

Development and Application of Microkinetic Models Leveraging Optimization Algorithms and Surrogate Models

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Abstract

Digitalization in catalysis research is a challenging endeavor due to its interdisciplinary scope, encompassing synthesis, characterization, and modeling. This thesis focuses on the development and application of digital tools to accelerate the workflows followed in numerical modeling. In particular, the development of microkinetic models is a crucial step in rational catalyst design and in gaining deeper insights from the reaction mechanism. However, the high-dimensionality of these models often poses a significant bottleneck in their development.

To address this, the work presented in this thesis introduces an optimization tool that integrates automation and established gradient-free optimization algorithms to accelerate the modeling process. The tool is applied across multiple catalytic systems and reactions, showcasing its versatility and potential to enhance model development in heterogeneous catalysis. A key application demonstrated in this thesis is the development of tailored models for the oxidation of methane under lean conditions over PdO-based catalysts, and using them to understand the effect of supports on the catalytic behavior.

In addition, the thesis also demonstrates the development of a deep learning-based surrogate model for methane oxidation over PdO/Al₂O₃ in a fixed bed reactor. This surrogate model is then used in performing gradient-based optimization of the simulation parameter representing the available active surface area against experimental performance data, to predict the dynamic changes in the catalyst properties under reaction conditions.

Kurzfassung

Die Katalyseforschung umfasst mehrere Bereiche wie die Synthese, Charakterisierung und Modellierung. Dieser interdisziplinäre Charakter macht die Digitalisierung des Forschungsfelds zu einer anspruchsvollen Aufgabe. Im Fokus der Aufmerksamkeit steht die Entwicklung und Anwendung digitaler Werkzeuge zur Beschleunigung der Arbeitsabläufe bei der numerischen Modellierung. Insbesondere die Entwicklung mikrokinetischer Modelle ist ein entscheidender Schritt für das rationale Katalysatordesign indem sie tiefere Einblicke in den Reaktionsmechanismus erlaubt. Die hohe Dimensionalität dieser Modelle stellt jedoch häufig eine erhebliche Herausforderung bei der Modellentwicklung dar.

Um diesem Problem zu begegnen, wird in dieser Arbeit ein Optimierungstool vorgestellt, welches einen Automatisierungsprozess und etablierte gradientenfreie Optimierungsalgorithmen integriert, um den Modellierungsprozess zu beschleunigen. Das Tool wird auf mehrere katalytische Systeme und Reaktionen angewendet und zeigt damit seine Vielseitigkeit und sein Potenzial zur Verbesserung der Modellentwicklung in der heterogenen Katalyse. Eine wichtige Anwendung, die in dieser Arbeit demonstriert wird, ist die Entwicklung maßgeschneiderter Modelle für die Oxidation von Methan unter mageren Bedingungen über PdO-basierten Katalysatoren und deren Anwendung zur Entwicklung eines Verständnisses über die Auswirkungen von Trägermaterialien auf das katalytische Verhalten.

Darüber hinaus zeigt die Arbeit die Entwicklung eines Deep-Learning-basierten Surrogatmodells für die Methanoxidation über PdO/Al₂O₃ in einem Festbettreaktor. Dieses Surrogatmodell wird anschließend verwendet, um eine gradientenbasierte Optimierung des Simulationsparameters durchzuführen, der die verfügbare aktive Oberfläche repräsentiert. Die Optimierung erfolgt anhand experimenteller Leistungsdaten, um die dynamischen Veränderungen der Katalysatoreigenschaften unter Reaktionsbedingungen vorherzusagen.

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Nomenclature

Latin Symbols

Symbol	Description	Unit
A	Area	m^2
A_k	Pre-exponential Arrhenius parameter	$[\text{cm}, \text{mol}, \text{s}]$
a_v	Surface area to volume ratio	m^{-1}
$\mathbf{b}$	Bias parameter in a neural network	—
c	Concentration	mol m^{-3}
D	Diffusion coefficient	$\text{m}^2 \text{s}^{-1}$
d	Diameter	m
E_a	Activation energy	kJ mol^{-1}
$F_{\text{cat/geo}}$	Ratio of catalytic to geometric surface area	—
G	Gibbs free energy	J mol^{-1}
H	Enthalpy	J mol^{-1}
K	Number of reversible reactions	—
k	Kinetic rate constant	$[\text{cm}, \text{mol}, \text{s}]$
k_{fs}	Fluid-solid mass transfer coefficient	m s^{-1}
$\mathcal{L}$	Loss function	—
L	Length	m
m	Mass	g

M_i	Molar mass of species i	g mol^{-1}
n	number of dimensions in the search space	—
N_s	Number of surface species	—
n_{ik}^-	Rate of consumption of species i through reaction k	$\text{mol m}^{-2} \text{s}^{-1}$
n_{ik}^+	Rate of production of species i through reaction k	$\text{mol m}^{-2} \text{s}^{-1}$
R	Gas constant	$\text{J K}^{-1} \text{mol}^{-1}$
$\mathcal{R}_g$	Set of all gas-phase reactions	—
R_k	Integrated rate of reaction k	mol m^{-2}
r_k	Local rate of reaction k	$\text{mol m}^{-2} \text{s}^{-1}$
$\mathcal{R}_s$	Set of all surface reactions	—
$\mathcal{S}$	Set of all species	—
S	Entropy	J K^{-1}
s^0	Sticking coefficient	—
$\mathcal{S}_g$	Set of gas-phase species	—
Sh	Sherwood number	—
$\dot{s}_i$	Surface reaction rate of species i	$\text{mol m}^{-2} \text{s}^{-1}$
$\mathcal{S}_M$	Set of third-body species	—
$\mathcal{S}_s$	Set of surface species	—
T	Temperature	K or $^{\circ}\text{C}$
t	Time	s
u	Velocity	m s^{-1}
$\mathbf{W}$	Weight parameter in a neural network	—
$\mathbf{x}$	Input vector in a neural network	—
X	Conversion	—
y	Output value	—
$\hat{y}$	Predicted output value	—
Y_i	Mass fraction of species i	K
z	Axial coordinate	m

Greek Symbols

Symbol	Description	Unit
α	Reflection parameter in Nelder-Mead method	—
β	Temperature dependency factor	—
Δ	Difference	—
δ	Shrink parameter in Nelder-Mead method	—
$\epsilon_{i,k}$	Model parameter for surface influence	—
η	Learning rate	—
γ	Expansion parameter in Nelder-Mead method	—
Γ_s	Surface site density	mol cm^{-2}
λ	Penalty weight	—
λ_j	Kinetic parameter vector of size j	—
μ	Mean value	—
ν	Stoichiometric coefficient	—
$\dot{\omega}_i$	Gas-phase reaction rate of species i	$\text{mol m}^{-3} \text{s}^{-1}$
ρ	Density	kg m^{-3}
σ_i	Number of sites occupied by species i	—
σ	Standard deviation	—
θ	Surface coverage	—
ε	Bed porosity	—
ϱ	Contraction parameter in Nelder-Mead method	—
ϑ	Neural network parameters	—

Indices

cat	catalytic
exp	experimental
f	forward reaction

geo	geometric
i	generic Index
j	generic Index
k	generic Index
m	generic Index
n	generic Index
np	catalyst nanoparticle
p	particle in a catalytic bed
ref	reference value
r	reverse reaction
sim	simulation
std	standardized value
surr	surrogate model

1 Introduction¹

In the modern world, catalytic materials are being extensively used in facilitating numerous chemical and biological reactions, with their impact on the chemical manufacturing sector being particularly significant [2]. The development of efficient catalysts has been pivotal in revolutionizing several important industrial processes. In the context of reducing anthropogenic environmental impacts as well, the field of catalysis plays a significant role [3, 4].

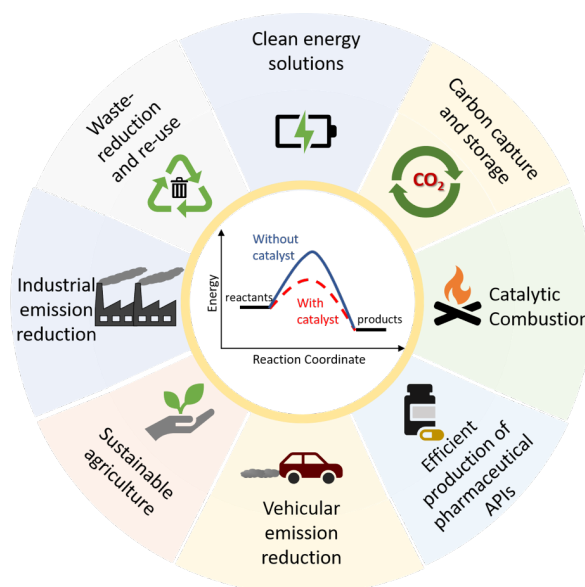


Figure 1.1: Various applications of catalytic materials. Figure reproduced from [1].

As industries globally strive towards carbon-neutral technologies, catalysis is enabling cleaner and environmentally responsible chemical processes (Fig.1.1). Research efforts are continually being made to support processes for carbon-capture and utilization [5],

¹Parts of this chapter are taken with permission from [1] Chacko, R. et al., “Interconnected Digital Solutions to Accelerate Modeling of the Reaction Kinetics in Catalysis”, ChemCatChem 2024, 16, e202301355, <https://doi.org/10.1002/cctc.202301355>, licensed under CC BY 4.0.

biomass conversion [6], and emission control [7–9]. To that extent, improving upon the process of development of new and advanced catalytic materials is of utmost importance. Emerging approaches, such as machine learning, and high-throughput experimentation are accelerating catalyst discovery [10–12]. Therefore, the digitalization of catalysis by integrating data-driven methodologies and automation in the research workflows is paramount to reducing development time, increasing efficiency, and enabling the transition of catalytic technologies from laboratory-scale to industrial applications [13, 14].

1.1 Digitalization in Catalysis Research

Catalysis deals with data that span a broad range of length and time scales while incorporating methods from a variety of disciplines such as organic, inorganic, physical, computational chemistry, and process engineering, thereby adding complexity to digitalization efforts [13, 15]. However, once realized the long-term impact would be monumental. As outlined in the GeCats whitepaper, “Digital Catalysis” would bridge the gap between theoretical and experimental approaches and provide opportunities for increased collaboration across disciplines and working groups, facilitating rational catalyst design [16].

The fundamental aspect to rational design of catalysts is to gain a deeper understanding of the mechanism of catalytic behavior [17]. This is accomplished through the diverse tools and methodologies in the “catalyst design toolbox” which includes advanced synthesis methods [18–20], sophisticated analytical techniques [21–24], and theoretical modeling approaches [25–29]. All these areas would greatly benefit from digitalization and efforts are therefore underway to build robust data frameworks and workflows that support the design process.

The materials sector has already witnessed significant strides [30–32] through initiatives such as the Materials Genome Initiative (MGI) [33], FAIRmat [34], and Novel Materials Discovery (NOMAD) [35]. In recent years, catalysis has experienced similar progress, driven by efforts like NFDI4Cat [36], DAPHNE4NFDI [37], CatApp [38], Catalysis-Hub [39], Catalyst Acquisition by Data Science [40]. These initiatives are lay-

ing the groundwork for digital catalysis, where the emphasis is also on building robust research data management (RDM) infrastructures. An RDM plan is necessary to enable data-reuse, facilitate collaboration and data exchange, and leverage advanced digital technologies such as machine learning. A key objective across these programs is to make data obtained at various stages of catalysis research Findable, Accessible, Interoperable, and Reusable (FAIR) [41], ensuring its use long after its generation, by the inclusion of rich metadata and the adoption of standardized data formats. Several strategies have been proposed to collect standardized data including use of ontologies for knowledge representation and Resource Description Framework (RDF) for metadata representation [42–46].

The diversity in the type of research data, ranging from experiments to characterization to theory, makes the development of a unified research data infrastructure particularly challenging [13]. To digitize catalyst synthesis and catalytic activity tests data, use of software tools that log all relevant data associated with the synthesis procedure is recommended [47]. Marshall et al. [15] have outlined strategies for the acquisition and storage of data from catalyst synthesis to functional analysis. Employing suitable Electronic Lab Notebooks (ELN) for data acquisition and use of standard protocols are key to ensure the generation of high-quality data [15, 48].

Another approach is the creation of a digital twin of test setups to track the changes made to the setup over time, while allowing data to be stored in repositories linked with the devices used to generate them. This concept is exemplified in the Adacta tool [49] developed within the NFDI4cat [36] initiative. Several reports have showcased the merits of using RDM strategies for handling diverse characterization data in catalysis [50, 51]. Similarly, tools for automation of the workflows followed in modeling studies and data-driven approaches have also gained increased attention [52–54]. Collectively, these efforts are paving the way towards autonomous catalyst discovery [55]. In particular in the modeling domain, interconnected digital solutions that deal with various aspects of catalysis research represent a crucial step towards better understanding the catalyst behavior. This is illustrated in Fig. 1.2, which demonstrates the role of interconnected tools in the process of development of kinetic models.

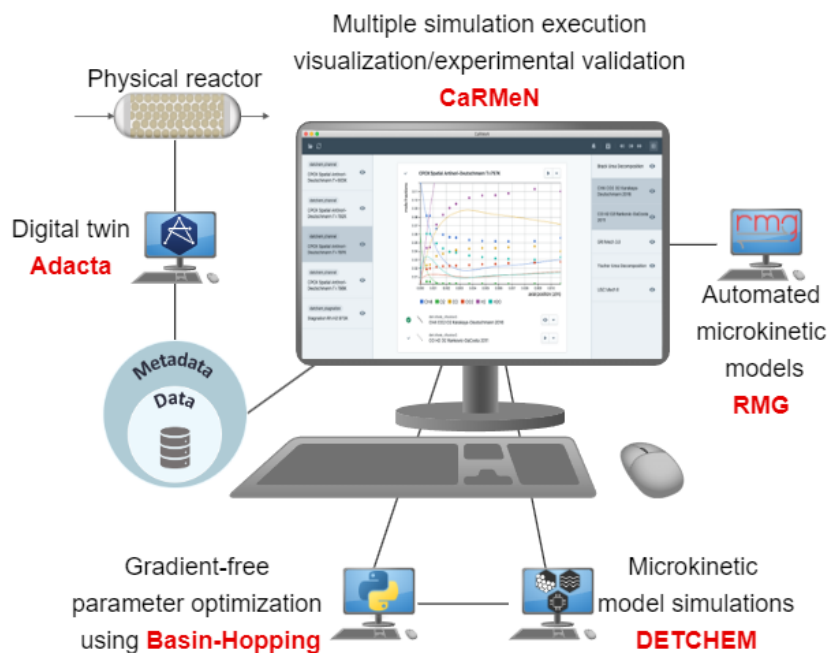


Figure 1.2: Interconnection of the various software and tools in kinetic model development. Figure reproduced from [1].

1.2 Objective and Outline of this Thesis

In this thesis, digitalization efforts towards use of automation, numerical algorithms and machine learning in the development and application of microkinetic models is demonstrated. Given that model development is a crucial step in gaining mechanistic insights and designing more efficient catalysts, leveraging digital tools and existing technologies can significantly accelerate the development process. This acceleration allows researchers to dedicate more time towards the application of these models. Additionally, this would also enable the adoption of such detailed models in industrial settings, where simplified models are often favored due to their rapid development.

The primary objective of this work was to develop tools that support the development of kinetic models and gain a better understanding of the surface chemistry. To this end, the initial focus was on developing and validating a protocol for the accelerated optimization of existing microkinetic models in response to new data or minor modifications in catalytic

materials. Subsequently, the potential of machine learning-based surrogate models was explored to better understand the catalytic performance under reaction conditions.

This thesis is structured into five chapters. The first two chapters provide a brief introduction to the topic and a description of the methods, the theoretical approaches used, and the governing equations for modeling. Chapter 3 outlines the optimization methodology and its application in optimizing two detailed microkinetic models for CO methanation over Ni/Al₂O₃ and NH₃ decomposition on ruthenium-based Ni-BCZY cermet catalyst. Chapter 4 describes the use of the optimization workflow in obtaining tailored mechanisms for two palladium-based supported catalysts to describe the effect of the supports on the catalytic behavior of PdO for methane oxidation under lean conditions. Finally, Chapter 5 demonstrates the development and application of a surrogate model trained with the help of simulated data obtained using a microkinetic model for methane oxidation on PdO/Al₂O₃ to better understand the dynamic nature of the active material during the light-offs. The experimental data for most of the applications presented in this work were sourced from published literature. An exception is the data related to ammonia decomposition on the cermet material used in Chapter 3, which was obtained through a collaborative project between Karlsruhe Institute of Technology (KIT) and the European Institute for Energy Research (EIFER). The experimental and characterization data were collected as part of the Master's thesis [56] of Tim Bastek from KIT, and the subsequent numerical investigations using the optimized model developed in this work, were carried out by Sadaf Davari from KIT. The paper [57] reporting the data and the model was published during the preparation of this thesis.

2 Theory and fundamentals

This chapter provides a description of the numerical techniques, methods, and the modeling equations. The content in this chapter are sourced from various textbooks and published literature [58–61].

2.1 Modeling of Heterogeneous Reactions

Understanding the kinetics of surface reactions in heterogeneous catalysis is essential in optimizing catalytic processes in both industrial and environmental contexts. Kinetics describe the rate at which chemical reactions occur and their numerical description spans a broad spectrum, ranging from global kinetic models to detailed microkinetic models (MKM). The global kinetic models are primarily phenomenological and used for application purposes instead of fundamental understanding [62]. In such models, only key species are considered and individual reaction steps occurring on the surface are lumped into global reactions, with empirically-calculated kinetic parameters that describe the behavior of the chemical system for a specific range of operating conditions. On the other hand, detailed microkinetic models incorporate all possible elementary steps happening on the surface without any prior assumptions about the rate-determining step or the most abundant reacting species [63]. Such models employ kinetic and thermodynamic parameters calculated based on first-principle methods. The elementary approach makes their application possible also at conditions that were not used during the development of the model.

A widely applied strategy in the microkinetic modeling framework is the mean-field approximation, which assumes a uniform distribution of surface species and active sites, neglecting any lateral interactions between adsorbates. This approach is in contrast to kinetic Monte Carlo (KMC) simulations [64], which model the temporal evolution of the catalytic system considering detailed spatial distribution of the adsorbates, however they are computationally expensive. Therefore, although the mean-field microkinetic models (MF-MKM) have lower accuracy than KMC models, the reduced computational cost and elementary approach makes mean-field microkinetic modeling a practical and powerful tool to investigate the complex chemical kinetics governing the catalyst performance and unravel the underlying mechanistic pathways. The following subsections detail the various equations used in this work for modeling the chemical kinetics and the reactor.

