Detailed Modeling of Flow-through Monoliths for Automotive Exhaust Gas Aftertreatment

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Multi-Scale Model of a Flow-Through Monolith

- Monolith Model
- Channel Model
- Washcoat Model
- Reaction Mechanism
Structure of DETCHEM

Model Level
- **BATCH + CSTR**: Prefectly Stirred Tank Reactors
- **Washcoat (optional)**
- **DETECHEM-Library**: Reaction Mechanisms, Thermodynamic Data, Transport Coefficients
- **MONOLITH**: Transient Temperature Profile of a Monolithic Catalyst
- **PLUG**: 1D Plug Flow
- **CHANNEL**: 2D Parabolized Model of a Laminar Flow
- **FLUENT**: Arbitrary Channel Geometry

Complexity vs. 2d / 3d

microscopic

macroscopic
Modeling heterogeneous reactions: Mechanistic approach (mean field approximation)

Adsorbed species are randomly distributed

Rate expression for single reaction results from averaging over inhomogeneities and lateral interactions

Surface coverage

\[ \Theta_i = \frac{c_i \sigma_i}{\Gamma} \]

\[ \frac{\partial \Theta_i}{\partial t} = \frac{\dot{s}_i M_i}{\Gamma} \]

Surface reaction rate

\[ \dot{s}_i = \sum_{k \in \mathcal{R}} v_{ik} k_{f_k} \prod_{j \in \mathcal{S}} c_j^{v_{jk}} \]

Rate coefficients

\[ k_{f_k} = A_k T^\beta_k \exp \left[ -\frac{E_{ak}}{RT} \right] f_k (\Theta_1, \ldots, \Theta_{N_s}) \]

\[ f_k (\Theta_1, \ldots, \Theta_{N_s}) = \prod_{i \in \mathcal{S}} \Theta_i^{\mu_{ik}} \exp \left[ \frac{E_{ik}}{RT} \Theta_i \right] \]

\[ k_{r_k} (T) = \frac{k_{f_k} (T)}{K_{c_k} (T)} \]
### Modeling heterogeneous reactions: Three-Way Catalyst (Pt/Rh)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Activity</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>TWC</td>
<td>Modeling</td>
<td>Rate</td>
</tr>
<tr>
<td>H2O + O2 + Pt</td>
<td>$7.00 \times 10^{-22}$</td>
<td>0.0</td>
</tr>
<tr>
<td>H2 + O2 + Pt</td>
<td>$9.80 \times 10^{-22}$</td>
<td>0.0</td>
</tr>
<tr>
<td>CH4 + O2 + Pt</td>
<td>$3.50 \times 10^{-22}$</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Washcoat Models

1D Reaction-Diffusion-Model:

\[
\frac{\partial \bar{J}_i}{\partial r} - \gamma \dot{s}_i = 0 \quad \text{with} \quad \bar{J}_i = -D_{\text{eff},i} \frac{\partial c_i}{\partial r}
\]

Can be solved analytically if

- One representative species with rate law \( \dot{s}_i = -k \cdot c_i \)
- Constant coefficients
- Gradients vanish at thickness \( L \)

\[
\dot{s}_{\text{eff},i} = -\bar{J}_i \bigg|_{r=0} = -D_{\text{eff},i} \lambda c_{i,0} \tanh(\lambda L) \quad \lambda = \sqrt{\frac{\gamma k}{D_{\text{eff},i}}}
\]

Compare to unlimited case:

\[
\dot{s}_{i,0} = -F_{\text{cat/geo}} k c_{i,0} = -\gamma L k c_{i,0}
\]

Effectiveness factor:

\[
\eta = \frac{\dot{s}_{\text{eff},i}}{\dot{s}_{i,0}} = \frac{\tanh(\lambda L)}{\lambda L}
\]
Parabolized Model (Boundary-Layer Equations)

Total mass flux
\[
\frac{\partial (\rho u)}{\partial z} = \frac{1}{r} \frac{\partial (r \rho v)}{\partial r}
\]

