New Approach to Washcoat Diffusion Resistance
Background and Overview

\[ \|D_{inv}\| = 0, \text{ "standard" problem} \]

\[ \|D_{inv}\| \text{ negligible} \]

\[ \|D_{inv}\| \text{ small, asymptotic solution} \]

\[ \|D_{inv}\| \text{ large, full numerical solution} \]

- \( \|D_{inv}\| \) small: practical regime
  - tractable, fast
Outline

• Simplest case -- single layer, no coverages
  – Motivation – zeroth order, “standard” problem: no concentration gradients in washcoat
  – How asymptotic solution works

• Extensions -- coverages, dual layers

• Discussion, magnitude estimates, sample results

• Status
Dimensionless equations (including scalings)

- Generally
  - simpler
  - proper for asymptotics
  - computations
- Specifically
  - length of reactor
  - warm-up time
  - characteristic temperature
  - characteristic species mass fractions (and coverages)
- $O(1)$ variables and coefficients for major terms of “standard” problem
- Effective diffusivities, washcoat thickness $\Rightarrow D_{\text{inv}}$
Equations for trace species vectors

channel:

\[ W \frac{\partial \omega_g}{\partial z} = K(\omega_s - \omega_g) \]
axial, \( 0 < z \leq 1 \)

washcoat at each \( z \):

\[ \frac{\partial^2 \omega}{\partial x^2} = -D_{inv} R \]
washcoat, \( 0 < x \leq 1 \)

boundary conditions:

\[ \frac{\partial \omega}{\partial x} = D_{inv} K (\omega_s - \omega_g) \]
\( x = 0 \), channel interface

\[ \frac{\partial \omega}{\partial x} = 0 \]
\( x = 1 \), substrate interface

• Integration + b.c. \( \Rightarrow \)

\[ K(\omega_s - \omega_g) = \bar{R} \equiv \int_0^1 R dx \]

, independent of \( \|D_{inv}\| \)

• Motivation: \( D_{inv} \rightarrow 0 \) \( \Rightarrow \)

“standard” problem
Asymptotic solution

- Extend zeroth order ($\|D_{inv}\| = 0$) solution to first order.
- Advantage – $2^{nd}$ order terms ($O(\|D_{inv}\|^2)$) neglected
- Fortunately tractable
Key points that enable asymptotic solution

- **Species:** \( \omega(x) = \omega_{\text{con}} + D_{\text{inv}} \omega_{\text{var}}(x) + O(\|D_{\text{inv}}\|^2) \)

- **Species rates:**
  \[ R(\omega(x)) = R(\omega_{\text{con}}) + \frac{\partial R}{\partial \omega_{\text{con}}} (\omega(x) - \omega_{\text{con}}) + O(\|D_{\text{inv}}\|^2) \]

  - In particular, point-wise:
    \[ R(\omega(x)) = R(\omega_{\text{con}}) + O(\|D_{\text{inv}}\|) \]

    Use in \( \frac{\partial^2 \omega}{\partial x^2} = -D_{\text{inv}} R \) to obtain \( \omega_{\text{var}}(x) \)

  - If \( \omega_{\text{con}} = \bar{\omega} \), \( \overline{R(\omega)} = R(\bar{\omega}) + O(\|D_{\text{inv}}\|^2) \)

    Use in \( K(\omega_s - \omega_g) = \overline{R(\omega)} = R(\bar{\omega}) + O(\|D_{\text{inv}}\|^2) \) to obtain \( \omega_{\text{con}} = \bar{\omega} \)

- **Reaction-diffusion solution:**
  \[ \omega(x) = \bar{\omega} + D_{\text{inv}} R(\bar{\omega}) \left[ \frac{1}{6} - \frac{1}{2} (1 - x)^2 \right] + O(\|D_{\text{inv}}\|^2) \]

  - In particular \( \omega_s(\bar{\omega}) = \bar{\omega} - D_{\text{inv}} R(\bar{\omega}) / 3 + O(\|D_{\text{inv}}\|^2) \)
Extensions

• Coverages
  – Assume any initial \( x \)-variations are \( O(\|D_{inv}\|) \)
  – Species rate argument generalizes to reaction rates and coverages:
    \[
    r(\omega, \theta) = r(\bar{\omega}, \bar{\theta}) + \left. \frac{\partial r}{\partial \omega} \right|_{\bar{\omega}, \bar{\theta}} (\omega - \bar{\omega}) + \left. \frac{\partial r}{\partial \theta} \right|_{\bar{\omega}, \bar{\theta}} (\theta - \bar{\theta}) + O(\|D_{inv}\|^2)
    \]
    – \( \theta \) drops out in favor of \( \bar{\theta} \)

