Simulation of absorption processes in nanoparticle catalysts

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In this contribution, we present a novel modeling approach for mass transport problems that connects the microscale with the macroscale. It is based on a proper investigation of the diffusion process in the catalytic pellets from which, after semi-analytic considerations, a source term for the macroscopic advection-diffusion process can be identified. For the special case of a spherical catalyst pellet, the parabolic partial differential equation at the microscale can be reduced to a single ordinary differential equation in time through the proposed semi-analytic approach. After the presentation of our model, we show results for its calibration against the macroscopic response of a mass transport experiment. Based thereon, the effective diffusion parameters of the catalyst pellet can be identified. Furthermore, we test the model’s robustness by applying significant noise to virtual experimental datasets.

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1 Introduction

Heterogeneous catalysis plays a key role in chemistry. In recent developments the catalyst’s size shrunk down to micro or even nano scale. While this leads to improved catalysis properties, such as the activity, it becomes at the same time harder to describe their behavior a priori. Hence, the microscale effects need to be captured properly in numerical simulations. In this contribution a computational description for the mass transport experiment of [1] with nano catalysts of [2] is presented.

2 Modeling and Numerics

Under the continuum assumption the macroscale obeys the advection-diffusion-reaction (ADR) equation

\[
\frac{\partial c}{\partial t} + \mathbf{w} \cdot \nabla c - \nabla \cdot (D \nabla c) = R.
\] (1)

Here, \(c, \mathbf{w}, D\) and \(R\) represent the macroscopic concentration, velocity, diffusion tensor and reaction term, respectively. The semi-discrete finite element formulation is obtained, if the strong form eq. (1) is multiplied with a test function \(\mathbf{v}\). Green’s formula is applied and finally, the infinite space \(V\) is substituted by the closed subspace \(V_h \subset H^1_0(\Omega)\) of piecewise linear polynomials, i.e.

\[
\int_\Omega \frac{\partial c}{\partial t} \, dV + \int_\Omega \mathbf{w} \cdot \nabla c \, dV + \int_\Omega \nabla \mathbf{v} \cdot D \nabla c \, dV = \int_\Omega R \mathbf{v} \, dV \quad \text{on } \Omega \times (0, T]
\] (2)

\[
c(x, t) = c_{\text{exp}}(t) \quad \text{on } \partial \Omega_D
\] (3)

with initial condition \(c(x, 0) = 0\) and final time \(T\). Dirichlet boundary condition \(c_{\text{exp}}(t)\) are the concentration measurements of the experiment, shown in Figure 1a with label “Exp. Input” and \(\partial \Omega_D\) is the top boundary of the computational domain. Due to the sharp advective flux in the second term of the weak form on the left hand side, standard Galerkin type discretizations suffer from instability. Hence, a suitable stabilization scheme needs to be added. In this contribution a Streamline-Upwind Petrov-Galerkin (SUPG) method is used [3], where \(\mathbf{v}\) is substituted by \(\mathbf{v} + \delta h \mathbf{w} \cdot \nabla c\). The reaction term \(R\) serves in this article as the connection between macro and micro scale and is defined as

\[R := k_\Gamma \left( \Gamma - c_\Gamma \right) \quad \text{where } \quad k_\Gamma c_\Gamma = \frac{1}{V} \int_\Omega c \, dV.
\] (4)

Two assumptions about the microscale are made, first off a linear distribution of the internal catalyst concentration \(c\) is assumed, which results in the right part of equation (4) and secondly, a spherical shape. Note that this can be extended to all regularly shaped and homogeneous catalyst morphologies. Here, \(c_\Gamma\) is the concentration at the catalyst boundary and is described by \(c\) which evolves according to a volume averaged microscopic transient diffusion equation, which is similar to eq. (1), however without the advective part, i.e.

\[
\frac{1}{V} \int_\Omega \frac{\partial c}{\partial t} \, dV = - \frac{1}{V} \int_\Omega \nabla \cdot (D \nabla c) \, dV \quad \text{Gauss' theorem yields } \quad \frac{1}{V} \int_\Omega \frac{\partial c}{\partial t} \, dV = \frac{1}{V} \int_{\partial \Omega} D \nabla c \cdot \mathbf{n} \, dA.
\] (5)

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In the second part of equation (5), the right hand side expresses the volume averaged outgoing concentration flux on the catalyst boundary and can be simplified due to the assumptions about the morphology and concentration distribution by

\[ k_T c_T = \frac{1}{V} D_{iso} \frac{\tau - c_T}{h} A, \]  

(6)

In equation 6 the fraction between \( \tau - c_T \) and \( h \) expresses the gradient at the boundary, where \( h \) represents the interface thickness. At both scales isotropic diffusion behavior is assumed. Hence, diffusion tensors \( \overline{D} \) and \( D \) can be expressed as \( \overline{D} = D_{iso} I \) and \( D = D_{iso} I \), respectively.

### 3 Results and Discussion

The model was calibrated by means of the CMA-ES algorithm [4], which yielded an almost perfect fit, that is visualized in Figure 1a. There were three fixed parameters, namely macro diffusion coefficient \( D_{iso} \), velocity \( \overrightarrow{w} \) and interface thickness \( h \). For the first fixed parameter a characteristic value of acetone was taken. The velocity was described by a constant value that was computed based on the experimental setup and interface thickness \( h \) was set one, such that if the true interface thickness is known, the optimized value of \( k_T \) can be recomputed. Both time derivatives were discretized by an implicit Euler scheme. The obtained optimized values can be found in Table 1. After that, the optimized set of parameters were taken and the concentration at two different spatial points were measured over time. The two spatial points are the middle and end of the domain at 2.5 cm and 5 cm, respectively. Then, Gaussian noise was applied to the simulation signal and the calibration was repeated, but this time the distorted simulation signal was the goal. For a consistent and sufficiently robust model, the optimized parameter should be obtained again, approximately. This is the case and can be seen in Table 2 with regards to the parameters and Figure 1b visualizes the fit with the corresponding distorted signal.

| Parameter | Value         | Unit |
|-----------|---------------|------|
| macro \( D_i \) | \( 1.14 \cdot 10^{-9} \) | \( \text{[m}^2/\text{s]} \) |
| micro \( D_i \) | \( 2.419 \cdot 10^{-14} \) | \( \text{[m}^2/\text{s]} \) |
| \( k \) | \( 19.303 \cdot 10^{-2} \) | [-] |
| \( k_T \) | \( 4.2 \cdot 10^{-6} \) | [-] |
| \( h \) | 1 | [m] |

**Table 1:** Fitted parameters for calibration procedure

| Parameter | Value         | Unit |
|-----------|---------------|------|
| macro \( D_i \) | \( 1.14 \cdot 10^{-9} \) | \( \text{[m}^2/\text{s]} \) |
| micro \( D_i \) | \( 4.902 \cdot 10^{-14} \) | \( \text{[m}^2/\text{s]} \) |
| \( k \) | \( 18.453 \cdot 10^{-2} \) | [-] |
| \( k_T \) | \( 8.9 \cdot 10^{-6} \) | [-] |
| \( h \) | 1 | [m] |

**Table 2:** Virtual lab fitted parameters

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