Abstract:

Machine learning assisted parameter estimation for optimal kinetic characterization of bifunctional heterogeneous catalysts

Co-supervisor 1: Prof. Jens-Uwe Repke, TU Berlin

Co-supervisor 2: Dr. Sebastian Matera, FHI Berlin

Estimating kinetic parameters from given experiments is a computationally demanding task, which is often riddled by infeasibilities, due to numerically solving complex, typically highly nonlinear, coupled transport-kinetic problems. This becomes even more severe, if we want to use the model to identify experimental operation conditions to increase the model accuracy (optimal experimental design, OED).
In this project, machine learning methods shall be employed to enable parameter estimation and optimal design applied for problems of two subsequent heterogeneously catalysed reactions taking place in one reaction chamber on different catalysts. Such problems are particularly demanding not only because the number of kinetic parameters increases but especially because the coupling introduces novel effects such as distance between active sites which need to be accounted for by more complex models, which potentially also increase the dimensionality of the design space. Stochastic models will be created to account for these effects and statistical analyses will be employed to reduce the parametric dimensionality of these models and the design space. Machine learning techniques will serve to create surrogates of the base transport-kinetic models, which will allow for dimensionality reduction of the mechanistic model and ensure the reliable solution of both parameter estimation and optimal experimental design problems.

Extended description version of the project:

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1. Overall goal of the project

The central objective of the proposed project is the development of an innovative general-purpose methodology implemented in an opensource software framework for the parameter estimation from and optimal design for experimental kinetic data at significantly reduced costs. Using CO_2 to methanol hydration coupled with a methanol to dimethyl ether (DME) conversion on two different catalysts as a prototypical example, the novel methodology shall be applied to optimally explore the high-dimensional design space. Particularly, it shall be investigated how the spatial catalyst arrangement can be exploited to shine light into the effects arising from the coupling of the two catalytic pathways. Especially, the case of preparation uncertainty will require to develop proper stochastic models, which, by their nature, will be computationally rather demanding and adaptive sparse grid quadrature will be employed here to perform the statistical averaging.
The primary challenge will be to achieve a high computational efficiency and algorithmic stability to address the complex scenarios of coupled reaction systems addressed in the CoE UniSysCat. To achieve this, methods like global sensitivity analysis (GSA) and subset selection will be used to reduce the dimensionality of the problem, thereby increasing the convergence rate of the involved iterative optimization algorithms. The other limiting factor is the evaluation of the base reactor model and machine learning techniques for high-dimensional problems like adaptive sparse grids or adaptive dynamic sampling will be employed to create computationally efficient surrogate models for performing parameter estimation and optimal experimental design.
Besides these methodological advances the project shall support the experimental studies on bifunctional heterogeneous catalysis conducted in the CoE, exemplified on the methanol synthesis from CO_2 followed by the dehydration to dimethyl ether. Two kinds of reactor setups shall be investigated, a Berty reactor and a fixed bed reactor. Emphasis will be put on the investigation of the spatial separation of active sites and the preparation uncertainty of core-shell particles, which both are expected to play a more prominent role than in conventional monofunctional catalysis.

2. State of the art

Parameter estimation (PE) has been in application for decades[1]. Common challenges in PE (and OED) are over-parameterization, convergence problems due to high nonlinearity, limitation of experimental data, effects of some parameters on model predictions may be small, or the effects of some parameters may be correlated, poor initial guess and last but least lack of identifiability[2]. Approaches to tackle these challenges have been proposed and exemplary been employed using Monte Carlo methods[3].

A crucial factor is to filter out unimportant parameters/design variables by global sensitivity analyses/subset selection and thereby reduce the dimensionality of the optimization problem in order to improve the convergence rate. During the last years, such methodologies have been developed in the Matera[4,5] (global sensitivity analysis) and the Repke[6] (subset selection) group. Essentially, such approaches provide the information how much the value of given parameter influences the output of a model.