2.1.1 Kinetic Modeling Equations

A detailed microkinetic model describing a heterogeneous catalytic system comprises of several elementary steps, such as the adsorption/desorption of gaseous species, association/dissociation reactions, and/or reactions between various surface intermediates occurring on the catalyst active sites. The set of gas-phase species and surface species involved are represented by the sets $\mathcal{S}_g$ and $\mathcal{S}_s$, respectively. The concentration of the i^{th} gas-phase species is represented by c_i . The concentration of surface species are related to their coverage fraction (θ) through Eq. 2.1,

$$\theta_i = \frac{c_i \sigma_i}{\Gamma_s} \quad (2.1)$$

where, σ_i is the number of surface sites occupied by one particle of species i and Γ_s is the surface site density of the specific surface. The coverage fractions of surface species and the free-sites must fulfill the following criteria,

$$\sum_{i \in \mathcal{S}_s} \theta_i = 1 \quad (2.2)$$

For any given reversible reaction, the rate of the forward reaction based on the forward rate constant k_f can be expressed as,

$$\frac{dc_i}{dt} = v_i k_f \prod_{j \in \mathcal{S}} c_j^{\tilde{v}_j'} \quad (2.3)$$

where, $v_i = (v_i' - v_i'')$ and $\tilde{v}_j'$ is the reaction order of each species in the set of all species in the system $\mathcal{S}$. v_i' and v_i'' represent the stoichiometric coefficient of the reactants and products, respectively. In microkinetic models each reaction is defined as an elementary step, therefore the reaction order is considered equal to the stoichiometric coefficient. Analogous to the forward reaction rate, the reverse reaction rate is defined based on the reverse rate constant k_r , such that,

$$\frac{dc_i}{dt} = -v_i k_r \prod_{j \in \mathcal{S}} c_j^{\tilde{v}_j''} \quad (2.4)$$

The kinetic rate constant (k_k) for the k^{th} elementary step is calculated based on the Arrhenius equation [65], with additional modifications [61, 66], such that,

$$k_k(T) = A_k \left(\frac{T}{T_{\text{ref}}} \right)^{\beta_k} \exp \left[-\frac{E_{a,k}}{RT} \right] \cdot \prod_{i \in \mathcal{S}_s} \exp \left[\frac{\epsilon_{i,k} \theta_i}{RT} \right] \quad (2.5)$$

where, A_k is the pre-exponential factor, $E_{a,k}$ is the activation energy, β_k is a fitting parameter for temperature dependency, R is the universal gas constant, and $T_{\text{ref}} = 1\text{K}$. The parameter ϵ in the last term in Eq. 2.5 incorporates the effect of lateral interactions between closely packed adsorbates in proximity, which may alter the activation energy of a given elementary step.

The surface reaction rate ($\dot{s}_i$) for species i can then be expressed as follows,

$$\dot{s}_i = \sum_{k \in \mathcal{R}_s} v_{ik} k_k \prod_{j \in \mathcal{S}} c_j^{\tilde{v}_{jk'}} \quad (2.6)$$

where, $\mathcal{R}_s$ is the set of all surface reactions. For adsorption reactions, the rates are modeled using Eq. 2.7 through sticking coefficients s_k^0 , i.e., the probability that a gaseous molecule colliding on the surface would get adsorbed [67].

$$\frac{dc_i}{dt} = v_i \frac{s_k^0}{\Gamma_s^{n_k}} \sqrt{\frac{RT}{2\pi M_i}} \left(\frac{T}{T_{\text{ref}}}\right)^{\beta_k} \exp\left(-\frac{E_{a,k}}{RT}\right) \prod_{j \in \mathcal{S}} \tilde{c}_j^{\tilde{\nu}_{jk'}} \quad (2.7)$$

Here, n_k is equal to 1 for molecular adsorption and 2 for dissociative adsorption. M_i is the molar mass of the gaseous species i . For a set of gas-phase reactions $\mathcal{R}_g$ and third-body species $\mathcal{S}_M$, the rate of production of a gas-phase species i can be calculated as

$$\dot{\omega}_i = \frac{dc_i}{dt} = \sum_{k \in \mathcal{R}_g} v_{ik} k_k \prod_{j \in \mathcal{S}_g \cup \mathcal{S}_M} \tilde{c}_j^{\tilde{\nu}_{jk}}. \quad (2.8)$$

2.1.2 Thermodynamic Consistency

At equilibrium, the rate of forward reaction is equal to the rate of backward reaction. Therefore, Eqs. 2.3 and 2.4 can be rearranged to give,

$$\frac{k_f(T)}{k_r(T)} = \prod_{j \in \mathcal{S}} c_j^{v_j} \quad (2.9)$$

A reaction mechanism is considered to be thermodynamically consistent, if Eq. 2.10 is fulfilled for all reversible reactions in the mechanism.

$$\frac{k_f(T)}{k_r(T)} = \prod_i (c_i^\ominus)^{v_i} \exp\left[-\frac{\Delta_R G}{RT}\right] \quad (2.10)$$

Here, $\Delta_R G$ is the Gibbs free energy change and $c_i^\ominus$ is the concentration of species i at standard pressure. The Gibbs free energy change for a reaction can be calculated in terms of the Gibbs free energy of each species, such that,

$$\Delta_R G(T) = \sum_i v_i G_i(T) = \sum_i v_i (H_i(T) - T \cdot S_i(T)) \quad (2.11)$$

The calculation of Gibbs energy requires availability of thermodynamic data to obtain the standard enthalpy (H) and entropy (S) values for a given temperature. Thermodynamic data is often made available in the form of NASA polynomial coefficients [68, 69], which contain two sets of 7 constants (b_1 to b_7 in Eqs. 2.12 and 2.13), with one set valid for low temperatures and the second set valid at high temperatures.

$$H_i(T) = R \left(b_{1,i}T + \frac{b_{2,i}}{2}T^2 + \frac{b_{3,i}}{3}T^3 + \frac{b_{4,i}}{4}T^4 + \frac{b_{5,i}}{5}T^5 + b_{6,i} \right) \quad (2.12)$$

$$S_i(T) = R \left(b_{1,i} \ln T + b_{2,i}T + \frac{b_{3,i}}{2}T^2 + \frac{b_{4,i}}{3}T^3 + \frac{b_{5,i}}{4}T^4 + b_{7,i} \right) \quad (2.13)$$

Therefore, for a given forward reaction rate constant, Eq. 2.10 can be used to calculate the rate constant for the reverse reaction. However, it is not as straight-forward for surface mechanisms, as the thermodynamic data for surface species are often unknown. This necessitates that the rate coefficients for the forward and reverse reactions be explicitly given, which satisfy Eq. 2.10 for all reversible reaction pairs.

Typically in a detailed microkinetic model for a heterogeneous system, the number of surface species are less than the total number of reversible reactions. Therefore, there are more number of equations similar to Eq. 2.10 than there are unknown thermodynamic functions $G_i(T)$. This implies that not all values of $k_f(T)$ and $k_r(T)$ can be chosen independently. This depends on the available degrees of freedom, which in the case of surface reactions equals the number of surface species (N_s) minus one. Therefore, for a mechanism with K pairs of reversible reactions, there needs to be at least $K - N_s + 1$ dependent rate coefficient values to avoid an overdetermined equations system.

In this work, the DETCHEM^{ADJUST} tool is used to obtain thermodynamic consistency in reaction parameters [70]. With the DETCHEM^{ADJUST} tool the user has the choice to either allow all reaction parameters to be minimally changed so that the mechanism is thermodynamically consistent or define only a subset of reactions whose parameters are allowed to be adjusted. In the second scenario if the number of reactions allowed to be modified are equal to $K - N_s + 1$, then the system of equations are deterministically solved to obtain the unknown thermodynamic functions and the dependent rate coefficients.

However, for an underdetermined system of equations, the DETCHEM^{ADJUST} tool tries to search for the solution that minimizes the changes in the rate constants.

2.2 Modeling Reactive Flow in a Packed Bed Reactor

2.2.1 DETCHEM Simulation Model

A bottom-up approach is followed in multi-scale modeling that starts with kinetic models with elementary steps which are integrated with mass and heat transfer models. In this work, all simulations are performed with the packed bed reactor model in the DETCHEM simulation package [71]. The DETCHEM package, written in Fortran, comprises several libraries which facilitate the modeling of various types of reactors. The core library in DETCHEM provides various subroutines for reading input files such as the mechanism input, thermodynamic data, etc., to calculate reaction rates, flow properties, and thermochemical properties for the species. These subroutines are used in the implementation of reactor models such as the packed bed reactor model, DETCHEM^{PBR}.

The DETCHEM^{PBR} code [72] models the reactor using a 1D heterogeneous model under plug flow assumptions. This implies that no changes in flow properties in the radial direction is assumed and that axial diffusion is considered negligible. Thus, the packed bed simulation model can be expressed as a system of ordinary differential equations (ODEs) as

$$\frac{d\rho u}{dz} = a_v \sum_{i \in \mathcal{S}_g} M_i \dot{s}_i \quad (2.14)$$

$$\rho u \frac{dY_i}{dz} + Y_i a_v \sum_{j \in \mathcal{S}_g} \dot{s}_j M_j = M_i (a_v \dot{s}_i + \dot{\omega}_i \varepsilon) \quad (2.15)$$

where, ρ is the density, u is the superficial velocity, z is the axial coordinate, a_v is the surface area to volume ratio, M_i is the molar mass of species i , Y_i is the mass fraction of species i and ε is the porosity of the catalyst bed. The surface and gas-phase rate of production of species i are calculated using Eqs. 2.6 and 2.8, respectively. In this work all the simulations are performed under isothermal conditions, therefore, the temperature

balance equations are not given. External mass transfer resistance between the bulk fluid and the particle surface is modeled by equation 2.16,

$$M_i \dot{s}_i = k_{i,fs} (\rho_{i,s} Y_{i,s} - \rho_i Y_i) \quad (2.16)$$

where, $k_{i,fs}$ is the fluid-solid mass transfer coefficient of species i and $Y_{i,s}$ is the mass fraction of species i on the solid surface. The mass transfer coefficient is calculated as,

$$k_{i,fs} = \frac{Sh_{fs} D_i}{d_p} \quad (2.17)$$

where, Sh_{fs} is the Sherwood number and D_i is the effective diffusion coefficient of species i and d_p is the average particle size in the bed.

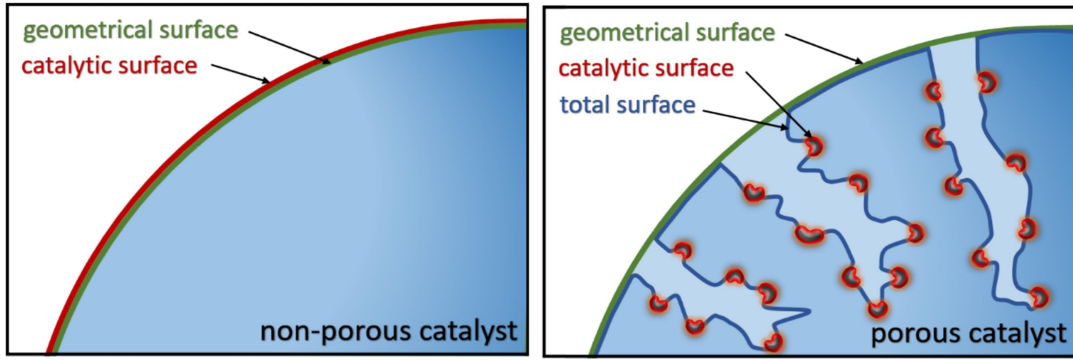


Figure 2.1: Illustration of the definition of surface area for non-porous and porous catalysts. Figure adapted from [73], licensed under CC BY 4.0.

In DETCHEM, the effect of increased surface area in the case of a porous catalyst is incorporated through the $F_{cat/geo}$ factor. This factor is defined as the ratio of the catalytic surface area available for adsorption to the geometric surface area as given in Eq. 2.18. The catalytic area A_{cat} is defined as the area of the active species in the catalyst bed and A_{geo} is the geometric surface area of the spherical bed particles, as illustrated in Fig. 2.1.

$$F_{cat/geo} = \frac{A_{cat}}{A_{geo}} \quad (2.18)$$

The available catalytic area may be determined experimentally by calculating dispersion through chemisorption experiments. The catalytic area may also be calculated based

on the average nanoparticle diameter of the active species d_{np} , obtained from imaging techniques, assuming spherical particles [74] such that,

$$A_{\text{cat}} = 0.5 \frac{m_{\text{active species}}}{\rho_{\text{active species}}} \frac{6}{d_{\text{np}}} \quad (2.19)$$

where, $m_{\text{active species}}$ is the mass of the active species calculated based on the catalyst loading and $\rho_{\text{active species}}$ is the density of the active catalyst species. It is assumed that the active species form spherical particles and half of the surface area is exposed to the bulk. The geometric area for a cylindrical packed bed reactor is calculated based on the surface area per unit volume of the solid fraction in the catalyst bed [75] such that,

$$A_{\text{geo}} = \frac{6(1 - \varepsilon)}{d_p} V_{\text{bed}} \quad (2.20)$$

$$A_{\text{geo}} = \frac{3\pi}{2} (1 - \varepsilon) \frac{D^2 L}{d_p} \quad (2.21)$$

where, ε is the bed porosity, D is the diameter of the reactor, L is the length of the reactor and d_p is the average diameter of particles in the catalyst bed.

2.2.2 Reaction Flow Analysis

Reaction flow analysis (RFA) is a useful technique in studying chemical kinetics to determine how much a particular reaction contributes towards the production or consumption of a species. RFA enables tracing the dominant reaction pathways that leads to the formation of a product by identifying important intermediate species and the pathways followed by them during the transformation of the reactants into the products. An integral rate analysis considers the overall contribution of a reaction along the full reactor length, while a local rate analysis examines the contributions towards formation or consumption at specific points in the reactor.

DETCHEM^{PBR} supports calculation of the integrated and local rates for each elementary step in a given reaction mechanism. The local rate (r_k) of the k^{th} reversible reaction is given by the following equation,

$$r_k = k_{fk} \prod_{j \in \mathcal{S}} c_j^{\tilde{v}_j'} - k_{rk} \prod_{j \in \mathcal{S}} c_j^{\tilde{v}_j''} \quad (2.22)$$

where, k_{fk} and k_{rk} are the rate constants for the forward and reverse step respectively. For integral RFA, the local rate is integrated for the duration of the residence time,

$$R_k = \int_0^t r_k dt \quad (2.23)$$

where R_k is the total rate in units mol m^{-2} . To calculate the rate of production (n_{ik}^+) or consumption (n_{ik}^-) of a species i , r_k is multiplied by the effective stoichiometric coefficient,

$$n_{ik} = (v_{ik}' - v_{ik}'')r_k \quad (2.24)$$

resulting in a matrix of dimensions ($N_s \times K$), where N_s is the total number of species and K represents the total number of reversible pairs of reactions. If n_{ik} is positive, then it indicates that the reaction contributes towards production of species (n_{ik}^+), and if negative, it contributes to its consumption (n_{ik}^-). To evaluate the overall impact of each reaction on a given species, it is useful to convert the absolute rates into percentages. Hence, normalization of the rate data is performed considering the formation and consumption rates separately. Thus, the percentage contribution of the k^{th} reaction towards the formation and consumption of species i are calculated by Eqs. 2.25 and 2.26, respectively.

$$n_{norm,ik}^+ = \frac{n_{ik}^+}{\sum_{k \in \mathcal{R}_s} n_{ik}^+} \times 100 \quad (2.25)$$

$$n_{norm,ik}^- = \frac{n_{ik}^-}{\sum_{k \in \mathcal{R}_s} n_{ik}^-} \times 100 \quad (2.26)$$

where, $\mathcal{R}_s$ is the set of all surface reactions.

2.2.3 Automation through CaRMeN

The process of comparison of simulated data with measured data involves several steps, namely: creation of input files for the various operating conditions, execution of multiple simulations, extraction and post-processing of the output data, and finally plotting the experimental and modeled data to obtain the comparison curves. The generation of input files includes creation of directories with files describing the flow properties in the form of a `moldata` file, thermodynamic information as NASA polynomial coefficients in the form of a `thermdata` file, species-related information as a `species.inp` file, mechanism-related information as a `mech.inp` file, and information on the configuration of the reactor setup and operating conditions in reactor-specific formats namely `pbr.inp` file.

During the development of a kinetic model, multiple simulations need to be performed which need to be quickly compared with experimental data and therefore, the simulation workflow benefits from automation. In this work, during the initial testing and the final validation of the developed kinetic models, the software CaRMeN (Catalytic Reaction Mechanism Network) [52, 53] was used to compare simulated data with the measured data. CaRMeN enables the acceleration of the simulation workflow by automating the labor-intensive tasks of setting up input files required for multiple simulations, parallelized execution and postprocessing of the outputs. Users of CaRMeN are able to specify simulation-related information in YAML files, and the software creates the input files in the required DETCHEM-specific format, executes the simulations, and displays the post-processed output of the simulation as comparison plots with the experimental data in the user-interface. Specifically for the simulation of a packed bed reactor, CaRMeN also supports the use of a template for the user-inputs and the experimental data in the form of a single Excel workbook, which contains validation checks to ensure valid data-entry and also automatically calculates the necessary simulation parameters based on the user-inputs. It not only allows easy data exchange across various working groups, but is also convenient for users who are not familiar with CaRMeN data formats.

At its core, CaRMeN follows a modular approach in creating the simulation configuration files as shown in Fig.2.2. It deconstructs a complete simulation input into subsets or

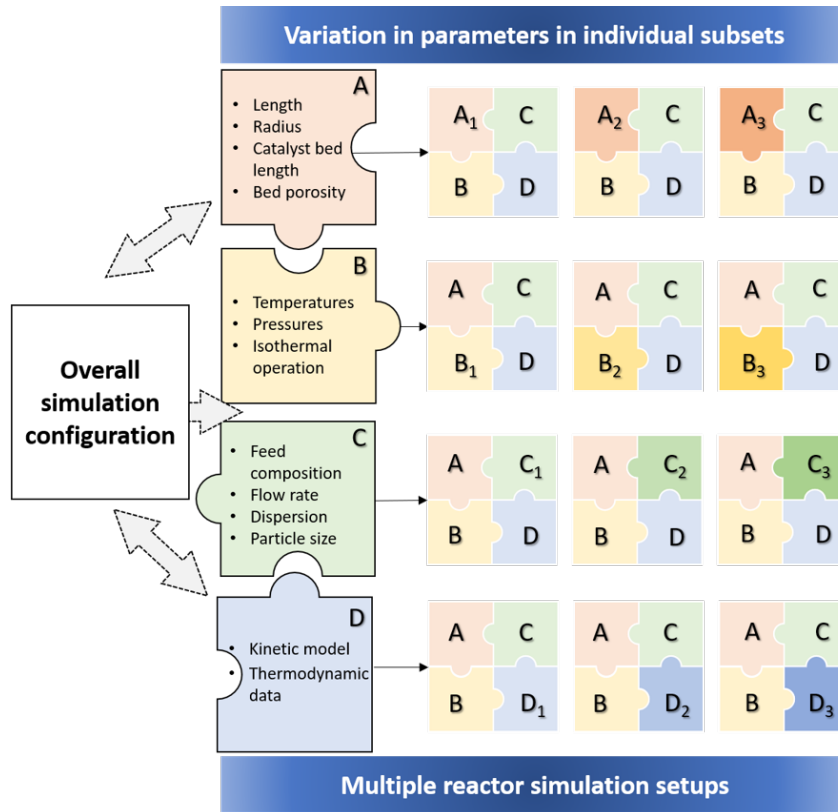


Figure 2.2: A pictorial representation of the modular approach followed in CaRMeN to create multiple simulations. Reprinted with permission from [1].

fragments that act as building blocks which may be reused and combined with other fragments. Due to this modular approach in creation of the simulation inputs, users are able to define the individual subsets containing parts of the simulation inputs and dynamically assemble them together within the user interface to run multiple simulations. For example, as depicted in the Fig. 2.2, a complete simulation configuration may be divided into subsets containing information regarding operating conditions and kinetic parameters, among others. It is a likely scenario, where multiple kinetic parameters may need to be tested, such as mechanisms for a given active catalyst from various literature sources, or when several experimental data with various feed ratios need to be compared with simulations using the same kinetic model. When such simulations need to be executed with several parameters remaining constant such as the reactor details, thermodynamic data, and other reactor operating conditions, then CaRMeN enables the reuse of the subset with constant values of simulation parameters, thereby reducing user effort in redefining the same information for each individual simulation. Such digital tools help

in accelerating the workflow of development of new models, and in reducing redundancy and errors.