Axial momentum flux
\[
\frac{\partial (\rho uu)}{\partial z} = -\frac{1}{r} \frac{\partial (r \rho vu)}{\partial r} - \frac{\partial p}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} \left( \eta \frac{\partial u}{\partial r} \right) + \rho g_z
\]

Enthalpy flux
\[
\frac{\partial (\rho u h)}{\partial z} = -\frac{1}{r} \frac{\partial (r \rho v h)}{\partial r} + u \frac{\partial p}{\partial z} - \frac{1}{r} \frac{\partial}{\partial r} (r q_r)
\]

Species mass flux
\[
\frac{\partial (\rho Y_i)}{\partial z} = -\frac{1}{r} \frac{\partial (r \rho v Y_i)}{\partial r} - \frac{1}{r} \frac{\partial}{\partial r} (r j_i) + M_i \dot{s}_i
\]

Coupling between surface reactions and flow field:
\[
j_{i,\text{wall}} = F_{\text{cat/geo}} \eta_i M_i \dot{s}_i
\]
MONOLITH
Temperature of the solid structure incl. canning by a 2D / 3D heat balance

CHANNEL or PLUG
1D or 2D-flow field simulations for a representative number of channels using boundary layer or plug flow equations

gas phase concentrations temperature
chemical source term transport coefficients

DETCHEM - Library
Thermodynamic and transport properties
Detailed reaction mechanisms for gas-phase & surface

DETCHEM\textsuperscript{MONOLITH}

Interaction of CHANNEL and MONOLITH

MONOLITH
(transient)

CHANEL
(steady state)

MONOLITH

\begin{align*}
\text{discretized grid} & \quad \times \text{channel density} \
& = \text{heat source term}
\end{align*}

\text{temperature profile}

\begin{align*}
-\lambda \frac{\partial T_{\text{gas}}}{\partial r} & \quad T_{\text{gas}} \
& \quad T_{\text{monolith}}
\end{align*}

channel section
Cluster-Agglomeration:
channels may differ in:
wall temperature profile
inlet conditions
⇒ discrete vectors
\[ x = (x_1, x_2, \ldots) \]

Clustering of “similar“ vectors

Vectors in one cluster are represented by an averaged vector

The text explains the concept of clustering in the context of flow-through monoliths, focusing on how different channels can vary due to wall temperature profile and inlet conditions. It illustrates this through a diagram showing how vectors representing these conditions are clustered, with each cluster represented by an averaged vector.
Structure of DETCHEM

- CSTR
- BATCH
- EQUIL
- MONOLITH
- PLUG
- CHANNEL
- DOC
- TWC
- NSC

Effectiveness Factor
Reaction-Diffusion-Equation
0-d Modelling:
Development of Detailed Surface Reaction Mechanisms

Steady-state experiments – gradient-free, differential reactor

- 450 ppm C\textsubscript{3}H\textsubscript{6}
- 1.42% CO
- 8% CO\textsubscript{2}
- 10% H\textsubscript{2}O

Monolith
20 x 30 mm

1000 ppm NO
1.4 / 0.8 / 0.4 % O\textsubscript{2}
balance N\textsubscript{2}

- Very fast numerical simulation
- Automated parameter fine-tuning available
- Individual mechanisms for Pt, Pd, Rh
TWC-Simulations (CSTR Model)
Platinum

CO

HC

NOx

rich
lean
stoic.
TWC-Simulations (CSTR Model)

Palladium

CO

HC

NO\textsubscript{x}

TWC

CSTR

rich

lean

stoic.
TWC-Simulations (CSTR Model)

Rhodium

CO

HC

NOx

Temperature [°C]

Rich  Lean  Stoic.
TWC-Simulations
Comparison of Channel Models

\[ T = 250 \, ^\circ\text{C} \]

- 60 ppm C\(_3\)H\(_6\)
- 400 ppm CO
- 200 ppm NO
- 40 ppm NO\(_2\)
- 12 % O\(_2\)
- 10 % H\(_2\)O
- 7 % CO\(_2\)

\[ F_{\text{cat/geo}} = 25 \]