Nevertheless, for complex systems like two subsequent heterogeneously catalysed reactions taking place in one reaction chamber on different catalysts found in the CoE UniSysCat the application of formerly proposed methods is limited due to increased complexity and the correlated increase in computational effort. The limiting factor for the computational efficiency is the repetitive evaluation of the costly physical/base model, especially when microkinetic models are used to represent the catalytic response. During the last years, we and others have developed surrogate (machine learning) models for the efficient representation of high-fidelity, costly models[4,7,8,9].

In the project, we will particularly explore the use of adaptive sparse grids, because they exhibit fast convergence also in higher dimension and allow for an adaptive, error controlled selection of the training data[4].

Bifunctional heterogeneous catalysis employs two kinds of catalytic particles, where the products from the first catalytic cycle serve as educts for the second. An exemplary system of coupled catalysis investigated in the scope of UniSyCat is the methanol synthesis from CO_2 followed by dehydration to DME. One research question in this field is how the distance between the two active sites affect the function of the overall process. One way to control this distance on mesoscopic scales is core-shell particles, and, during the last months, we have developed a reduced order mathematical model for the particles (Brösigke, Repke, Matera, in preparation). This allows for running corresponding reactor simulations at comparable costs as for single shell particles, if all particles in the chamber would be identical. In reality, the synthesis of identical particles is not possible and deriving a model which accounts for this uncertainty will be part of the project.

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3. Specific aims and how they may be reached

The main objective of this work is the development of a novel methodology for efficient kinetic parameter estimation for complex chemical reaction systems taking place at different catalytic active sites. Both the Repke group and the Matera group will provide methods from previous or other ongoing projects dealing with that matter. Moreover, the inhouse (Repke group) modeling library MOSAICModeling provides a platform for generic (meaning independent from commercial/proprietary software) source code generation with interfaces to programming languages e.g. python or C++.

The next step will be to extend our model for ideal particles to a more realistic stochastic model, which accounts for the preparation uncertainty. Due to this, every particle will be different, for instance, by having a different catalyst loading in the active shells or different diameter. This has not much impact in single shell particles, where essentially only the total amount of catalyst (per macroscopic volume) has an impact on the outcome of a reactor model. However, for core shell particles, the kinetic response depends on such mesoscale details. The catalytic response, which is to be coupled to the reactor models, must thus be obtained from an ensemble of different particles. This requires averaging over a probability distribution of different particles, i.e. over core-shell models running at different sets of such mesoscale parameters. Besides the standard Monte Carlo sampling for testing, we will employ sparse grids for this, which we expect to perform superior for such numerical integration in medium high dimensions. The result is the effective catalytic response, i.e. turnover frequencies, of the particles as a function of the partial pressures and temperature at the surface of the particles, the kinetic parameters and the parameters defining the uncertainty.

This kind of model will be applied to the methanol synthesis from CO_2 followed by the dehydration of methanol to DME using parametric kinetic models from literature[10,11]. For simplicity, we will firstly restrict to cases, where the particles are assumed to be spherically symmetric and the only source of uncertainty are the diameters of the different shells, their catalyst loading and the transport coefficients of the porous matrix (assuming Knudsen diffusion with an uncertain distribution of pore diameters and porosity). Posing reasonable bounds for all input parameters, a subsequent GSA will serve to reduce the dimensionality of the space of input variables of the stochastic model. Besides this, the GSA will already provide useful insight into the problem, e.g. how much the preparation uncertainty influences the catalytic response.

Even with efficient sparse grid averaging, the solution of the stochastic particle model will be computationally demanding especially in the context of parameter estimation and OED. We will therefore interpolate the output of the stochastic model as function of the most important input variables using locally and dimension adaptive sparse grids[4]. The efficient surrogate for the particle model will be coupled to reactor models such as the CSTR and fixed bed reactor model. The thereby hybrid physical/surrogate models will then again be analyzed using GSA in order to identify whether the macroscopic transport masks the dependence on some parameters and which effects are still present on the particle level. After the subsequent dimensionality reduction, the hybrid models will be employed to analyze and guide the experimental studies on the CO_2 to DME problem conducted in the scope of the existing EC^2 project “Fundamental experimental Investigations on mass transfer between different catalytic centers situated in porous matrices”, which collaborates between the groups of Thomas, Schomäcker, Matera and Repke.

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