2.3 Optimization Techniques

During the development of kinetic models, it is a common approach to optimize kinetic parameters based on measured data. Typically this optimization is conducted using numerical techniques which offer a convenient and robust alternative to manual fitting of the parameters [76–81]. Many optimization algorithms have been used in the literature, ranging from gradient-based methods to heuristic algorithms [82–89]. The overall goal in all methods is to minimize or maximize a given objective function such as, the residual error between the modeled and the measured outputs.

2.3.1 Basin-Hopping

In this work, the global optimization method Basin-Hopping [90] was used to optimize detailed kinetic models. Fig. 2.3 visualizes the basic principle behind this method. The method attempts to find the global solution to a given objective function by hopping from one local solution point to another point in the search space which might lead to a better solution. This hopping refers to the exploration step in the global search. Additionally, the algorithm uses a local-search method that may or may not use gradients to search for the local solution, after each hop, known as the exploitation step. A user-defined value of step size defines the range of each hop. A local solution is accepted or rejected based on the metropolis criterion [91], where a solution is always accepted if the value of the objective function is lower than the previously best value, or accepted with a probability calculated based on the difference in the current and the best objective function values.

Basin-Hopping has inherent stochasticity in it since the hopping point at each iteration is randomly decided in between the range determined by the step size value. Therefore, the method does not guarantee reaching a global solution. Additionally, reproducibility

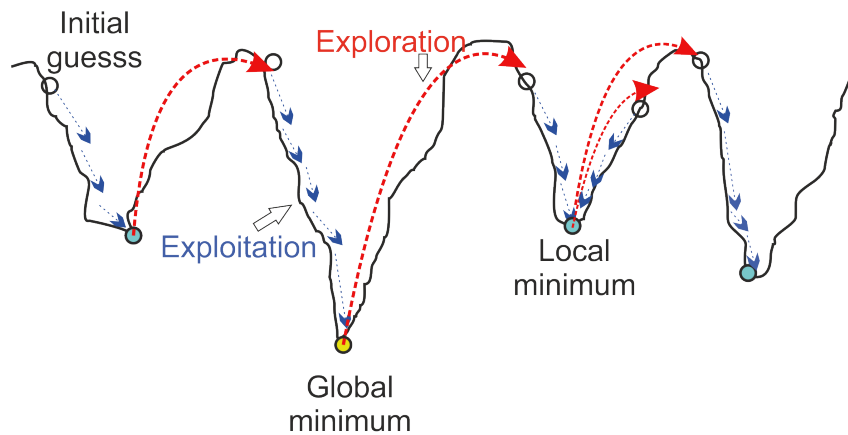


Figure 2.3: Search for a global minimum through Basin-Hopping. Figure reprinted without changes from [92].

of results is difficult as consecutive runs with the same value of step size and number of iterations may not lead to the same solution. However, this stochasticity may also lead to a better solution with multiple runs. In spite of these challenges, Basin-Hopping has proven to be useful in optimization of multi-modal objective functions, especially with high-dimensional search spaces [90, 93, 94]. The main advantage of Basin-Hopping is that due to its hopping mechanism, it avoids getting stuck at a local minimum or maximum. In this work, the Nelder-Mead method [95] was used as the local search method, which is described in detail in the following subsection. The Nelder-Mead method is a gradient-free method, it may be used with any simulation code, without needing to solve additional ODEs which would require significant computational resources for high-dimensional problems. This approach makes it easier to setup a general automation code for the optimization workflow irrespective of what reactor set up was used to measure the experimental data.

2.3.2 Nelder-Mead Method

The Nelder-Mead method, also known as the Simplex search method is a heuristics-based method to obtain the local optimum value of an objective function. It uses a set of heuristics to obtain the solution rather than relying on gradients information to direct

the search. The Nelder-Mead method uses a “simplex” to search the parameter space. A simplex is a geometrical shape containing $n + 1$ vertices, where n represents the number of dimensions of the search space. In this work, n refers to the total number of independent kinetic parameters to be optimized.

The method begins with an initial simplex, which is reshaped or moved towards the optimal region in the search space during the optimization procedure. The initial simplex is created using the initial guess of the parameters. The first vertex of the simplex is the point of initial guess (here, the initial mechanism parameters) and then each subsequent vertex is formed by making a small change in one of the parameter values, such that if $\vec{x}_1$ is the initial guess, then the $(i + 1)^{th}$ vertex of the simplex is calculated using the i^{th} dimension unit vector $\vec{u}_i$, through the following equation,

$$\vec{x}_{i+1} = \vec{x}_1 + h(\vec{x}_1, i) * \vec{u}_i \quad \forall i \in \{1, \dots, n\}. \quad (2.27)$$

Here, $h(\vec{x}_1, i)$ is defined as 0.05 if the coefficient of $\vec{u}_i$ in the definition of $\vec{x}_1$ is non-zero, otherwise it is defined as 0.00025. These values follow the default simplex-generation heuristics used in Scipy [96] and MATLAB [97]. More generally, $h(\vec{x}_1, i)$ represents an estimate of the characteristic length scale of the problem [98] in the i^{th} dimension, namely, the magnitude of perturbation in the parameter that produces a non-negligible change in the objective function. In this work, the value of 0.05 corresponds to a 5 % change in the kinetic parameter value, which is a reasonable estimate of the scale at which the change in the objective function is meaningful.

After the initial simplex generation, the method tries to make modifications in the current simplex at each iteration, so as to shift it towards the point with the lowest value of the objective function. The method uses a series of steps during each iteration namely, (i) ordering, (ii) computation of the centroid, and (iii) transformation of the simplex. The ordering step involves sorting the vertices of the simplex based on the value of the objective function $f(\vec{x}_i)$ ranging from the best to the worst:

$$f(\vec{x}_1) \leq f(\vec{x}_2) \leq \dots \leq f(\vec{x}_n) \leq f(\vec{x}_{n+1}). \quad (2.28)$$

In the context of a minimization optimization task, the best vertex is the one with the lowest objective function value, and the worst-performing vertex has the highest objective function value. The consecutive steps are used to replace the vertex with the worst performance with a better performing point. For this, a centroid $\vec{x}_c$ is calculated considering all the vertices except the worst-performing vertex followed by the transformation step, which uses the centroid to guide the generation of the next vertex.

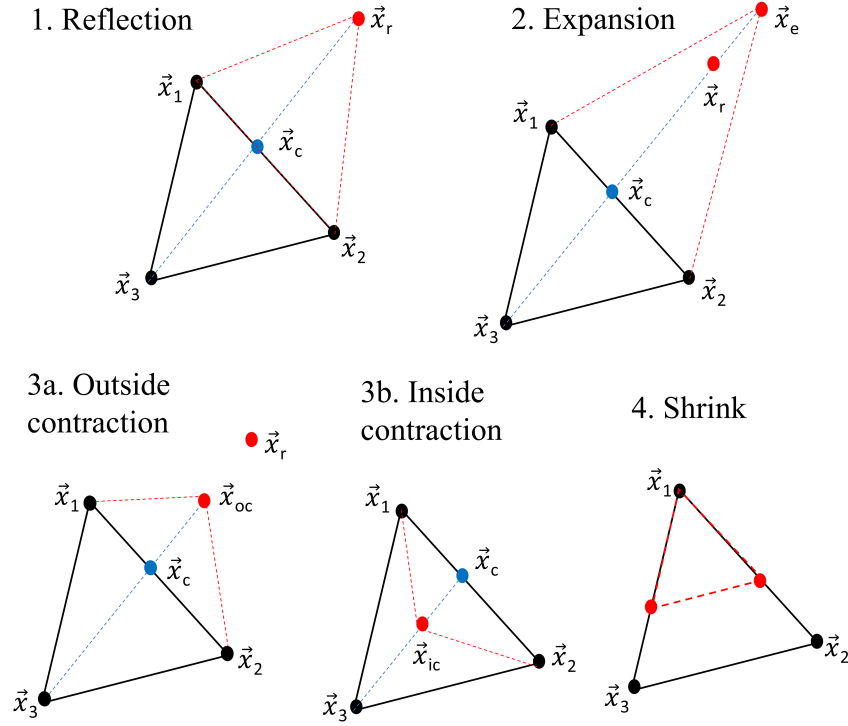


Figure 2.4: Schematic representation of the transformation operations used in the Nelder-Mead method for $n = 2$.

The transformation step consists of a variety of operations, as illustrated in Fig. 2.4 for a two-dimensional problem. The first operation that attempts to replace the worst-performing vertex ($\vec{x}_{n+1}$) is the reflection operation, where a new reflected point $\vec{x}_r$ is generated using,

$$\vec{x}_r = \vec{x}_c + \alpha(\vec{x}_c - \vec{x}_{n+1}) \quad (2.29)$$

where, α is the reflection parameter. The reflection operation aims to move the simplex in a direction away from the sub-optimal region around the worst-performing vertex. As shown in Fig. 2.4(1) for $n = 2$, $\vec{x}_r$ “mirrors” the worst-performing point $\vec{x}_3$ across the

centroid $\vec{x}_c$. If the newly generated point gives a lower value of the objective function than the second worst-performing vertex, i.e. $f(\vec{x}_1) \leq f(\vec{x}_r) \leq f(\vec{x}_n)$, then the new vertex replaces the worst-performing vertex ($\vec{x}_{n+1}$) and the algorithm begins a new iteration. If the newly generated vertex performs even better than the best vertex ($\vec{x}_1$) then the algorithm tries to look for further solutions in the same direction by performing the expansion operation. It is defined as,

$$\vec{x}_e = \vec{x}_c + \gamma(\vec{x}_r - \vec{x}_c) \quad (2.30)$$

where $\vec{x}_e$ is the expansion point and γ is the expansion parameter. As shown in Fig. 2.4(2) for $n = 2$, $\vec{x}_e$ further explores the same direction of $\vec{x}_r$. If $\vec{x}_e$ is better than $\vec{x}_r$, then $\vec{x}_{n+1}$ is replaced by $\vec{x}_e$, otherwise it is replaced by $\vec{x}_r$, and a new iteration is performed.

In the event that the objective function value for the reflected point is not better than the second worst point, i.e. $f(\vec{x}_r) \geq f(\vec{x}_n)$, then there are two possible operations for transformation. First, if $f(\vec{x}_r) < f(\vec{x}_{n+1})$, implying that the reflection direction is promising, then outside contraction is performed (Fig. 2.4(3a)),

$$\vec{x}_{oc} = \vec{x}_c + \varrho(\vec{x}_r - \vec{x}_c) \quad (2.31)$$

where, ϱ is the contraction parameter. Second, if $f(\vec{x}_r) \geq f(\vec{x}_{n+1})$, implying that the direction of the reflection point is not ideal, then the contracted point is computed on the inside of the simplex (Fig. 2.4(3b)) as,

$$\vec{x}_{ic} = \vec{x}_c + \varrho(\vec{x}_{n+1} - \vec{x}_c). \quad (2.32)$$

If the contracted point is better, then it replaces $\vec{x}_{n+1}$ and a new iteration is performed. If the contraction operation also did not lead to a better performing point, then a shrink operation is performed, which replaces all the points in the simplex except for the best vertex (Fig. 2.4(4)). Therefore, for $2 \leq i \leq n + 1$, the i^{th} vertex is calculated as,

$$\vec{x}_i = \vec{x}_1 + \delta(\vec{x}_i - \vec{x}_1) \quad (2.33)$$

where, δ is the shrink parameter. The scalar parameters used in the above operations are based on the adaptive implementation proposed by Gao and Han [99] where the parameters are calculated based on the number of dimensions to make the Nelder-Mead method suitable for high dimensional problems. According to the adaptive implementation, for $n \geq 2$,

$$\alpha = 1, \quad \gamma = 1 + \frac{2}{n}, \quad \varrho = 0.75 - \frac{1}{2n}, \quad \delta = 1 - \frac{1}{n}. \quad (2.34)$$

2.4 Artificial Neural Networks

This section aims to give a brief overview of artificial neural networks (ANN) with an emphasis on how they are used for regression tasks. A more comprehensive discussion of the architectures and model training procedure followed in this work is given in Chapter 5. The primary inspiration for the fields of artificial intelligence (AI) and machine learning (ML) is to enable machines to mimic human intelligence to perform a variety of complex tasks. An ANN is a foundational model in the domain of deep learning, which is a subset of machine learning, that is designed to replicate the behavior of biological neurons in human brain. An ANN consists of a network of interconnected artificial neurons, each with associated weights and biases that are learned during model training. According to the universal approximation theorem, an ANN can approximate any function, given enough number of neurons and layers in the network [100]. This makes them highly versatile for complex regression and pattern matching tasks. Regression problems fall under the category of supervised learning, where the model learns to approximate a function that relates a set of input and output variables.

The training procedure for a typical regression problem simply involves optimizing the weights and biases associated with the network, by minimizing the difference between the predicted and the actual outputs for a given set of inputs. The key issue in machine learning is making sure that the trained weights are generalized enough to not only perform well on the training data but also on unseen data, i.e., data not experienced by the model during training. This is also how ML training differs from a “true” optimization task,

since ML training aims to reduce this generalization error on test data, while training its parameters by minimizing a cost function that is calculated on a different set of data. If the model performs well on training data, but does not generalize well on other testing data, then such a model is considered to be an overfitted model. In contrast, a model that does not predict well even on the training dataset is an underfitted model. A model is said to have trained well if the prediction error on the training dataset is low and the difference between the prediction errors of the training and the testing dataset is also low. The complexity of the network architecture also plays a crucial role in determining if the model would tend to overfit or underfit. The complexity of the model directly translates to the capacity of the model to learn. If the true complexity of the prediction task is less than the model's capacity to learn, then the model would tend to overfit, by just memorizing all the outputs. Similarly, if the true complexity is higher than the model's capacity to learn then it would tend to underfit. Regularization techniques are often used during training to reduce overfitting and improve generalization.

Most ML algorithms including ANNs have hyperparameters, which determine the configuration of the model and the number of trainable parameters in the model. These hyperparameters are not adapted during the model training but are rather set beforehand. However, one needs to determine the optimal values for these hyperparameters to obtain the best model. This is where a validation dataset is useful which is typically obtained by randomly splitting the training dataset into two disjoint sets. This validation dataset is distinct from the testing dataset mentioned above, which is only used to estimate the generalization error of a model once the training is complete. The purpose of the validation dataset is to guide the selection of hyperparameters, by training various combination of hyperparameter settings and comparing model performance on same set of samples. Commonly used approaches for hyperparameter tuning include grid search or random search. A grid search involves defining a range for each hyperparameter and discretizing the hyperparameter domain into a grid. A new model is trained at each point on the grid representing a combination of hyperparameter values, and the performance is tested. The grid point showing the best performance is then considered the optimal combination of hyperparameters. Such an approach on one hand is thorough, since it

spans all combinations, but it is also slow because many models need to be trained to find the optimal set. Random search is similar to grid search, however instead of using all points on the grid, only a subset of randomly selected points are tested. This results in a fast but less accurate approach.

2.4.1 Gradient-based Optimization for Neural Network Training

A simple fully connected network would involve an input layer, a hidden layer and an output layer, where every neuron within a layer gets input from all the neurons from the previous layer. The hidden layers typically also include activation functions, which are used to incorporate non-linearity in the model. The choice of the activation function is done based on the type of prediction of task. Several activation functions exist such as sigmoid (or logistic function), tanh, and ReLU. As the task complexity becomes more demanding, the complexity of the neural network may also grow beyond the simple feed forward architectures, such as deeper networks with more hidden layers, convolutional layers, recurrent layers, or transformers.

The output ($\mathbf{z}^{[1]}$) from a hidden layer of size h can be expressed in terms of the input vector ($\mathbf{x} \in \mathbb{R}^n$), the weights $\mathbf{W}^{[1]} \in \mathbb{R}^{h \times n}$, and biases $\mathbf{b}^{[1]} \in \mathbb{R}^h$, as

$$\mathbf{z}^{[1]} = \phi(\mathbf{W}^{[1]}\mathbf{x} + \mathbf{b}^{[1]}) \quad (2.35)$$

where $\phi(\cdot)$ is the activation function. The predicted scalar output ($\hat{y}$) from the output layer would be calculated as,

$$\hat{y} = \mathbf{W}^{[2]}\mathbf{x} + \mathbf{b}^{[2]} \quad (2.36)$$

where, $\mathbf{W}^{[2]} \in \mathbb{R}^{1 \times h}$ are the weights and $\mathbf{b}^{[2]} \in \mathbb{R}$ are the biases of the output layer. A loss function is used as a performance measure for the model, where mean squared error (MSE) is commonly used for regression tasks. For a training dataset with N samples with a true output value of y_i the MSE loss function is defined as,

$$\mathcal{L} = \frac{1}{N} \sum_{i=1}^N (y_i - \hat{y}_i)^2 \quad (2.37)$$

The network parameters are updated typically through gradient descent algorithm [101] where the parameters are changed in the negative direction of the derivative of the loss function with respect to the network parameters, such that,

$$\vartheta \leftarrow \vartheta - \eta \cdot \frac{\partial \mathcal{L}}{\partial \vartheta} \quad (2.38)$$

where, ϑ are the network parameters (could be weights or biases) and η is the learning rate. The process of using an input $\mathbf{x}$ to obtain the predicted output $\hat{y}$ and the loss function $\mathcal{L}$, is known as the forward propagation step, as information flows forward through the network. The back-propagation step then allows the information from the loss function to flow backward through the network in order to compute the gradients. Automatic differentiation is used to calculate the partial derivatives needed for the update step, by breaking down the complex functions used during the forward propagation step into a sequence of basic operations and systematically applying the chain rule.

Traditional gradient descent-based optimization of the network parameters use a constant value of learning rate to update the network parameters which may lead to issues such as slow convergence and sensitivity to learning rate choice. A very low learning rate at the start of the training would lead to very slow model training, while a very high learning rate would lead to larger updates in the parameters which might lead to completely missing the minimum point. Thus, learning rate schedulers are necessary to more efficiently guide the update. More advanced optimizers such as Adam (Adaptive Moment Estimation) [102] were proposed to handle these challenges. Adam optimizer works by adaptively adjusting the learning rate for each parameter using estimates of the mean and variance of the gradients. This enables Adam to adapt to the shape of the loss functions and make more efficient steps towards minimizing the error. As a result, Adam has become the default optimizer in many deep learning applications.

3 Kinetic Parameter Optimization

using Basin-Hopping: A Proof of Concept¹

Microkinetic modeling is a powerful tool for rational catalyst design and understanding the underlying surface phenomena. It is often necessary to fit existing microkinetic models to new experimental data under different conditions or for similar catalytic systems that share the same elementary steps but differ slightly in the values of the rate parameters. In such cases, the large number of tunable kinetic parameters in the microkinetic model is a limiting factor in optimizing the models. This chapter presents the development of an automated optimization workflow used for fitting the rate parameters in microkinetic models, that helps accelerate the microkinetic model development. Details regarding the various steps in the optimization workflow and illustrative examples for the optimization procedure are described. It is shown that the use of an automated approach in executing the simulations necessary for the calculation of the objective function during the optimization procedure helps in accelerating the development of a microkinetic model. The use of a gradient-free optimization algorithm Basin-Hopping enables creation of a generalized workflow that can be easily extended to any simulation framework or catalytic system.