• Dual washcoat layers
  – Each layer has own reactions, species \( \left( \omega^{(1)}, \omega^{(2)} \right) \), coverages \( \left( \bar{\theta}^{(1)}, \bar{\theta}^{(2)} \right) \), etc.
  – Overall rate balance
    \[
    K(\omega_s - \omega_g) = R^{(1)}(\bar{\omega}^{(1)}, \bar{\theta}^{(1)}) + R^{(2)}(\bar{\omega}^{(2)}, \bar{\theta}^{(2)})
    \]
    – Reaction-diffusion equations remain analytically solvable
    – Additional (nonlinear) equations \( \left( \bar{\omega}^{(2)} \right) \) from continuity at interface between layers
Limitations

- Asymptotics not designed for scaled $\omega_i$ small, $\sim O(\|D_{inv}\|)$ $x$-variations
  - Normally below ppm detection limit or below absolute error tolerance of numerics
- Large diffusion resistance regime
  - too thick washcoat or too small $D_{eff}$
  - Asymptotics often surprisingly good.
Estimate $\|D_{inv}\|$  

\[
D_{inv} = \begin{bmatrix}
D_r / D_{eff,1} & 0 \\
D_r / D_{eff,2} & D_r / D_{eff,2}
\end{bmatrix}
\]

- Reference effective diffusivity, \( D_r = (SV)_{ref} \delta^2 / f_{wc} \) [m$^2$/s]  
  \[ \delta^2 / f_{wc} \approx D_h \delta / 4 \approx 7.5 \times 10^{-9} \] [m$^2$] (square channels, \( D_h = 1\) mm, \( \delta = 30 \) µm)  
  - \((SV)_{ref}\) : consistency with other equations. Should approximate actual \( SV \approx 15\) s$^{-1}$  
  - \( D_r \approx 1.1 \times 10^{-7} \)

- Commonly measured range, \( D_{eff} = O(10^{-6}) \) [m$^2$/s] :  
  “sweet spot” – \( \|D_{inv}\| \) small, but not negligible.
Comparison with Data

- Single-layer Pt NH₃-oxidation catalyst. Then add Fe-zeolite SCR

Published Experimental Results *

* Scheuer, et al. App Cat B: Environmental, 111-112 (2012) pp. 445-455 (Figure 5)
Comparison with 1+1D

- CO oxidation
- 3.2 liter reactor
- 400 cpsi
- 27000 1/hr SV
- 1000 ppm CO
- 10% O₂
- 500 K Inlet Temp.

\[ R_{CO} \left( \frac{mol}{m^3_{reactor s}} \right) = \frac{3.55 \times 10^6 \exp\left(\frac{-9782}{T}\right) C_{CO} C_{O_2}}{\left(1 + 248 \exp\left(\frac{-615}{T}\right) C_{CO}\right)^2} \]
Summary

• Fast
  – Similar to “standard” problem

• Respects reaction scheme
  – approximation only exploits diffusion resistance

• Can be structured close to “standard” problem, especially single layer

• Solid mathematics – not *ad hoc*

• Not for large diffusion resistance -- large catalyst underutilization

• No boundary, asymptotics degrades gradually

• Captures dominant effects from small-to-moderate diffusion resistance
Status

• Publication ASAP
  – Manuscript: finishing touches
  – Full disclosure – you should be able to implement
    • Single layer especially not difficult

• Single layer with coverages in GT-Power last fall (version 7.4)

• Dual layer
  – Full functionality next fall (full release)
  – “Beta”
Backups
Qualitative Comparison to Literature

• Scheuer et. al. (2012) compares ammonia oxidation between a catalyst with a single platinum layer and one with Fe-zeolite SCR layer over a platinum layer

• GTI has already calibrated an AOC mechanism (single platinum layer) to this paper’s data
  – Mechanism and comparison available in ASC_GTI_2013.gtm example

• GTI used its two-site SCR mechanism (also available as example) for the top layer in this study

• Knowns:
  – Inlet conditions, 10 micron Pt washcoat thickness, 71 micron SCR washcoat thickness, 300,000 1/hr SV

• Assumptions:
  – Both washcoats use tortuosity = 3, washcoat porosity = 40%, 5 micron pore diameter
Washcoat Profiles

603 K, Normalized Axial Location = 0.1

- **NH3**
- **N2O**
- **NO**

**Graph Details:**
- **Y-Axis:** ppm
- **X-Axis:** Washcoat Depth, microns
- Points of Interest:
  - **NH3:** Decreasing linearly to very low levels near 75 microns.
  - **N2O:** Increasing linearly from a low value near 0 ppm to a higher level as depth increases.
  - **NO:** Exhibits a peak at around 75 microns before decreasing linearly towards the bottom of the graph.