and periodic states
(v) Light-off behavior
(vi) Bifurcation analysis
(vii) Microkinetic models vs. global kinetic models

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