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3.1 Background and Motivation

The primary advantage of using microkinetic models is that all possible elementary reactions occurring on the surface are considered in the model without making any a priori assumptions about the rate determining step (RDS) or the most abundant species on the surface. It is necessary to avoid such assumptions so as to have a generalized kinetic model capable of accurately extrapolating the kinetic behavior across a wide range of operating conditions. The challenges of employing such a comprehensive approach include, the identification of an expansive set of elementary steps occurring on the catalyst surface and the estimation of associated kinetic parameters to accurately model the reaction kinetics. Automated reaction mechanism generator programs [54, 103] are a viable strategy to obtain an expansive reaction network which can act as an initial reaction mechanism with the possibility of further refinement. The determination of the associated kinetic parameters for these steps can be done through first principle-based computations, semi-empirical methods, and/or experimental approaches.

First-principle simulations include ab initio quantum chemistry methods such as density functional theory (DFT) and transition state theory (TST), which can be used for parameter estimation. However, these methods are computationally expensive, and estimating the energy parameters for every possible elementary step across all relevant conditions becomes highly demanding [104]. Therefore, hybrid parameter estimation approaches are commonly employed where DFT computations are supplemented with semi-empirical techniques like unity bond index-quadratic exponential potential (UBI-QEP) in combination with some fitting to experimental data. Purely experimental approaches would involve extraction of the parameters from individual surface science experiments such as temperature-programmed desorption (TPD). Such an approach also requires optimization of the rest of the kinetic parameters against experimental catalytic performance measurements. Additionally, the estimated parameters may have inherent uncertainties [17] that require optimization of the parameters within the known uncertainties to be able to accurately predict the catalyst behavior under experimental conditions [105].

Additionally, the use of different supports with an active catalyst may alter the kinetics and the catalytic performance. This effect can stem from the direct participation of the support or indirectly through modifications in the shape and size of the metal nanoparticles, through charge transfer, metal-support interactions, or stabilization of ionic metal species [106]. Generally, such an impact is modeled implicitly in the kinetic parameters and not as additional elementary steps, especially when there is no direct participation of the support. A direct estimation of rate parameters considering the influence of the supports using first-principles is difficult and computationally demanding due to the complex electronic structure of the supports. Hence, the microkinetic models developed for an active metal generally need to be optimized to take into account the effect of supports when experimental measurements are made with catalysts supported on other materials.

The optimization of kinetic parameters in a microkinetic model, with its high dimensionality, is a complex optimization problem, wherein the objective function is to minimize the residuals between experimentally measured and modeled data, within the realistic bounds for the parameters. Additionally, the process is made more complex if calculation of gradients of the highly non-linear objective function is needed. Various optimization algorithms [83–89] have been used in the literature in an attempt to have an optimized model that is able to reveal more information about the catalytic behavior and the reaction mechanism on the catalyst surface. Global optimization methods, such as differential evolution and genetic algorithms have gained much attention, however many of these methods tend to get stuck in local minima [107], especially when the objective function landscape is noisy. In order to circumvent these challenges, Basin-Hopping algorithm is employed in this work.

As described in Section 2.3.1, the Basin-Hopping algorithm uses a combination of exploration and exploitation strategies to potentially find an optimal solution [90]. The exploitation step is crucial in finding the local minima after each hop performed in the exploration step. There are several possible choices for the local-search algorithm, such as Nelder-Mead method [95], Powell’s conjugate direction method [108], or Limited-memory Broyden-Fletcher-Goldfarb-Shannon (L-BFGS) method [109]. The L-BFGS method is useful when the objective function is differentiable, however for applications such as ki-

netic parameter optimization, the calculation of derivatives is not trivial, making it unsuitable for current application. The Nelder-Mead method, a heuristics-based algorithm is a more appropriate choice in this case, as it is not only gradient-free but also performs well for high-dimensional use-cases, due to its adaptive implementation of the algorithm parameters, as described in detail in Section 2.3.2. Therefore, the use of Basin-Hopping together with the Nelder-Mead method offers an efficient and completely gradient-free method for kinetic parameter optimization.

3.2 Methodology

The key step in the optimization procedure is the calculation of the objective function, which entails running multiple simulations to generate the model outputs that can be compared with the corresponding experimental data. In contrast to a gradient-based method, where the search for an optimal solution is guided by the gradients of the objective function with respect to the kinetic parameters to be optimized, Basin-Hopping approaches the objective function as a black-box, relying solely on its output values without requiring any knowledge of its internal structure or derivatives. Therefore, it can be used in conjunction with any simulation code, modeling any type of reactor or chemical system, thus providing a general optimization workflow. The results presented in this thesis are primarily focused on using Basin-Hopping to optimize detailed surface mechanisms with experimental data measured in a packed bed reactor. However, the protocol can be followed to optimize any type of model kinetics including lumped kinetic models incorporating data from multiple reactor setups.

In this work, a Python-based [110] script was developed to automate and accelerate the overall workflow for the optimization process. The DETCHEM simulation package [71], specifically the DETCHEM^{PBR} code was used to generate the simulation outputs, that models a packed bed reactor as a one-dimensional heterogeneous model under plug flow assumptions, using detailed microkinetic models for the surface rate calculation. The governing equations for the reactor model are described in Section 2.2.1. The script au-

tomates the various steps for calculation of the objective function during the parameter search at each iteration. The various steps include, creation of specific input files necessary for the simulations, parallelized execution of the multiple simulations, reading and post-processing of the generated outputs, followed by the calculation of the chosen objective function.

3.2.1 Choosing the Type of Objective Function

In the case of Basin-Hopping, the choice of the objective function is not very critical as the algorithm uses the value of the objective function only to determine if the current parameter set may be accepted as an optimal solution, via the Metropolis criterion [91]. Similarly within Nelder-Mead, the local-search method, only the value of objective function is compared with other points in the simplex to determine which point should be replaced in the simplex, and does not explicitly use the objective function value to calculate the next point. However, it may be necessary to use an appropriate objective function based on the task at hand, in order to better interpret the fit from the values of the objective function during the optimization process. A general rule of thumb would be to use such an objective function that even significantly different experiments contribute to the objective function value in the same manner.

In this work, since conversions were used, the objective function was chosen to be the sum of the absolute deviations between the experimental and simulated data, as expressed below in Eq. 3.1

$$f(\lambda_j) = \sum_{n=1}^N \left| \left(X_{i,\text{sim}}^{T_n}(\lambda_j) - X_{i,\text{exp}}^{T_n} \right) \right| \quad (3.1)$$

where, λ_j is a vector of size j denoting the total kinetic parameters for a given microkinetic model, $X_{i,\text{sim}}^{T_n}$ is the simulated end-of-pipe conversion of reactant species i , and $X_{i,\text{exp}}^{T_n}$ is the experimental conversion of reactant species i at temperature T_n . N represents the total number of experimental data points to be used in the objective function.

3.2.2 Experimental Data for Objective Function Calculation

The selection of both the number and type of experimental data points to be included in the objective function depends on the specific problem. One crucial aspect for consideration is to include only those data points where significant dependency exists on the kinetic parameters and where the catalytic performance is not limited by heat transfer or mass transfer effects. An initial sensitivity analysis may be helpful in determining the range of operating conditions where the reactor outputs are in a kinetic-control regime, in addition to finding the most sensitive kinetic parameters in the microkinetic model.

The experimental data is to be provided for the objective function calculation in the form of an Excel sheet containing tabulated data with each column header denoting the type of data present, such as temperature, axial coordinate, time, and/or various species concentration. Each experimental data file may contain only the data corresponding to a particular feed type and operating condition except temperature. Therefore, a single data file may include for a particular feed composition, multiple end-of-pipe measurements when the reactor is either operated isothermally or subject to a temperature ramp, or spatially-resolved measurements for every temperature and axial point in the reactor. Different feed compositions, catalytic bed properties, reactor configurations, or operating conditions other than temperature such as pressure or flow conditions, require additional files as input to the Python script.

The number of experimental data points provided in the data file(s), determine the number of simulations that would be executed during the calculation of the objective function. It is important to consider that a unique solution for the parameter optimization problem may not be found if the number of experimental points are lower than the number of kinetic parameters needed to be optimized, leading to an over-parameterized (or under-determined) system. However, due to the high dimensionality of the microkinetic models it is not practical to include that many data points in the objective function, as it would lead to a significant increase in the computational time needed to calculate the objective function. This would significantly limit the practical application of the fitting process.

Therefore, achieving a reliable mechanism requires balancing the number of data points included with the computational effort needed to perform the optimization.

In order to overcome the risks of an over-parameterized system, the following strategies are useful. One way to avoid an over-parameterized system is to reduce the number of parameters to be fitted, by optimizing only the kinetically significant parameters and keeping the rest of the parameters constant. In other cases, when an under-determined system cannot be avoided, the experimental data should be divided into a fitting set and a validation set, to reduce the risk of overfitting. The fitting set is used for the objective function calculation and the validation set is used to see if the parameter sets are generalizable to other operating conditions and are able to reasonably predict the activity under these conditions. Additionally, imposing reasonable bounds and constraints to the parameters would also be useful in obtaining parameters that are within physically realistic ranges. In this thesis, since examples are shown for optimizing large microkinetic models with limited experimental data, the latter approaches are used to minimize the risk of overfitting.

3.2.3 Implementation with DETCHEM

As described above, the number of experimental points provided determines the number of simulations that would be executed during the objective function call. The Python script developed in this work employs the DETCHEM simulation suite to execute the reactor simulations. The DETCHEM code requires a folder comprising the input files needed for simulation, containing various details such as the reactor configuration details, the mechanism information, and the transport and thermodynamic properties of the species involved. Hence, each experimental data point corresponding to a unique set of operating conditions requires its own folder containing its associated input files, which would also contain the generated output data after a simulation is executed. Depending on the type of experimental data points provided for the objective function calculation, several files need to be dynamically generated during the various iterations of the optimization

procedure. The DETCHEM program allows including the various information needed for the simulations in separate input files in specific text-based formats.

Generally, the mechanism-related information is provided in the `mech.inp` file containing the elementary steps and their associated Arrhenius kinetic parameter values. Here as an initial guess, these values are provided by the end-user, obtained either from similar mechanisms for other catalytic systems or from initial estimates from the various parameter estimation methods discussed earlier. The script uses regular expressions matching to extract the numerical values of the parameters to be optimized from the text-based input files and for subsequent creation of the new mechanism files. During the optimization procedure at each iteration when a new parameter set is explored, a new `mech.inp` file is created in each directory. The species-related information specifying the gas-phase and surface-phase species, the transport properties, and the thermodynamic data containing the coefficients for the NASA polynomials are provided by the end-user as `species.inp`, `moldata`, and `thermdata` files, respectively. The information contained in these files typically do not change during the optimization procedure. The reactor-specific input data is provided as a separate file, depending on the type of reactor code used, such as in the case of packed bed reactor model the input file is named `pbr.inp`. This file needs to be updated depending on the experimental data. For example, if multiple end-of-pipe data at several temperatures are provided as experimental data for a single feed composition, then only the wall temperature input in the `pbr.inp` needs to be updated in the appropriate directories. In case several data points are provided for various feed compositions at multiple temperatures, then both the wall temperature and inlet conditions need to be updated. However, if only a spatially resolved measurement is provided at a single temperature and feed composition, the `pbr.inp` file remains fixed throughout the optimization procedure.

During the initial development stage of the optimization script, only the DETCHEM^{PBR} code was compatible, as the inputs needed for the setup of the optimization routine were obtained with the help of the CaRMeN Excel template used specifically for the packed bed reactor simulations, described in Section 2.2.3. However, as the need arose for a more generalized script that may be extended to other reactor codes available in the

DETCHEM simulation package, then the script was updated to utilize a user-defined reactor template file in the DETCHEM-specific format, as used by DETCHEM users for running simulations. This template file needs to have placeholder texts (or strings) for values that need to be updated during the optimization procedure. The placeholder string should be a valid Python identifier, prefixed with the “\$” sign, with the identifier string matching the column headers as specified in the experimental data files. The script was then updated to utilize the standard `Template` class in the Python `string` module, to substitute the placeholder strings within the reactor template file with the actual values, as provided in the experimental data at each iteration during the optimization procedure. In addition to the reactor-specific template file, the user needs to provide all the other input files needed for the simulation mentioned earlier that do not change during the optimization procedure, along with the initial mechanism file.

3.2.4 Independent Parameter Optimization and Thermodynamic Constraints

While developing microkinetic models, it is important to make sure that thermodynamic consistency is maintained [111]. As outlined in Section 2.1.2, the thermodynamic consistency for surface mechanisms is complex due to the unavailability of the thermodynamic properties of surface species. Therefore, if the model consists of K pairs of reversible reactions with N_s surface species, parameters corresponding to $K - N_s + 1$ number of reactions need to be calculated to satisfy the thermodynamic constraints [70], while the rest may be independently chosen. The deterministic calculation of the dependent parameters is accomplished with the help of the DETCHEM^{ADJUST} tool and is used within the optimization script to maintain thermodynamic consistency.

There are multiple ways to use the DETCHEM^{ADJUST} tool during the optimization procedure. The first method is the one described above where the minimum number of reactions i.e. $K - N_s + 1$ are deterministically calculated through DETCHEM^{ADJUST} and only the independent parameters are optimized independently via the optimization algorithm. Therefore, at each iteration, the search space consists of only the independent parameters

which are modified algorithmically, followed by calling the DETCHEM^{ADJUST} tool which outputs a thermodynamically consistent parameter set and consequently a `mech.inp` file, which is used for running the simulations for the objective function calculation. The second method involves the user specifying the elementary reactions that need to be independently modified by the algorithm. The DETCHEM^{ADJUST} tool may be called to either calculate all the rest of the parameters or only the parameters for the dependent steps ($K - N_s + 1$). In the latter scenario, there would be a certain number of elementary steps that would remain constant throughout the optimization procedure. Both the methods are useful in reducing the dimensionality of kinetic parameter search space while ensuring thermodynamic consistency of the mechanism throughout the optimization procedure.

3.2.5 Overall Optimization Workflow

The Basin-Hopping algorithm was implemented in the kinetic parameter optimization script using the `Scipy` library [96] for Python [110]. As described in Section 2.3.1, the algorithm performs stochastic hops during the exploration step, which is constrained by a user-defined step size. The step size value is a crucial parameter in the optimization routine as it determines the total volume of the search space during each iteration. A large step size would lead to a large search space with a low probability of landing near a potential minimum. If the deviations between the initial model and the experimental data are not large then it is prudent to keep a small step size. For larger deviations, a smaller step size with more number of Basin-Hopping iterations would be appropriate. It is to be noted that the step size value constraints the changes in the independent parameters only during a single iteration, relative to the current value of the parameter. As the algorithm proceeds, with each hop, the search space may move significantly away from the initial point, and the parameters may attain values that lie outside the step size relative to their initial values.

In the default `Scipy` implementation, step size is the maximum displacement of the value of a parameter in either direction. However, due to the varying orders of magnitude among different kinetic parameters, the default step-taking method was adapted. For each

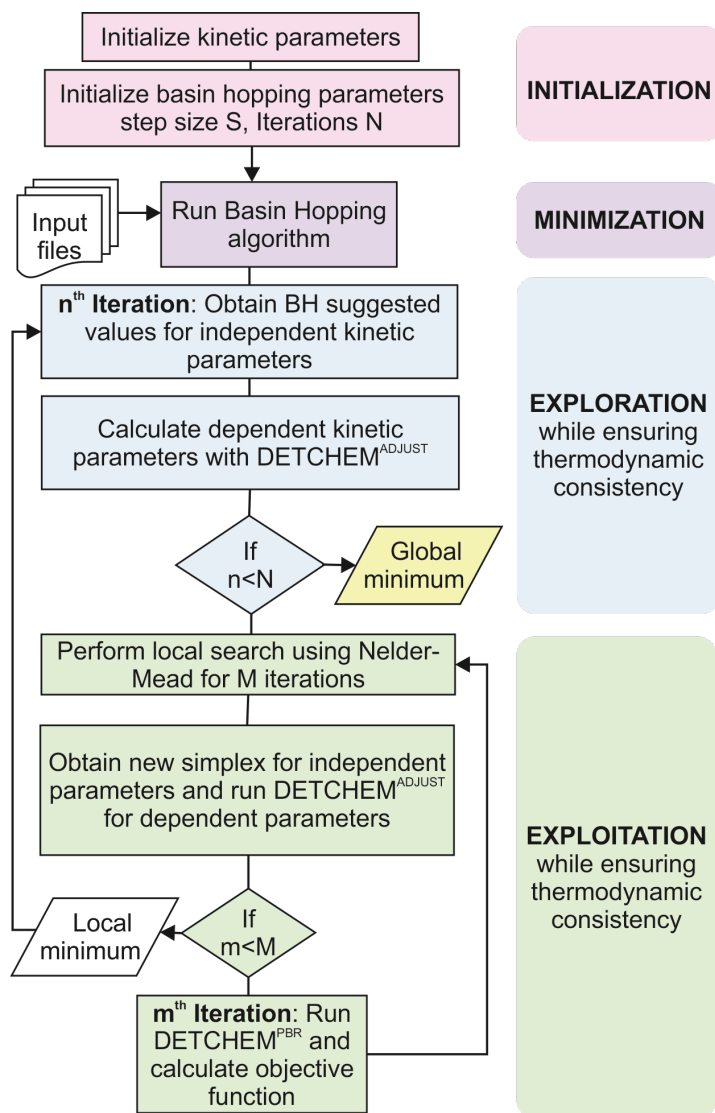


Figure 3.1: Overall optimization workflow. Figure reprinted without changes from [92].

parameter, a random value is drawn from a uniform distribution within the step size range ensuring equal probability for increases and decreases. This value then determines the magnitude and direction of the update. The hops are made proportionally to their current values, resulting in relative adjustments that scale with magnitude. For pre-exponential factors, updates are applied in logarithmic space. Additionally, bounds were imposed for each parameter type to ensure that the optimized parameters are within realistic ranges, for example, the activation energies were restricted to a maximum absolute change of 30 kJ mol^{-1} . Inclusion of such bounds is necessary in addition to defining an appropriate

value of step size because the local search method, Nelder-Mead is an unconstrained method, and it may lead to unrealistic values for some parameters during the local search.

Other crucial user-defined parameters for the optimization procedure are the number of iterations for the global and the local search, i.e., the number of Basin-Hopping iterations and the number of Nelder-Mead iterations, respectively. The number of iterations for the global search determines the number of hops that would be performed during the overall procedure. The local minimization stops when either the changes in the objective function values and parameter values fall below 1×10^{-4} or the number of local search iterations are exceeded.

The overall workflow is illustrated in Fig. 3.1. The user needs to initialize the values for step size, the number of iterations, and prepare the necessary input files. The mechanism file has to be initialized with parameters marked for independent optimization and those marked for thermodynamic adjustment. The user also has the option to specify the type of parameters to be optimized, for example, fitting only the activation energies. The independent parameters are suggested by either Basin-Hopping through random perturbation or through Nelder-Mead method based on the simplex-based search, followed by the calculation of parameters specified by the user for thermodynamic adjustment through DETCHEM^{ADJUST}. Based on the computational resources available, the simulations needed for the objective function calculation are performed in parallel. The script uses the `multiprocessing` library for parallelization. During each iteration, after all parallel simulations needed are executed, the output files are read and the objective function is calculated. For spatially resolved experimental data, interpolation of data is done to obtain the species concentrations at a given axial point. To avoid unnecessary computational effort, an optional early stopping criterion was also implemented for the global search, such that if a better solution is not found after a user-defined number of iterations, then the global search is terminated. If used, this value should be set sufficiently high to minimize the likelihood of prematurely terminating the search and missing a better solution.

