



# Reduction of microkinetic reaction models for reactor optimization exemplified for hydrogen production from methane



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## HIGHLIGHTS

- We present a new reduction technique for complex chemical reaction networks.
- This easy-to-use method is universal and ensures conservation of mass.
- We exemplify the reduction technique for a C<sub>1</sub> microkinetic reaction network.
- The significantly reduced reaction network shows still an excellent agreement.

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## ABSTRACT

Sustainable and efficient processes require optimal design and operating conditions. The determination of optimal process routes, however, is a challenging task. Either the models and underlying chemical reaction rate equations are not able to describe the process in a wide ranges of reaction conditions and thus limit the optimization space, or the models are too complex and numerically challenging to be used in dynamic optimization. To address this problem, in this contribution, a reduction technique for chemical reaction networks is proposed. It focuses on the sensitivity of the reaction kinetic model with respect to the removal of selected reaction steps and evaluates their significance for the prediction of the overall system behavior. The method is demonstrated for a C<sub>1</sub> microkinetic model describing methane conversion to syngas on Rh/Al<sub>2</sub>O<sub>3</sub> as catalyst. The original and the reduced microkinetic model show excellent qualitative and quantitative agreement. Subsequently, the reduced kinetic model is used for the optimization of a methane reformer to produce a hydrogen rich gas mixture as feed for polymer electrolyte membrane (PEM) fuel cell applications.

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## 1. Introduction

As economical and ecological aspects play a significant role in the design of chemical production processes, model-based optimization is crucial for the rational derivation of the best process route and optimal equipment for efficient and sustainable production [1,2].

Reliable process optimization requires quantitative and sufficiently accurate information about the underlying physical and chemical phenomena. With increasing computational power, new

theoretical approaches and advanced numerical algorithms, it is now possible to use microkinetic multi-step descriptions of chemical reactions, based on first principles, for reaction engineering purposes. Today, such microkinetic models for reaction systems with small molecules, e.g. ammonia [3] and nitrogen oxides [4–6] have been derived. Recently, the interest in C<sub>1</sub> chemistry, especially methane conversion into syngas components, has grown considerably. Microkinetic models for methane catalytic partial oxidation [7], reforming [8–11], oxidative coupling [12], and CO/H<sub>2</sub> oxidation [13] are available, but also models that are able to deal with multiple chemical regimes for methane conversion at the same time [14–17].

But the high complexity of detailed microkinetic reaction models turned out to be a challenging feature, especially for model-based reactor optimization. The microkinetic rate

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## Notation

### Latin

Symbol	Description (unit)
$A$	pre-exponential factor (– or 1/s)
$a$	specific surface area ( $\frac{1}{m}$ )
$c_i$	concentration of component $i$ ( $\frac{mol}{m^3}$ )
$\hat{c}_i = \frac{c_i}{c_{i,0}^g}$	dimensionless concentration of component $i$ (–)
$D_i$	diffusion coefficient of component $i$ ( $\frac{m^2}{s}$ )
$E_A$	activation energy ( $\frac{J}{mol}$ )
$\hat{j}_i = \frac{j_i}{c_{i,0}^g k_m^{ref}}$	dimensionless external molar dosing flux (–)
$k$	reaction rate constant (reaction specific)
$k_m$	mass transfer coefficient ( $\frac{m}{s}$ )
$\hat{k}_m = \frac{k_m}{k_m^{ref}}$	dimensionless mass coefficient (–)
$M_i$	molar mass ( $\frac{kg}{mol}$ )
$N$	number of ... (–)
$n$	molar mass flux ( $\frac{mol}{s}$ )
$\hat{n} = \frac{n}{c_{i,0}^g k_m^{ref}}$	dimensionless molar mass transfer flux (–)
$n_{Sc}$	exponent of Schmidt-number in Sherwood-correlation ( $Sh = K_{Sh} Re^{n_{Re}} Sc^{n_{Sc}}$ ) (–)
$p$	total pressure (Pa)
$R$	universal gas constant ( $\frac{J}{molK}$ )
$r_j$	rate of reaction $j$ ( $\frac{mol}{m^2s}$ )
$T$	temperature (K)
$t$	time (s)
$\chi_i$	molar fraction of component $i$ (–)