N. Mladenov, J. Koop, S. Tischer, O. Deutschmann accepted at Chemical Engineering Science (2009)
TWC (Monolith Model)
Validation Under Engine Test Bench Conditions

Experimental data by J. Eberspächer GmbH & Co. KG
(Ref.: S. Tischer et al. Environmental Catalysis Conference 2005)

New European Driving Cycle (NEDC, 1176 s)

For kinetic measurement desired:
slow heat-up of catalyst

Monoliths: Cordierite (400/6.5), coated with various loadings of Pt, Pd, Rh
Cummulative Emissions (NEDC)
Platinum 40 g/ft³

- CO
- HC
- NOₓ

- before cat
- experiment
- simulation

Time [s]
Cumulative Emissions [g]
Cummulative Emissions (NEDC)
Palladium/Rhodium (5:1) 60 g/ft³

- before cat
- experiment
- simulation

Cummulative Emissions (NEDC)

- before cat
- experiment
- simulation

CO

HC

NOx

TWC
Influence of Spatial Non-Uniformity

Non-uniform flow distribution at converter front face

Temperature after 40 s
Non-uniform flow distribution

Temperature after 40 s
Uniform flow distribution

**DETCHEM + FLUENT**

**Arbitrary Channel Geometry**

- **a**: 1.000 mm
- **b**: 0.886 mm
- **c**: 0.905 mm, R0.2 mm
- **d**: 0.1 mm, 1.000 mm
- **e**: 0.886 mm
- **f**: 0.905 mm, R0.2 mm

- Washcoat not discretized
- No washcoat diffusion limitation
- Use porous media model for washcoat
C$_3$H$_6$ profiles at lean conditions at 250°C (steady-state operation)

N. Mladenov, J. Koop, S. Tischer, O. Deutschmann accepted at Chemical Engineering Science (2009)
NO profiles at lean conditions at 250°C (steady-state operation)

N. Mladenov, J. Koop, S. Tischer, O. Deutschmann accepted at Chemical Engineering Science (2009)
Reduction of NO\textsubscript{x} emissions of lean operated engines: Principles of a NO\textsubscript{x} storage/reduction catalyst (NSC)

Lean phase – O\textsubscript{2} rich

Rich phase – O\textsubscript{2} deficit
Temperature of the solid structure incl. canning by a 2D / 3D heat balance

**MONOLITH**

Temperature and *storage concentrations*

- **CHANNEL or PLUG**
  - 1D or 2D-flow field simulations for a representative number of channels using boundary layer or plug flow equations

- transient
- quasi-steady-state

- temperature profile at the wall

**DETCHEM - Library**

- Thermodynamic and transport properties
- Detailed reaction mechanisms for gas-phase & surface

- gas phase concentrations temperature
- chemical source term transport coefficients
- concentration of storage species
- heat source term
  - time scale ~ 1 s
  - residence time < 100 ms

- chemical source term of storage species
- transient
- quasi-steady-state

**NSC**
NO\textsubscript{x} storage catalyst: Lean/Rich Cycle (60s/5s) for Pt/Ba/Al\textsubscript{2}O\textsubscript{3} at 350°C

Good agreement between simulations and experiments for both lean/rich cycling and axial profiles.


Summary

Detailed elementary-step reaction kinetics (TWC, NSC, DOC)

0-d and 1-d washcoat models

Fast tools to solve 0-d and 1-d problems suitable for parameter optimization

1-d and 2-d channel models

Transient 2/3-d monolith model with storage

Interface to FLUENT (Ansys) for modeling of arbitrary channel geometries
Acknowledgements

- J. Eberspächer GmbH & Co. KG, Esslingen
- Daimler AG, Stuttgart
- Daniel Chatterjee
- Jan Koop
- Luba Maier
Simulation of NEDC (600 - 1176 s)
Platinum 40 g/ft$^3$

- CO
- $C_3H_6$
- NO

Cumulative Emissions [g]
- before cat
- experiment
- simulation

Inlet Temperature [°C]

Time [s]

CO
$C_3H_6$
NO

TWC