The following subsections illustrate the methodology with two applications, where the automated optimization procedure is used to optimize detailed microkinetic models for methanation of carbon monoxide (CO) on a nickel catalyst and for decomposition of ammonia (NH₃) on a cermet material.

3.3 Illustrative Example I: Methanation

Methanation of carbon oxides, first reported by Sabatier and Severens [112] in 1902, is an essential chemical process with diverse applications. It is a key step in the removal of trace amounts of CO from hydrogen feedstocks for use in ammonia production plants [113] and fuel cell applications requiring high purity hydrogen [114]. Beyond purification, there has been increased interest in the production of synthetic natural gas (SNG) through methanation using hydrogen obtained via renewable energy sources [115]. This offers a practical route for renewable energy storage and utilization, since methane is compatible with existing natural gas infrastructure [116].

Methanation of CO, and of CO₂ which may be formed due to water-gas shift reaction, is an exothermic process, hence low temperatures are favored thermodynamically. However, from a kinetic standpoint, at low temperatures the rates are too low for practical application. Therefore, catalytic methanation is performed at temperatures higher than 250 °C, typically in fixed bed reactors with nickel-based catalysts [117]. Although Ni-based catalysts are prone to coke deposition and formation of hotspots within the reactor due to high exothermicity of the reaction, for industrial applications, they are useful due to their low cost, high activity and selectivity towards CH₄ [117, 118]. Hence, when designing reactors for practical applications, it is essential to model the reaction kinetics accurately under a wide range of conditions.

To that extent, Schmider et al. [119] recently developed a microkinetic model for CO and CO₂ methanation over Ni. The model consists of 42 elementary steps with 5 gas-phase and 14 surface species, considering several reaction pathways for conversion of CO and CO₂ into CH₄ and H₂O. The model parameters are thermodynamically consistent and

are validated with a variety of experimental data under diverse conditions for various supported nickel catalysts. For methanation of CO, two main pathways are defined in the model, namely the carbide pathway and the hydrogen-assisted CO dissociation pathway. The carbide pathway involves direct dissociation of the adsorbed CO species into surface carbide species, which are subsequently hydrogenated to form methane on the surface. The hydrogen-assisted pathway involves the formation of a formyl intermediate which then dissociates to form the surface carbide species. Since the microkinetic model by Schmider et al. [119] is a general reaction mechanism for Ni-based catalysts, small adjustments to kinetic parameters to improve accuracy are necessary to consider the effect of supports [120].

3.3.1 Optimization of Methanation Model

The microkinetic model for methanation of CO and CO₂ over Ni [119] consists of 42 elementary steps with additional coverage dependent activation energies defined for steps involving adsorbed CO and adsorbed carbide (C(s)) species, leading to a total of 128 kinetic parameters available for fitting. Out of the 42 reactions, 8 were chosen to be dependent reactions with the help of the DETCHEM^{ADJUST} tool. Basin-Hopping was used to algorithmically optimize 104 parameters independently including the coverage dependent parameters, and the rest of the parameters were deterministically calculated using DETCHEM^{ADJUST} for ensuring thermodynamic consistency.

The experimental data for the calculation of objective function was taken from the literature [121] corresponding to a feed mixture containing a 3:1:1 molar ratio of CO, H₂ and N₂, with a gas hourly space velocity (GHSV) of 30 000 mL g⁻¹ h⁻¹ between 450–900 K, in a packed bed reactor with an average particle size of 630 µm in the catalytic bed, containing 0.5 g of 20 % Ni/Al₂O₃ catalyst. The step size for the Basin-Hopping hops was kept as 0.1, meaning a maximum of 10 % change was allowed in the parameter values at each hop. The number of Basin-Hopping iterations and Nelder-Mead iterations were specified as 25 and 50, respectively. The number of iterations for early stopping of the global search was set to be 6. The objective function was calculated using Eq. 3.1 with 9 experimental data

points of end-of-pipe CO conversion at various temperatures. The overall optimization procedure of the microkinetic model took approximately 52.5 min to complete.

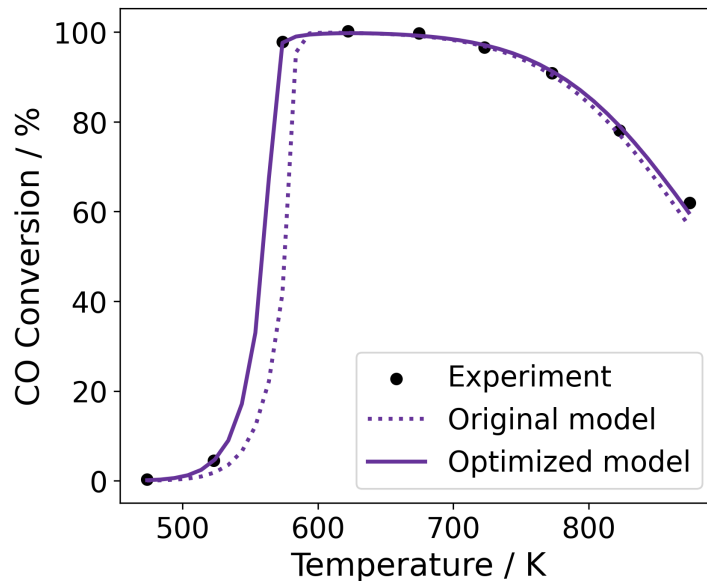


Figure 3.2: Experimental data for CO methanation ($\text{CO:H}_2=3:1$) over 20 % Ni/ Al_2O_3 [121] compared with simulated data using the original kinetic parameters from Schmider et al. [119] and using the optimized parameters through Basin-Hopping. Figure redrawn from [92].

As illustrated in Fig. 3.2, the simulated conversion of CO with the original kinetic parameters from Schmider et al. [119] closely follow the experimental data, except at 573 K where the experimental data shows a conversion of 97.8 %, while the simulated conversion is only 41.7 %. However, after the optimization of the parameters to reflect the activity of Ni supported over Al_2O_3 catalyst, a much better fit was obtained with the experimental data at all conditions. The optimized model is able to reproduce the steep increase in activity at temperatures between 520–600 K and the loss in activity due to thermodynamic limitations at temperatures higher than 700 K.

Fig. 3.3 showcases how the objective function value progresses during the optimization procedure. The dashed vertical lines represent the hopping point, characterized by a sudden change in the objective function value. The points marked with a red star represent the value of the objective function at each of the local minima points during the Nelder-Mead search. As depicted in Fig. 3.3, the search ran for 8 Basin-Hopping iterations, after which the search was terminated due to 6 consecutive unsuccessful iterations, where

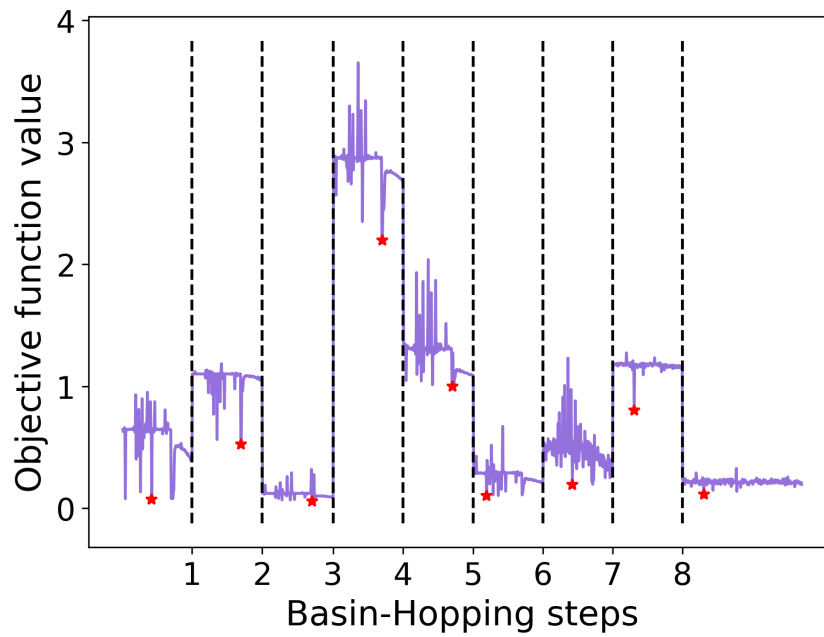


Figure 3.3: Change in the objective function value during the parameter search. Local minima points depicted with red star markers. Figure redrawn from [92].

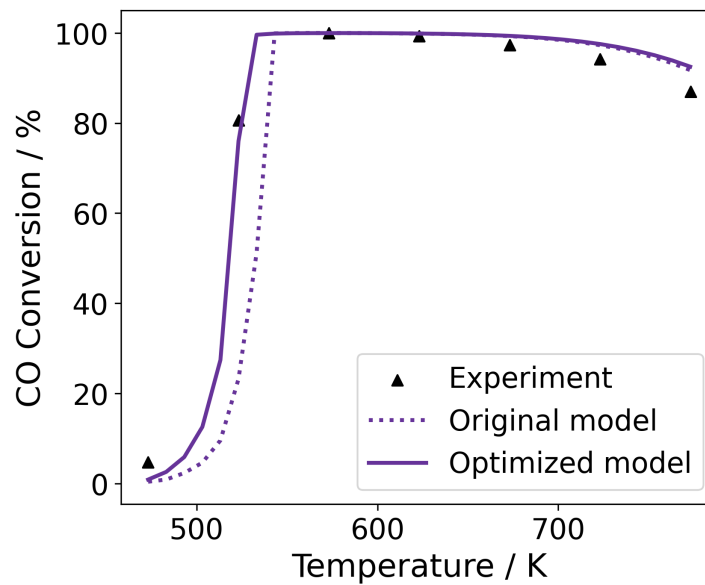


Figure 3.4: Validation of the optimized mechanism parameters using experimental data from Rahmani et al. [122]. Experimental conditions: $\text{CO}:\text{H}_2=1:3$ over 20 % $\text{Ni}/\text{Al}_2\text{O}_3$. Figure redrawn from [92].

no new global minimum was found. The initial value of the objective function calculated using Eq.,3.1 was 0.646, based on the conversions predicted by the model using the original kinetic parameter values. During the first Nelder-Mead search, a local minimum with an objective function value of 0.074 was observed. A lower value of 0.058 was later identified after the second hop, representing the global minimum within the explored parameter space. Consequently, the kinetic parameter values corresponding to this minimum was considered to be the best fit for the experimental data [121].

As described in Section 3.2.2, to ensure that the model parameters were not overfitted to the experimental data used during the optimization process, another set of experimental data was used to validate the model parameters. The validation experimental data was taken from the study of Rahmani et al. for CO methanation on 20 % Ni/Al₂O₃ in a packed bed reactor [122]. The reaction feed mixture consists of CO and H₂ in 1:3 molar ratio with a GHSV of 9000 mL g⁻¹ h⁻¹. Fig. 3.4 shows the comparison between the experimental and simulated data using the original and optimized model parameters. The model with the optimized parameters performs well on the validation data and is able to reproduce the performance of the Ni/Al₂O₃ catalyst at the given operating conditions better than the original model. However, both the models overpredict the performance slightly at higher temperatures. Since certain values related to the experimental setup had to be assumed such as the dispersion of the catalyst, this could have led to the overestimation of the activity. It is also possible that since the study [122] does not mention dilution of the catalytic bed or the feed mixture, hotspots may have formed in the catalytic bed, resulting in reduction of the catalytic performance at higher operating temperatures.

3.3.2 Convergence Study

Basin-Hopping being a stochastic optimization method, allows escape from local minima and explore regions where a potential global minimum may exist. However, its stochastic nature also implies that convergence to a true global solution cannot be guaranteed. To increase the probability of reaching a global solution, the number of iterations for the global search need to be high enough. In the earlier section, the optimization results have

been shown when the number of Basin-Hopping iterations were set as 25 with an early stopping criterion. This was done to minimize the computational effort needed for the optimization procedure. Although the execution of the multiple simulations needed for the objective function calculation is parallelized in the script, the search iterations have to be executed sequentially, hence a high number of iterations may lead to significant computational time without much gain in accuracy. Therefore, to assess this trade-off between the computational cost and solution accuracy, a convergence study with an increased number of iteration was performed. The results of the convergence study are summarized in Table 3.1.

Table 3.1: Summary of various runs of the Basin-Hopping algorithm for optimization of kinetic parameters for methanation reaction over Ni.

Algorithm parameters	Successful hops	Hop after which best solution is obtained	Best objective function value
25 hops, step size 0.1, Nelder-Mead iterations 50	8 (based on the early-stopping criterion)	2	0.058
300 hops, step size 0.1, Nelder-Mead iterations 50	267 (due to solver errors at higher iterations)	58	0.055
300 hops, step size 0.1, Nelder-Mead iterations 50	300	95	0.062

The results demonstrate that with high number of Basin-Hopping iterations, as the algorithm moves away from the initial guess, the simulations with the new kinetic parameters may encounter solver errors in regions of stiffness, preventing successful evaluation of the objective function. Due to the inherent stochasticity, multiple runs do not lead to the same solution. However, the results indicate the best solutions are reached much earlier, making large number of hops unnecessary. The best solution was reached after 58 hops with an objective function value of 0.055, corresponding to only about a 5 % gain in accuracy. This suggests that in applications where the kinetic parameters need to be optimized to only incorporate the effects of small changes to the catalytic system, a relatively small

number of Basin-Hopping iterations is sufficient to obtain parameters sets that provide reasonable fits to the experimental data.

3.3.3 Mechanism Parameter Comparison after Optimization

The optimized parameters for the microkinetic model for Ni/Al₂O₃ are given in Table 3.2 tabulating the Arrhenius parameters for each elementary step. For the adsorption reactions, the corresponding values of sticking coefficients are given, which are dimensionless, while for the rest of the steps the pre-exponential factors are given in units that depend on the order of the reaction. Specifically, for bimolecular reactions, the unit of pre-exponential factor has units of cm² mol⁻¹ s⁻¹, while for unimolecular reaction steps it is expressed in s⁻¹.

Fig. 3.5 compares the parameter values after optimization with the original values reported by Schmider et al. [119]. The comparison shows that the order of the pre-exponential factors remains the same, with relatively larger modifications in the temperature-dependency parameter β and the activation energies. The algorithmic optimization of the independent parameters result in absolute changes in the range of 0.1 to 12 % compared to the original values. The parameters modified by the DETCHEM^{ADJUST} tool showed relatively larger changes, highlighting the need to consider less significant reactions for thermodynamic adjustment.

It is also notable that although the initial deviation between the experimental and simulated data was relatively small and significant only in a small range of temperature, all the parameters needed to be altered to get the best fit. This strongly highlights the complex relationship between the parameters associated with various competing pathways and the catalytic performance under various conditions. Such complexities cannot be realized by using a manual fine-tuning approach, and therefore underscores the need of using algorithmic approaches. This example has demonstrated clearly the use of Basin-Hopping in accelerating the kinetic model development process and the overall workflow that addresses the challenges associated with tuning high-dimensional microkinetic models.

Table 3.2: Optimized kinetic parameters for CO methanation over Ni/Al₂O₃.

Reaction	Independently modified	Optimized parameters		
		s^0 or A ([cm,mol,s])	E_a (kJ mol ⁻¹)	β
H ₂ + 2(s) → 2H(s)	yes	1.22 × 10 ⁻²	0	0
2H(s) → H ₂ + 2(s)	yes	5.05 × 10 ²¹	101.6	-0.149
CH ₄ + (s) → CH ₄ (s)	yes	0.039	0	0
CH ₄ (s) → CH ₄ + (s)	yes	2.76 × 10 ¹⁵	39.6	0.085
H ₂ O + (s) → H ₂ O(s)	yes	0.116	0	0
H ₂ O(s) → H ₂ O + (s)	yes	1.75 × 10 ¹²	63.0	-0.029
CO ₂ + (s) → CO ₂ (s)	yes	5.97 × 10 ⁻⁵	0	0
CO ₂ (s) → CO ₂ + (s)	yes	4.99 × 10 ⁷	28.0	0.021
CO + (s) → CO(s)	yes	0.381	0	0
CO(s) → CO + (s) [‡]	yes	1.05 × 10 ¹²	111.9	-0.114
CO ₂ (s) + (s) → CO(s) + O(s)	yes	1.55 × 10 ²³	79.0	-0.947
CO(s) + O(s) → CO ₂ (s) + (s) [‡]	yes	5.99 × 10 ¹⁹	127.4	0
CO(s) + (s) → C(s) + O(s) [‡]	yes	2.67 × 10 ¹⁴	113.4	0
C(s) + O(s) → CO(s) + (s) [§]	yes	2.60 × 10 ¹⁸	150.3	0
CO(s) + H(s) → C(s) + OH(s) [‡]	yes	2.66 × 10 ¹⁸	111.9	-0.228
C(s) + OH(s) → CO(s) + H(s) [§]	yes	2.18 × 10 ¹⁸	63.0	0.143
CO(s) + H(s) → HCO(s) + (s)	yes	6.50 × 10 ²¹	135.0	-0.911
HCO(s) + (s) → CO(s) + H(s) [‡]	yes	2.19 × 10 ²⁰	0.16	-0.022
HCO(s) + (s) → CH(s) + O(s)	yes	5.84 × 10 ¹⁵	72.5	0.026
CH(s) + O(s) → HCO(s) + (s)	yes	3.54 × 10 ¹⁹	117.7	-0.022
C(s) + H(s) → CH(s) + (s) [§]	yes	1.50 × 10 ²⁴	154.6	-0.437
CH(s) + (s) → C(s) + H(s)	no	3.15 × 10 ²²	28.1	0.403
CH(s) + H(s) → CH ₂ (s) + (s)	yes	3.17 × 10 ²⁵	90.0	-0.09
CH ₂ (s) + (s) → CH(s) + H(s)	yes	6.14 × 10 ²⁴	83.8	0.087
CH ₂ (s) + H(s) → CH ₃ (s) + (s)	yes	8.62 × 10 ²²	55.6	-0.051
CH ₃ (s) + (s) → CH ₂ (s) + H(s)	yes	5.84 × 10 ²⁴	99.1	0.046
CH ₃ (s) + H(s) → CH ₄ (s) + (s)	yes	3.78 × 10 ²¹	70.5	-0.049
CH ₄ (s) + (s) → CH ₃ (s) + H(s)	no	3.79 × 10 ¹⁷	57.4	1.333
H(s) + O(s) → OH(s) + (s)	yes	1.02 × 10 ²⁴	102.0	-0.187
OH(s) + (s) → H(s) + O(s)	no	8.55 × 10 ¹⁹	16.3	0.184
H(s) + OH(s) → H ₂ O(s) + (s)	yes	2.58 × 10 ²⁰	45.0	0.074
H ₂ O(s) + (s) → H(s) + OH(s)	no	1.91 × 10 ²¹	83.1	-0.11
2OH(s) → H ₂ O(s) + O(s)	yes	1.13 × 10 ²⁰	84.5	0.241
H ₂ O(s) + O(s) → 2OH(s)	no	9.95 × 10 ²⁴	208.4	-0.314
H(s) + CO ₂ (s) → COOH(s) + (s)	yes	1.32 × 10 ²⁵	110.1	-0.387
COOH(s) + (s) → H(s) + CO ₂ (s)	yes	1.29 × 10 ²⁰	34.4	0.499
COOH(s) + (s) → CO(s) + OH(s)	yes	6.70 × 10 ²³	50.0	-0.209
CO(s) + OH(s) → COOH(s) + (s) [‡]	no	2.23 × 10 ²¹	88.3	0.223
COOH(s) + H(s) → HCO(s) + OH(s)	yes	4.01 × 10 ²³	107.4	-1.256
HCO(s) + OH(s) → COOH(s) + H(s)	no	4.50 × 10 ¹⁹	10.9	0.065
2CO(s) → CO ₂ (s) + C(s) [‡]	yes	6.78 × 10 ¹³	262.9	0.523
CO ₂ (s) + C(s) → 2CO(s) [§]	no	1.70 × 10 ²¹	251.4	-0.424

Note: (s) represents an empty surface site. ‡ represents coverage dependency of 51.9 kJ mol⁻¹ on CO(s) and § represents coverage dependency of 98.7 kJ mol⁻¹ on C(s).