### Greek

$\Gamma_{Rh}$	active site density ( $\frac{mol}{m^2}$ )
$\epsilon$	error (–)
$\epsilon$	void fraction (–)
$\Theta$	surface coverage (–)
$\nu_{ij}$	stoichiometric coefficient of component $i$ in reaction $j$ (–)
$\sigma_i$	chemical production rate of component $i$ ( $\frac{kg}{m^2s}$ )
$\tau = a^{gc} k_m^{ref} t$	dimensionless time (–)

### Superscripts

$c$	catalyst
$g$	gas phase
$gc$	gas/catalyst interface
$k$	index number
$ref$	reference

### Subscripts

$0$	initial state at $t = 0$
$Com$	components
$final$	final state
$i$	component index
$j$	reaction index
$Re$	reactions
$t$	total

expressions are strongly nonlinear functions of temperature, gas phase concentrations and catalyst surface coverages and interdependent. Furthermore, the reaction rates often cover many orders of magnitude, which results in bad model scaling and ill-posed numerical problems. For this reason, comparative simulation studies [18–22], but only few rigorous optimizations are found in literature to improve the design of catalysts, reactors and processes. E.g., for the ammonia synthesis Jacobsen et al. [23] derived an optimal catalyst on the atomistic scale based on volcano curves computed from first principles.

The objective of the present work is to combine microkinetic models and rigorous reactor optimization. To overcome the before mentioned numerical issues, a new reduction technique for microkinetic reaction network models based on network-wide analysis of errors in the predicted reaction rates is proposed. Previous reduction techniques for chemical reaction networks are based on progressive species reduction with reparametrization [24], element flux analysis [25], integer linear programming [26], principle component analysis [27] and reaction route graphs [28–30].

Progressive species reduction with parametrization of the reaction rates uses a global error function to gradually reduce the number of species in the reaction model with element flux analysis. Afterward the model parameters are re-estimated within their uncertainty region using a genetic algorithm. Although this procedure opens a very elegant path for reparametrization of the reaction model, genetic algorithms need be used with great caution, as the results may strongly depend on the configuration of the genetic algorithm. This further increases computation and implementation complexity significantly. Element flux analysis considers the fluxes of one element, e.g. carbon, from one molecule to another and judges the significance of a reaction by comparing the magnitude of the element fluxes between different reactions. The larger the element flux, the more significant the reaction will be. However, this method requires the considered element to be present in every reaction. If this is not the case, this reaction cannot

be compared with the others properly. This limits the method to reaction systems that share a common element.

Reaction and species elimination with integer linear programming (ILP) is an automated, optimization-based reduction method. Besides integer formulation that is in general hard to handle, this method requires additional solvers and optimization routines. Furthermore, the mass balance of the reduced system is not ensured.

From a systems engineering point of view, the reaction route graphs are very fascinating. The authors [28–30] established an analogy between reaction networks and electrical circuits. By considering reactions as chemical resistors, this information can be used to identify major barriers within the reaction network. In analogy to electrical engineering, they are able to use this information to derive a chemical reaction that behaves as an equivalent resistance. For small systems, the authors were even able to determine analytical solutions. Unfortunately, this method is difficult to use for complex chemical reaction networks, as the determination of the reaction route graphs is very difficult.

All these previous approaches are not fully suitable for use in rigorous dynamic optimization, where universal and computationally cheap methods are desirable. To avoid reparametrization issues and complex numerical methods, we here aim for an easy-to-use reduction approach based on sensitivity analysis that does not require special network properties or problem statements.

The present work is structured as follows. First, a methodology for preprocessing and reduction of a given microkinetic model is derived, demonstrated and discussed in detail. For these purposes, the microkinetic model proposed by Maestri et al. [14], which describes the conversion of methane to syngas components on Rh/Al<sub>2</sub>O<sub>3</sub> as catalyst, is used as example of industrial relevance. In the second step, a validation of the reduced kinetic model is carried out. Finally, the reduced kinetic model is utilized for rigorous reactor optimization. For this purpose, we apply the Elementary Process Functions (EPF) methodology proposed by our group [1,2].

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