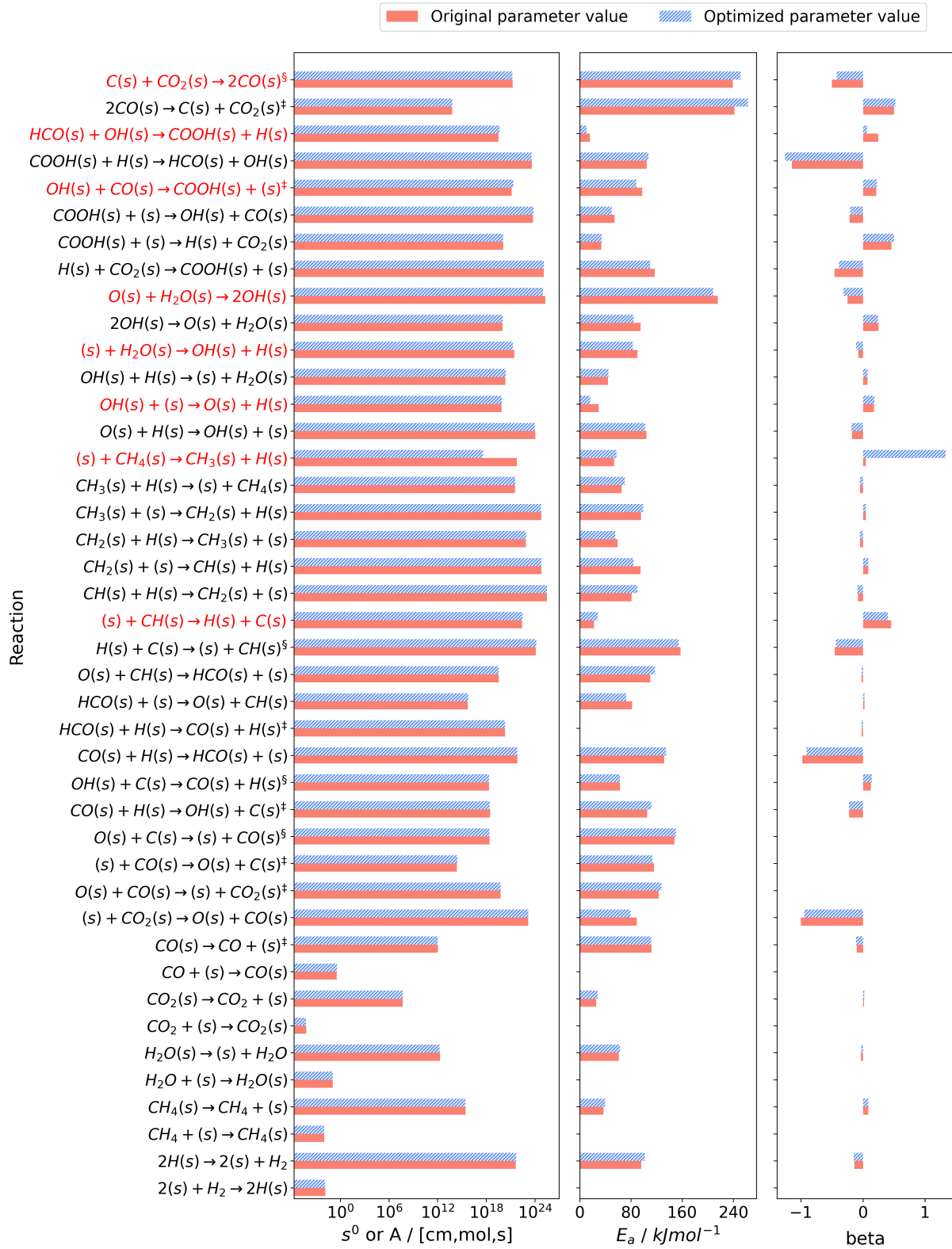


Figure 3.5: Comparison between the original and optimized parameters for the microkinetic model for Ni/Al₂O₃. Reactions in red were modified by DETCHEM^{ADJUST} to ensure thermodynamic consistency. Figure redrawn from the supporting information of [92].

3.4 Illustrative Example II: Ammonia Decomposition

This section presents another illustrative example demonstrating the use of the optimization script in the development of a kinetic model for ammonia decomposition over a bimetallic catalytic system. In addition to being one of the most important industrial chemicals, ammonia (NH_3) is gaining increased interest in the energy sector due to its potential to be used as a clean fuel and energy carrier [123]. Ammonia offers several advantages as a hydrogen carrier, including a high volumetric hydrogen density, ease of liquefaction, and safe transportability due to its low vapor pressure and high boiling point [124]. Hence, efficient NH_3 decomposition is necessary for its practical application as a hydrogen carrier.

Protonic ceramic cells (PCC) are promising energy conversion systems that function reversibly as fuel cells and electrolysis cells, and exhibit great performance at low operating temperatures (450–650 °C) [125]. In direct ammonia-fed protonic ceramic cells (NH_3 -PCC), NH_3 can be fed directly at the anode to obtain hydrogen as fuel [126, 127]. PCCs typically use a composite material made of ceramic and a sintered metal known as a cermet as their fuel electrode, to improve the thermal durability and conductivity. Nickel-based cermet materials such as $\text{Ni-BaCe}_{0.8}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (Ni-BCZY) are commonly used as anodes in PCCs, where Ni provides active sites for the electrochemical reactions, while BCZY facilitates proton conduction and stability of the cell [128]. In NH_3 -PCCs, the metallic Ni also acts as a catalyst for decomposition of NH_3 into H_2 and N_2 [126].

To ensure optimal fuel utilization and power output, and minimize catalyst poisoning due to unreacted NH_3 , efficient ammonia decomposition at the anode is a pre-requisite [126]. Ruthenium (Ru) exhibits superior catalytic activity for ammonia decomposition compared to nickel, and is a suitable candidate for improving the efficiency of the decomposition reaction [129, 130]. Furthermore, the use of barium (Ba) as a promoter for ammonia synthesis is established [131]. Hence, experimental measurements [56] obtained with several catalytic samples containing various compositions of Ba and Ru supported on a Ni-BCZY cermet in a packed bed reactor were used to study the effect of addition of Ru on the catalytic performance of the cermet (Ni-BCZY) for PCC application [57]. In this work,

the experimental data corresponding to the sample with the following composition was used: 0.5 wt.-% of Ru, 1 wt.-% of Ba, and the Ni-BCZY cermet contained 60 wt.-% of NiO before reduction of the cermet [56, 57].

3.4.1 Ammonia Decomposition Kinetic Model

Cermet-based catalyst samples differ from conventional supported metal catalysts in that the metallic phase in a cermet is integrated throughout the bulk of the material, whereas in supported metal catalysts the active metal is present as discrete nanoparticles dispersed on the support surface. Therefore, a catalyst sample prepared by wet-impregnation of Ru on a powdered Ni-BCZY cermet has dispersed ruthenium nanoparticles as active sites for ammonia decomposition, in addition to the catalytically active surface from the exposed nickel on the surface of the Ni-BCZY cermet powder. Hence, in order to model the activity of such a catalyst two surfaces need to be considered with each surface having a distinct value for the available catalytic area, which needs to be estimated through appropriate characterization techniques. The role of Ba is limited as a promoter and does not provide additional active sites for the decomposition reaction [131].

The microkinetic model for NH_3 synthesis using gaseous N_2 and H_2 over ruthenium was first reported by Hinrichsen et al. [132], containing 6 reversible surface reactions, which are also applicable for NH_3 decomposition due to the principle of thermodynamic reversibility, and have been widely accepted as the reaction mechanism for synthesis/decomposition of ammonia [133–137]. The reaction steps include dissociative adsorption/desorption of gaseous N_2 and H_2 , sequential dehydrogenation reactions, and adsorption/desorption of NH_3 on the metal surface site [132]. The initial kinetic parameters for the Ru surface were taken from the study of Zhang et al. [131] where, the impact of alkaline earth metals such as Ba on the activity of Ru supported on yttria-stabilized zirconia (YSZ) ceramic was investigated, for synthesis of ammonia. The kinetic model from Zhang et al. [131] has additional coverage dependencies defined for adsorbed nitrogen and hydrogen species. For the nickel surface, the initial model parameters were taken from the model proposed by Zhu et al. [138], where the kinetic parameters were obtained by tuning the parameters

with experimental data for a Ni/BaZrO₃ catalyst. In order to simulate the behavior of the Ba-promoted Ru/Ni-BCZY sample, the elementary steps for both surfaces were used with the initial parameter values.

3.4.2 Optimization Strategy for Bimetallic Catalysts

The catalytic performance of the Ba-promoted Ru/Ni-BCZY was simulated in a packed bed reactor through the kinetic model described above considering both metal surfaces using the DETCHEM^{PBR} code. The available active area was incorporated in the simulations through Eq. 2.18. Since the amount of metals in the catalyst sample differed significantly, the active area for individual metals needed to be characterized properly. The active area for Ru in the bimetallic sample was calculated using Eq. 2.19 from the nanoparticle diameter which was estimated to be approximately 4.78 nm through Energy-Dispersive X-ray spectroscopy (EDX) [57]. For nickel surface, the dispersion of the metal was estimated to be 13 % through H₂ temperature-programmed desorption (H₂-TPD) by characterizing only the cermet powder without Ru [57]. The sample characterization and testing were not within the scope of this thesis and details of the methods may be found here [57].

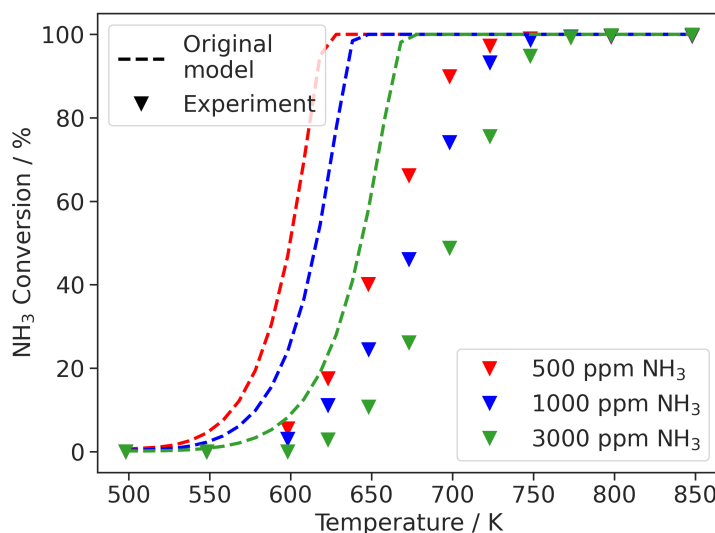


Figure 3.6: Simulated catalyst performance with the initial model parameters for the bimetallic catalyst Ba/0.5Ru/Ni-BCZY [56, 131, 138]. Figure redrawn from the supporting information of [57].

Fig. 3.6 compares the simulated data using the original kinetic parameters [131, 138] with the experimental data at various concentrations of ammonia in the feed. The results show that the model overpredicts NH_3 conversion for all feed concentrations, indicating the need for optimization of the kinetic parameters. This outcome is expected as the original parameters were obtained for different catalyst systems which may not reflect the activity of ruthenium dispersed on the cermet.

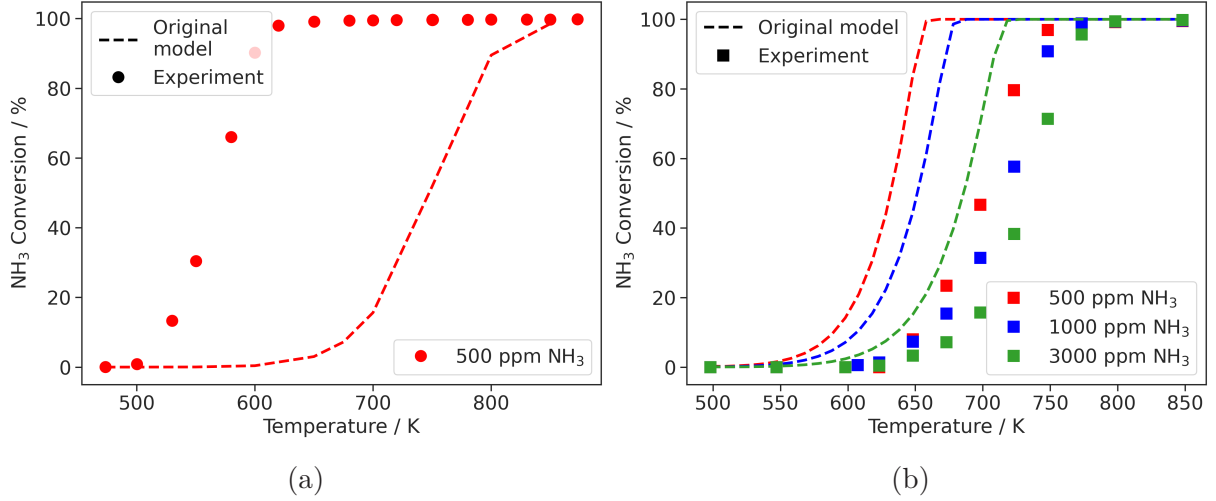


Figure 3.7: Comparison of the experimental conversions [56] with simulated conversion using original parameters with various concentration of NH_3 at the inlet in a packed bed reactor with sample (a) containing only Ba-promoted Ru supported on YSZ [131] (b) containing only the Ni-BCZY cermet powder [138]. Figure (b) adapted from [57].

To determine whether the kinetic parameters associated with Ru or Ni surface should be adjusted, simulations were first performed with catalytic samples containing only Ru and only Ni. Fig. 3.7a shows the experimental and simulated catalytic performance of Ba-promoted Ru supported on YSZ, and Fig. 3.7b compares the same for a sample containing only Ni-BCZY powder. While Fig. 3.7a shows that the kinetic model [131] significantly underpredicts the conversion of NH_3 on the ruthenium surface, Fig. 3.7b shows overprediction of activity on the nickel surface using the kinetic model [138].

Since Fig. 3.7 showed deviations with kinetic models for both the surfaces, this implied that model parameters for both surfaces need to be tuned to reflect the activity of the bimetallic catalyst sample. Moreover, it is possible that the activity of Ru may also be affected by the use of Ni-BCZY support. Hence, first the model parameters for the

nickel surface were optimized using the experimental data corresponding to feed containing 1000 ppm of NH_3 . The experimental data corresponding to 500 ppm and 3000 ppm of NH_3 were used for validation of the optimized parameters. The step size for the Basin-Hopping hops was kept as 0.05, the number of hops as 25 with 200 Nelder-Mead iterations during the local search. The objective function was calculated using Eq. 3.1. The desorption of NH_3 from the Ni surface was found to be kinetically less significant during the preliminary sensitivity analysis and was therefore considered to be the dependent step for thermodynamic adjustment through DETCHEM^{ADJUST} tool. The parameters associated with the remaining 11 reactions were allowed to be algorithmically modified. The results with the optimized model are presented in Fig. 3.8a, which shows a better match with the experimental data. The model underpredicts the activity at 3000 ppm of NH_3 in the feed which could be the result of underestimation of the active surface area of the catalyst sample. The optimization script required around 2.3 h for the fitting process and ran 80 604 simulations with DETCHEM^{PBR} during the routine.

Once the kinetic parameters reflecting the activity of the Ni surface present in the cermet powder were obtained through the optimization routine described above, the parameters for the Ru surface in the bimetallic model were optimized while the nickel surface param-

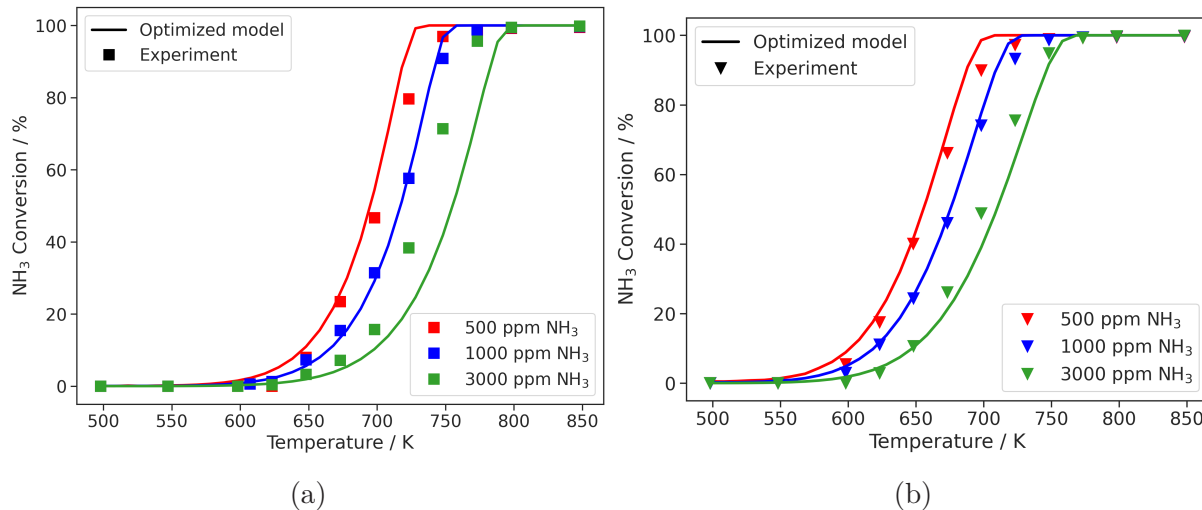


Figure 3.8: Comparison of the experimental conversions with simulated conversion using optimized kinetic parameters at various feed concentration of NH_3 for sample (a) containing only Ni-BCZY cermet powder (b) with Ba-promoted Ru on Ni-BCZY cermet powder. Figure redrawn from [57].

Table 3.3: Optimized kinetic parameters for NH₃ decomposition of ammonia on a Ba-promoted Ru supported on Ni-BCZY cermet.

Reaction	Independently modified	Optimized parameters		
		s^0 or A ([cm,mol,s])	E_a (kJ mol ⁻¹)	beta
NH ₃ + Ni → NH ₃ -Ni	yes	1.82×10^{-5}	0.02	-0.097
NH ₃ -Ni → NH ₃ + Ni	no	9.89×10^{12}	50.35	-0.825
NH ₃ -Ni + Ni → NH ₂ -Ni + H-Ni	yes	1.84×10^{20}	66.09	0.198
NH ₂ -Ni + H-Ni → NH ₃ -Ni + Ni	yes	5.26×10^{19}	26.08	-0.201
NH ₂ -Ni + Ni → NH-Ni + H-Ni	yes	5.70×10^{19}	12.21	0.174
NH-Ni + H-Ni → NH ₂ -Ni + Ni	yes	9.22×10^{19}	78.27	-0.155
NH-Ni + Ni → N-Ni + H-Ni	yes	6.11×10^{19}	28.83	0.141
N-Ni + H-Ni → NH-Ni + Ni	yes	6.28×10^{20}	103.55	0.169
2N-Ni → N ₂ + 2Ni	yes	1.83×10^{16}	129.43	-0.136
N ₂ + 2Ni → 2N-Ni	yes	1.43×10^{-6}	53.95	0.0
2H-Ni → H ₂ + 2Ni	yes	5.92×10^{20}	103.94	-0.11
H ₂ + 2Ni → 2H-Ni	yes	1.87×10^{-3}	0.0	0.0
NH ₃ + Ru → NH ₃ -Ru	yes	1.15×10^{-5}	0.0	0.0
NH ₃ -Ru → NH ₃ + Ru	yes	2.51×10^{11}	72.45	0.087
NH ₃ -Ru + Ru → NH ₂ -Ru + H-Ru	yes	1.36×10^{20}	$76.90 + 0.83\theta_{\text{H-Ru}}$	0.0
NH ₂ -Ru + H-Ru → NH ₃ -Ru + Ru	yes	3.58×10^{19}	16.10	0.081
NH ₂ -Ru + Ru → NH-Ru + H-Ru	yes	8.91×10^{19}	$15.65 + 0.83\theta_{\text{H-Ru}}$	-0.085
NH-Ru + H-Ru → NH ₂ -Ru + Ru	yes	5.25×10^{19}	84.93	0.1
NH-Ru + Ru → N-Ru + H-Ru	yes	6.31×10^{19}	$33.44 + 0.83\theta_{\text{H-Ru}}$	0.216
N-Ru + H-Ru → NH-Ru + Ru	no	2.02×10^{22}	$101.6 - 9.02\theta_{\text{N-Ru}}$	-0.38
2N-Ru → N ₂ + 2Ru	yes	2.08×10^{17}	$143.70 - 18.03\theta_{\text{N-Ru}}$	-0.297
N ₂ + 2Ru → 2N-Ru	yes	3.01×10^{-6}	35.87	0.0
2H-Ru → H ₂ + 2Ru	yes	3.75×10^{20}	$91.82 - 1.67\theta_{\text{H-Ru}}$	0.734
H ₂ + 2Ru → 2H-Ru	yes	3.91×10^{-3}	0.0	0.0

ters were kept fixed, in order to only optimize the activity of ruthenium when supported on the Ni-based cermet. The protocol followed for the optimization routine was same as that described above for the Ni surface. Only the Ru surface reaction parameters including the coverage-dependent parameters were optimized using the experimental data corresponding to 1000 ppm NH₃ in the feed. The reverse reaction of the last dehydrogenation step (i.e., N-Ru + H-Ru → NH-Ru + Ru) was considered to be the dependent reaction, and the parameters for this step were calculated deterministically by DETCHEM^{ADJUST}. The earlier optimized parameters associated with the Ni surface, reflecting the activity of the cermet were kept constant throughout. As the Fig. 3.8b shows, after optimization of the Ru related steps, the overall bimetallic kinetic model is able to accurately simulate the catalytic performance of the bimetallic sample at all conditions. During this process, the script executed 124,308 simulations and required approximately 3 h to complete. The optimized parameters are presented in Table 3.3 for both the surfaces.

3.5 Limitations

The methodology presented here performs reasonably well in refining detailed microkinetic model parameters. However, it has several important limitations. First and foremost is the need for a good initial guess for the mechanism, meaning that the initial microkinetic model must include all relevant reaction pathways for the catalytic system and any changes in the catalyst for which the optimization is performed do not alter the underlying mechanism. The examples showcased in this thesis adhere to these assumptions.

Additionally, it must be recognized that the fitting process may mask the influence of other effects, such as mass-transfer limitations or catalyst deactivation. Therefore, these effects should be carefully considered when performing simulations during the optimization process. Furthermore, it is imperative to use high-quality experimental data with minimal noise, and the assessment of the model–experiment fit should account for inherent measurement uncertainties to avoid overfitting. It is the responsibility of the user to provide a sufficient number of experimental points for the optimization to ensure that the optimized mechanism is reliable and valid for a wide range of conditions.

Furthermore, to maintain thermodynamic consistency, very large changes in the dependent reaction parameters may be necessary, hence a sensitivity analysis should be conducted to identify kinetically insignificant reactions which may be designated as dependent. However, a key limitation of this approach is that linear dependencies among the already-selected dependent reactions can restrict which reactions may be treated as independent, thereby reducing the flexibility of the optimization process. Additionally in this work, the presented examples are focused solely on accurately predicting the conversion trends of the reactants, for which the temperature-dependent behavior was monotonic. The feasibility of the approach when multiple species must be simultaneously optimized with non-monotonic trends remains to be evaluated.

3.6 Conclusions and Summary

This chapter described the development and implementation of the optimization workflow with the DETCHEM simulation model to optimize kinetic parameters in detailed microkinetic models. The inherent challenges associated with optimizing large kinetic models were discussed and the necessity of gradient-free algorithmic optimization was highlighted via two illustrative examples.

To address the complexity and manual effort typically involved in dealing with large microkinetic models, a Python-based automation script was employed. The script accelerates the process by generating the necessary simulation input files for DETCHEM, executing the multiple simulations in parallel, and postprocessing the output data to compare simulated results with the experimental observations across various operating conditions. Moreover, the overall workflow followed ensures thermodynamic consistency throughout the optimization process, requiring minimal input from the end-user. The global optimization algorithm Basin-Hopping was chosen for refining the kinetic parameters as the method is gradient-free and suitable for high-dimensional applications. To complement this, the Nelder-Mead method, another gradient-free optimization method was employed as the local search method within the Basin-Hopping framework.

The first application highlighted the use of the algorithm for fine-tuning a large microkinetic model originally developed as a general mechanism for CO/CO₂ methanation on Ni-based catalysts, comprising of various competitive pathways for Ni/Al₂O₃. The optimization explored the high-dimensional search space comprising 128 kinetic parameters, where all the independent parameters were algorithmically modified and the remaining dependent parameters were deterministically calculated to ensure thermodynamic consistency. Despite the large dimensionality of the methanation model, the optimization process required less than an hour to complete, due to fast simulation times and parallel execution. Furthermore, a convergence study involving a high number of Basin-Hopping iterations revealed that, for such applications where the refinement is necessary to incorporate only minor changes to the catalyst (here, the use of inert support), the computational cost of an extensive exploration of the search space does not yield a proportional gain

in accuracy. This highlighted the importance of balancing optimization complexity with practical efficiency.

The second application showcased the use of the optimization protocol in developing a kinetic model for decomposition of NH_3 on a Ba-promoted Ru catalyst supported over a Ni-BCZY cermet. Since both Ru and Ni exhibit catalytic activity for ammonia decomposition, the microkinetic model needed elementary steps for both surfaces. However, existing literature models were inadequate for accurately capturing the behavior of the cermet-based bimetallic catalyst. Therefore, the optimization script was first used to refine the kinetic parameters of the nickel surface to accurately simulate the performance of the Ni-BCZY cermet alone. These optimized parameters were then held constant during the subsequent optimization of the bimetallic model, where only the kinetic parameters related to the Ru surface were adjusted to match the performance of the Ba/Ru/Ni-BCZY catalyst. This two-step strategy enabled the use of different sets of experimental data for selectively optimizing subsets of reaction steps. Due to large discrepancies between the initial model predictions and the experimental data, more iterations were needed, resulting in higher computational time compared to the methanation example.

The results with the optimized model parameters in both the applications showed increased accuracy in the simulated data. The automated workflow significantly reduced the time and effort compared to a manual fitting process. It was showcased that since the number of parameters to be tuned are larger than the amount of experimental data, which is typically the case when dealing with large microkinetic models, the use of a separate set of validation data is essential and ensured that the optimized model parameters were generalizable and capable of simulating the catalyst behavior under conditions beyond those used for fitting. Therefore, the overall optimization workflow leveraging Basin-Hopping is a convenient and suitable method for refining existing detailed microkinetic models with new experimental data or assist in developing new microkinetic models for similar catalytic systems.

4 Modeling the Effect of Supports in PdO-Based Methane Oxidation Catalysts¹

This chapter presents the use of the optimization workflow described in Chapter 3 to extend an existing microkinetic model to more accurately model new experimental data for oxidation of methane over palladium-based catalysts. The primary aim of this work was to numerically investigate the effect of using different supports, namely SnO₂ and ZrO₂ with PdO catalyst for methane oxidation under lean conditions, in the presence and absence of water in the reaction mixture. In order to study the behavior of these supported catalysts under these operating conditions, new microkinetic models were required as existing models were unable to accurately predict the experimentally observed behavior of the catalysts. The chapter outlines briefly the methodology followed for the optimization process and discusses how the resulting optimized models were used to understand the underlying mechanism and the various surface species that drive the catalytic performance under various conditions for both the supported catalysts.

¹Parts of this chapter are taken with permission from [139] Chacko, R. et al., “Microkinetic Modeling of Support Effects in PdO-Based Methane Oxidation Catalysts”, ACS Catalysis 2025, 15, 9, 6937-6952, <https://doi.org/10.1021/acs.jpcc.2c08179>, licensed under CC BY-NC-ND 4.0

4.1 Motivation

Methane is a major greenhouse gas and its efficient removal from the exhaust gas of natural gas engines and emissions from chemical and energy production sectors is crucial in mitigating its environmental impact [140–142]. Alumina-supported PdO catalysts remain the premier choice for total oxidation of methane under lean conditions at low temperatures, due to their high activity [143, 144]. However, these catalysts also suffer from rapid decline in activity during long-term operation and pronounced inhibition in the presence of water [145–149]. Several strategies to overcome the inhibition and deactivation behavior have been proposed, including the addition of Pt to Pd-based catalysts [150–152], use of different support materials [153–156], or forced dynamic reactor operation by using short-reducing pulses [157–159].

The inhibition in the presence of water is said to be a result of hydroxyl formation and subsequent blocking of active sites, which leads to a shift in activity towards higher temperatures [149, 160, 161]. The accumulation of hydroxyls is also observed on the support materials [160, 162]. Previous experimental investigations have demonstrated that supports such as zirconia which have higher oxygen mobility, can help in increasing the activity of the palladium catalyst, although the support alone does not have activity for methane activation [161]. Pd supported on SnO₂ has been shown to outperform even Pt-Pd/Al₂O₃ catalyst due to strong metal-support interactions and high oxygen mobility in SnO₂ [163]. Therefore, the use of these support materials presents an opportunity to enhance catalytic activity. However, to fully ascertain the role of these supports, the development and application of kinetic models that are able to reflect their experimental behavior are essential.

Although several global kinetic models have been proposed in the literature [154, 164–167], their limited generalization beyond the specific conditions under which they were developed restricts their use in obtaining a comprehensive understanding of the underlying reaction mechanism. Therefore, microkinetic models offer a better alternative, as they are valid under a broad range of operating conditions and can help in studying the catalyst under various reaction conditions. Moreover, if a microkinetic model exists for a similar

catalytic system, they can be extended to new experimental datasets. However, since microkinetic models have large number of elementary steps and consequently large number of parameters to be estimated, algorithmic procedures are necessary in obtaining these parameters [92], while making sure thermodynamic consistency is not violated [111].

In the context of methane oxidation, Stotz et al. [168] proposed a microkinetic model for PdO catalyst, however, it does not account for the influence of the support material. The choice of different supports affects the PdO particle sizes, which in turn influences its reducibility [169–172]. Given that the reaction proceeds via Mars-van-Krevelen mechanism [145, 169, 173], the effect of the particle size on the activity is crucial, as oxygen is more strongly bonded to smaller particles than larger ones [170]. Therefore, the kinetic model needs to be refined to account for the influence of different supports. In this work, the effect of supports is investigated by obtaining new tailored parameter sets for the supported catalysts PdO/SnO₂ and PdO/ZrO₂, by leveraging Basin-Hopping for optimization of the kinetic parameters as described in the previous chapter.

4.2 Kinetic Model for Methane Oxidation over PdO

The microkinetic model for oxidation of methane used in this work, reported by Stotz et al. [168], was developed based on surface energies derived from DFT [174] for PdO/Al₂O₃. The model is a dual-site mechanism considering two active sites in the (101) facet of PdO namely, the coordinatively unsaturated (cus) Pd_{cus} and O_{cus} sites. In this work, the Pd_{cus} and O_{cus} sites are represented as “a” sites and “b” sites, respectively. The reaction network encompasses 23 surface species, 4 gas-phase species, and 39 reversible reactions. The schematic representation of the reaction mechanism is shown in Fig. 4.1.

The mechanism consists of steps related to the Mars-van-Krevelen [145, 169, 173] redox mechanism for reduction of the lattice oxygen, formation of oxygen vacancies (represented as the surface species, vac–b), and regeneration through incorporation of oxygen in the lattice from gas phase. Gas phase reactions are not considered in the model as they become relevant only at high temperatures. The model primarily aims to simulate the

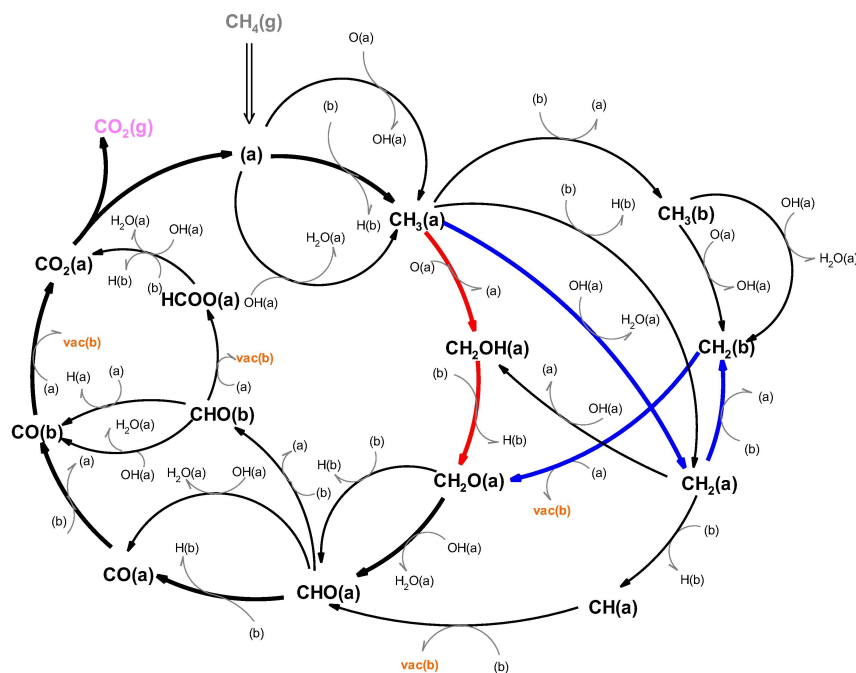


Figure 4.1: Schematic of the methane oxidation mechanism on PdO proposed by Stotz et al. [168]. Reprinted from Journal of Catalysis, 370, H. Stotz, L. Maier, A. Boubnov, A.T. Gremminger, J.-D. Grunwaldt, O. Deutschmann, Surface reaction kinetics of methane oxidation over PdO, 152-175, Copyright (2019), with permission from Elsevier.

inhibitory effect in the presence of water, which is pronounced under lean-burn conditions at low temperatures ($T < 500$ K). The effect of support was not considered as alumina was the only support used in the initial model development by Stotz et al. [168].

4.3 Methodology

The experimental data for oxidation of methane under lean conditions, on PdO catalysts supported over ZrO_2 and SnO_2 , in the presence and absence of water were taken from the study of Keller et al. [149]. The corresponding experimental conditions are briefly described here. The reacting gas mixture consisted of 3200 ppm of CH_4 , 10 vol.% O_2 , 0–12 vol.% of H_2O in balance N_2 . The catalytic light-off tests were performed in a packed bed reactor with a catalytic bed containing 300 mg of the supported PdO catalyst with a metal loading of 2.3 %, and 700 mg of quartz, resulting in a bed length of approximately 1.3 cm. The internal diameter of the reactor was 8 mm. These tests were conducted

under a linear temperature ramp of 3 K min^{-1} starting from 500 to 800 K and a GHSV of $80\,000 \text{ h}^{-1}$.

Due to the variation in supports, the nanoparticle sizes of PdO differed, resulting in distinct values of catalytic surface area for each supported catalyst, which were calculated using Eq. 2.19. The value of the simulation parameter $F_{\text{cat/geo}}$ was obtained through Eq. 4.1, where $\varsigma = 2$ is the (a-b) site-pair conversion factor, as defined by Stotz et al. [168].

$$F_{\text{cat/geo}} = \frac{1}{\varsigma} \frac{A_{\text{cat}}}{A_{\text{geo}}} \quad (4.1)$$

The ZrO_2 supported catalyst exhibited a lower catalytic surface area with a nanoparticle size of $5.1 \pm 1.6 \text{ nm}$ compared to SnO_2 -based catalyst which showed a nanoparticle diameter of $4.1 \pm 1.2 \text{ nm}$. To minimize mass transfer limitations, the particle size in the catalytic bed were kept in the range of $125\text{--}250 \mu\text{m}$. Additionally, the dilution of both the reaction mixture and the catalytic bed helped ensure minimal temperature gradients throughout the reactor.

The kinetic parameters associated with the elementary steps in the microkinetic model [168] were optimized for the experimental data [149] with other supported catalysts using the workflow described in Chapter 3 using Basin-Hopping [90]. The model parameters to be independently optimized by the algorithm were selected based on an initial sensitivity analysis of the kinetic parameters at the temperature corresponding to 10 % conversion (T_{10}) of methane. For PdO/SnO_2 , 60 elementary steps were chosen as independent reactions that were allowed to be algorithmically optimized, the parameters associated with the remaining 18 steps were deterministically calculated by DETCHEM^{ADJUST}, based on thermodynamic consistency as described in Section 3.2.4. Correspondingly for PdO/ZrO_2 , 49 elementary steps were independently modified and the rest were obtained through DETCHEM^{ADJUST}. The step size for the exploration step for both the supports was chosen to be 0.01. The number of iterations for Basin-Hopping was set as 10 and for the local search using the Nelder-Mead method was set to be 20.

For both supported catalysts, only a part of the experimental data corresponding to certain concentrations of water fed at the inlet, were used for the fitting process. For the

optimization of the mechanism for PdO/SnO₂, the experimental data corresponding to 0 vol.% and 1 vol.% H₂O were used for fitting, while for PdO/ZrO₂, 0 vol.% and 12 vol.% H₂O data were used. The rest of the experimental dataset was used only for validation of the optimized mechanism, to ensure the mechanism was not overfitted to the fitting data. Since the original model [168] comprised 78 elementary steps, it involved tuning 234 kinetic parameters, resulting in a large search space. To reduce the computational burden during the optimization process, the objective function through Eq. 3.1 was evaluated only at temperatures corresponding to 10 %, 50 %, and 90 % methane conversion, represented as T₁₀, T₅₀, and T₉₀, respectively.

Packed bed reactor simulations were performed at all experimental conditions for both the supports using the DETCHEM^{PBR} simulation model. The governing equations for the reactor model are provided in Section 2.2.1. The simulated coverages of various surface species along the length of the reactor and the gas phase mole fractions at reactor outlet were obtained as simulation outputs at various temperatures and feed conditions. After an optimized set of parameters for both supports were obtained, a reaction flow analysis using the integrated rates of each reversible reaction was performed at T₁₀, T₅₀, and T₉₀ for both supported catalysts. The methodology for the reaction flow analysis is outlined in Section 2.2.2, where the individual steps were implemented through a Python-based script.

4.4 Results and Discussion

4.4.1 Optimization of Kinetic Parameters for the Supported Catalysts

Fig. 4.2 compares the experimental conversion of methane with the simulated values using the original microkinetic model from Stotz et al. [168], at various concentrations of water fed at the inlet. The results indicate that the original model parameters could not accurately capture the experimental trends on both the supports. The simulations for the

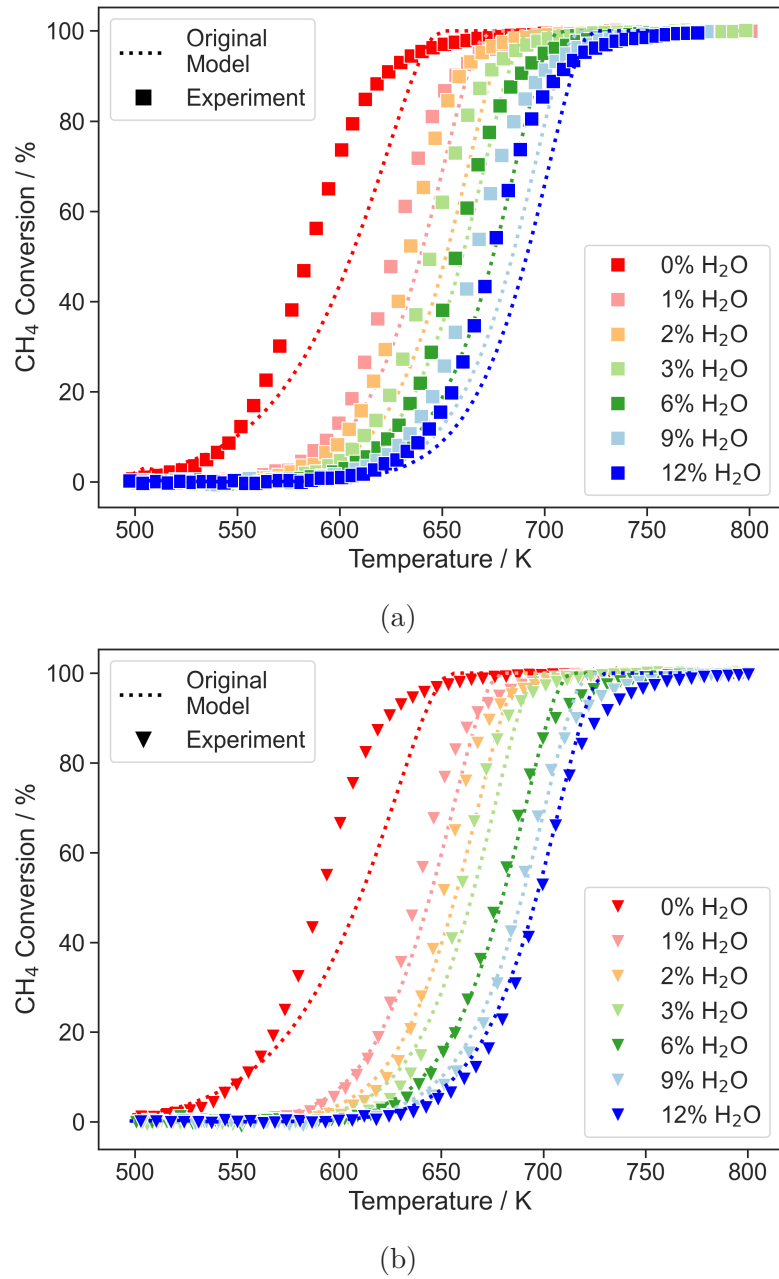


Figure 4.2: Comparison of the experimental conversions with simulated conversions using the original parameters [168] at various concentration of H₂O at the inlet in a packed bed reactor with catalyst sample (a) PdO supported over SnO₂ (b) PdO supported over ZrO₂. Feed conditions: 3200 ppm CH₄, 10 vol.% O₂, 0–12 vol.% H₂O in N₂. Figure adapted from [139].

PdO/SnO₂ catalyst predict lower conversion values at all operating conditions (Fig. 4.2a), while for PdO/ZrO₂ the parameters underpredict the conversion values primarily for the dry feed (Fig. 4.2b). According to literature [161, 163], both SnO₂ and ZrO₂ lack intrinsic activity towards methane activation at low temperatures. PdO supported on SnO₂ ex-

hibits higher catalytic activity and reduced water inhibition, attributed to the reducibility of the support and its ability to remove hydroxyls from Pd surface [175]. Consequently, the kinetic model developed for PdO/Al₂O₃ underestimates the catalytic performance of PdO/SnO₂. Similarly, PdO/ZrO₂ also shows better performance than PdO/Al₂O₃ due to improved metal-support interactions [176]. Additionally, the particle size of PdO on the supported material plays a significant role in catalytic activity. Smaller particles lead to higher dispersion and catalytic surface area, which may enhance conversion, while larger particles may provide more accessible oxygen for oxidation [170]. Initial simulations with the model for PdO/Al₂O₃ (Fig. 4.2) accounted for the effect of varying surface area with variation in supports, through the parameter $F_{\text{cat/geo}}$ (as outlined in Section 2.2.1). Therefore, the deviations between the simulations and the experimental performance suggest that the kinetic model requires further refinement.

Since the support is not directly participating in the conversion of methane by providing more active sites, additional elementary steps are not required. Rather, optimization of just the kinetic parameters for the elementary steps is sufficient to improve the simulated performance, based on the experimental data. Therefore, Basin-Hopping [90] was used to optimize the kinetic parameters for the various elementary steps for both supported catalysts, while maintaining thermodynamic consistency of the entire microkinetic model. During the automated optimization workflow, DETCHEM^{PBR} was executed multiple times to evaluate the objective function. Overall, 13,914 DETCHEM^{PBR} simulations were performed for the optimization of the SnO₂-supported catalyst model parameters, requiring approximately 4.6 h to complete on an AMD Ryzen Threadripper 3990X processor with 64-cores with a boost clock of 4.3 GHz. Correspondingly, for the ZrO₂-supported catalyst, since lesser number of reaction steps were independently optimized, the optimization routine was completed in approximately 2.11 h with a total of 13,326 DETCHEM^{PBR} simulations. Although the global minimum obtained in the 10 hops of Basin-Hopping [90] offered the best fit to the experimental data, the workflow also yielded several local minima. These were carefully analyzed to identify the most physically realistic solution, which is also closest to the original model. Simulations were conducted with these parameters,

as they better represented the underlying system behavior despite not being the best fit statistically.

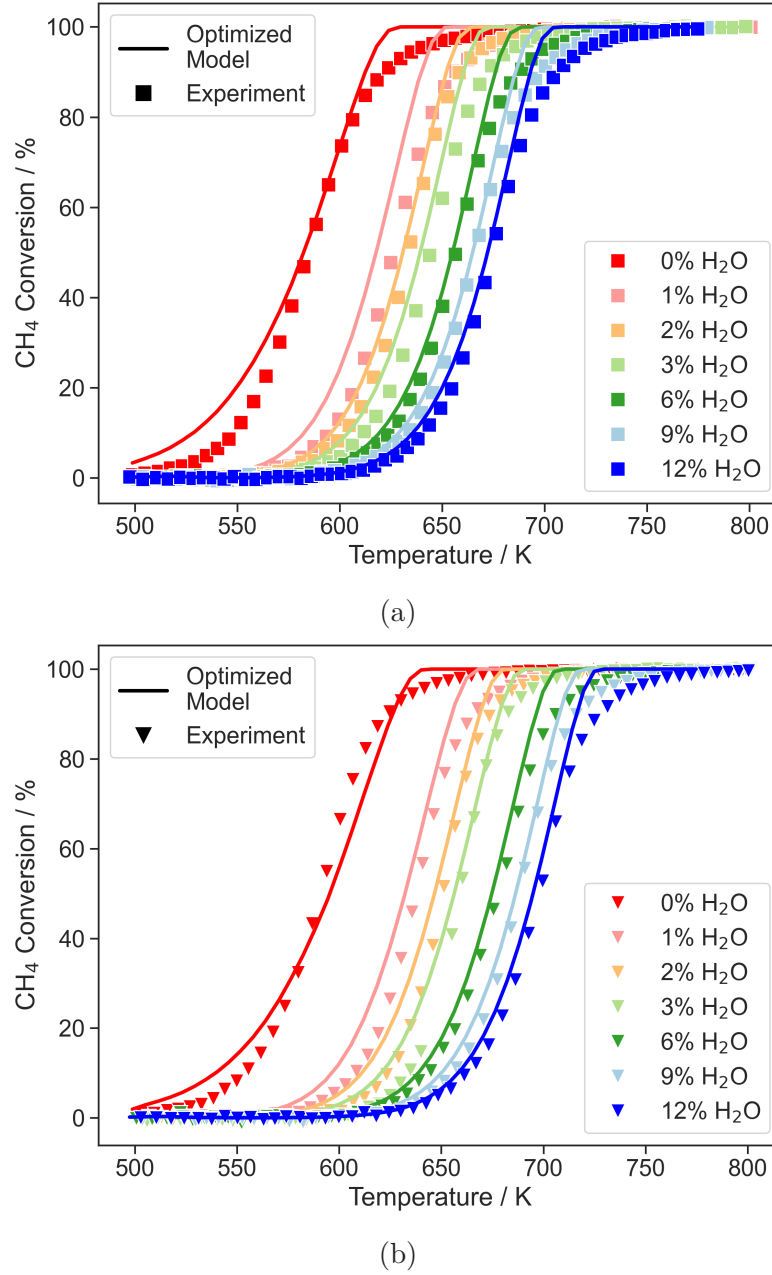


Figure 4.3: Comparison of the experimental conversions with the simulated conversions using the optimized parameters at various concentration of water in a packed bed reactor with catalyst (a) PdO supported over SnO₂ (b) PdO supported over ZrO₂. Feed conditions: 3200 ppm CH₄, 10 vol.% O₂, 0–12 vol.% H₂O in N₂. Figure adapted from [139].

Fig. 4.3 demonstrates the improved simulated performance for both the supported catalysts using the optimized model parameters. The simulations with the optimized pa-

parameter sets were able to capture the experimental trends better than the original model at all operating conditions. The larger deviations at higher temperatures beyond 90 % conversion of CH_4 most likely stem from internal mass transfer limitations. However, internal mass transfer was not considered during the simulations, as these effects were not significant under the conditions investigated in this work, according to the Weisz-Prater criterion [177]. The Weisz-Prater number at T_{10} and T_{50} for both supported catalysts was less than 0.3, while at T_{90} the values were between 0.5 and 0.6. Hence, it was concluded that at higher temperatures, the internal mass transfer resistances may have an influence, but were not severely limiting the catalytic performance.

The optimized parameter sets for both the supported catalysts are listed in Tables 4.1 and 4.2. The pre-exponential factors in both the tables are expressed in units [cm, mol, s] as DETCHEM [71] uses concentrations of surface species in defining the rate expressions. Therefore, for all of the bimolecular reactions, the units are $\text{cm}^2 \text{mol}^{-1} \text{s}^{-1}$, and for the unimolecular reactions (specifically R4r, R5r, R7r and R8r) the units are s^{-1} . The sticking coefficients (s^0) for the adsorption reactions and β which represents the temperature dependency parameter in the modified Arrhenius expression are dimensionless parameters. The activation energies are provided in kJ mol^{-1} . The listed values are given for a surface site density of $3.553 \times 10^{-9} \text{mol cm}^{-2}$ and a reference temperature (T_{ref} , in Eq. 2.5) of 1 K. The following sections present an analysis of surface coverages and reaction pathways, followed by a discussion of the changes in reaction parameters observed after optimization.

Table 4.1: Optimized kinetic parameters for PdO supported over SnO_2

Nr.	Reaction	s^0 or A ([cm, mol, s])	β	E_a (kJ/mol)
R1f	$\text{CH}_4 + a + b \rightarrow \text{CH}_3-a + \text{H}-b$	0.0459	-0.001	34.23
R1r	$\text{CH}_3-a + \text{H}-b \rightarrow \text{CH}_4 + a + b$	1.03×10^{21}	0.002	96.49
R2f	$\text{CH}_4 + \text{OH}-a + a \rightarrow \text{CH}_3-a + \text{H}_2\text{O}-a$	0.015	0.001	28.77
R2r	$\text{CH}_3-a + \text{H}_2\text{O}-a \rightarrow \text{CH}_4 + \text{OH}-a + a$	7.21×10^{19}	-0.004	94.71
R3f	$\text{CH}_4 + \text{O}-a + a \rightarrow \text{CH}_3-a + \text{OH}-a$	0.0305	0.007	26.28
R3r	$\text{CH}_3-a + \text{OH}-a \rightarrow \text{CH}_4 + \text{O}-a + a$	2.66×10^{20}	-0.03	191.23
R4f	$\text{O}_2 + a \rightarrow \text{O}_2-a$	0.0568	0	0
R4r	$\text{O}_2-a \rightarrow \text{O}_2 + a$	6.65×10^{15}	-0.031	63.29
R5f	$\text{O}_2 + \text{vac}-b \rightarrow \text{O}-b$	0.0569	0	0
R5r	$\text{O}-b \rightarrow \text{O}_2 + \text{vac}-b$	7.01×10^{15}	-0.027	159.86
R6f	$\text{H}_2\text{O} + \text{O}-a + a \rightarrow 2\text{OH}-a$	0.139	0	0
R6r	$2\text{OH}-a \rightarrow \text{H}_2\text{O} + \text{O}-a + a$	3.21×10^{21}	0.013	199.38
R7f	$\text{H}_2\text{O} + a \rightarrow \text{H}_2\text{O}-a$	0.142	0	0
R7r	$\text{H}_2\text{O}-a \rightarrow \text{H}_2\text{O} + a$	6.31×10^{12}	0.045	100.38
R8f	$\text{CO}_2 + a \rightarrow \text{CO}_2-a$	0.0504	0	0
R8r	$\text{CO}_2-a \rightarrow \text{CO}_2 + a$	3.98×10^{14}	0.029	65.73
R9f	$\text{CH}_3-a + b \rightarrow \text{CH}_3-b + a$	1.5×10^{22}	0.008	129.63
R9r	$\text{CH}_3-b + a \rightarrow \text{CH}_3-a + b$	3.74×10^{22}	0.245	173.10

Table 4.1 Optimized kinetic parameters for PdO supported over SnO₂ (continued)

Nr.	Reaction	A ([cm, mol, s])	β	E_a (kJ/mol)
R10f	CH ₃ -b + O-a → CH ₂ -b + OH-a	1.24×10^{22}	0.012	34.24
R10r	CH ₂ -b + OH-a → CH ₃ -b + O-a	1.69×10^{22}	-0.012	308.90
R11f	CH ₃ -b + OH-a → CH ₂ -b + H ₂ O-a	1.42×10^{22}	-0.004	34.84
R11r	CH ₂ -b + H ₂ O-a → CH ₃ -b + OH-a	1.05×10^{22}	0.004	210.50
R12f	CH ₃ -a + O-a → CH ₂ OH-a + a	3.55×10^{21}	0.016	31.28
R12r	CH ₂ OH-a + a → CH ₃ -a + O-a	3.68×10^{22}	0.237	320.45
R13f	CH ₃ -a + OH-a → CH ₂ -a + H ₂ O-a	2.04×10^{21}	0.004	73.21
R13r	CH ₂ -a + H ₂ O-a → CH ₃ -a + OH-a	1.17×10^{22}	-0.004	114.87
R14f	CH ₂ -a + O-a → CH ₂ OH-a + a	3.34×10^{21}	-0.004	12.73
R14r	CH ₂ OH-a + a → CH ₂ -a + O-a	3.26×10^{21}	0.257	161.22
R15f	CH ₂ OH-a + b → CH ₂ O-a + H-b	1.95×10^{22}	0.012	12.66
R15r	CH ₂ O-a + H-b → CH ₂ OH-a + b	3.35×10^{20}	-0.012	57.24
R16f	CH ₂ O-a + OH-a → CHO-a + H ₂ O-a	5.53×10^{21}	0.012	51.46
R16r	CHO-a + H ₂ O-a → CH ₂ O-a + OH-a	2.08×10^{22}	-0.012	57.24
R17f	CHO-a + OH-a → CO-a + H ₂ O-a	5.96×10^{22}	0.008	65.57
R17r	CO-a + H ₂ O-a → CHO-a + OH-a	9.15×10^{21}	-0.008	264.64
R18f	CH ₃ -a + b → CH ₂ -a + H-b	1.81×10^{21}	0	123.35
R18r	CH ₂ -a + H-b → CH ₃ -a + b	4.95×10^{22}	0	161.34
R19f	CH ₂ -a + b → CH ₂ -b + a	1.25×10^{22}	0	13.32
R19r	CH ₂ -b + a → CH ₂ -a + b	3.98×10^{21}	0.253	190.78
R20f	CH ₂ -a + b → CH-a + H-b	3.80×10^{22}	0.008	115.49
R20r	CH-a + H-b → CH ₂ -a + b	2.90×10^{22}	-0.008	167.94
R21f	CH-a + b → CHO-a + vac-b	2.10×10^{21}	0.008	24.54
R21r	CHO-a + vac-b → CH-a + b	1.832×10^{20}	0.246	206.16
R22f	CH ₂ -b + a → CH ₂ O-a + vac-b	2.12×10^{22}	0.008	91.76
R22r	CH ₂ O-a + vac-b → CH ₂ -b + a	2.46×10^{20}	-0.008	9.02
R23f	CH ₂ O-a + b → CHO-a + H-b	3.33×10^{21}	0.008	70.38
R23r	CHO-a + H-b → CH ₂ O-a + b	5.97×10^{22}	-0.008	209.74
R24f	CHO-a + b → CO-a + H-b	1.10×10^{23}	0.004	55.33
R24r	CO-a + H-b → CHO-a + b	8.02×10^{22}	-0.004	250.7
R25f	CHO-a + b → CHO-b + a	2.73×10^{22}	0.018	76.01
R25r	CHO-b + a → CHO-a + b	7.01×10^{21}	-0.017	95.56
R26f	CHO-b + a → CO-b + H-a	2.77×10^{21}	-0.002	142.39
R26r	CO-b + H-a → CHO-b + a	2.14×10^{21}	0.002	267.83
R27f	CO-a + b → CO-b + a	1.32×10^{21}	0.011	33.98
R27r	CO-b + a → CO-a + b	2.23×10^{21}	-0.011	15.90
R28f	CO-b + a → CO ₂ -a + vac-b	1.39×10^{21}	0.01	42.74
R28r	CO ₂ -a + vac-b → CO-b + a	9.54×10^{20}	-0.01	79.20
R29f	H-b + a → OH-a + vac-b	1.90×10^{22}	0	126.37
R29r	OH-a + vac-b → H-b + a	4.20×10^{21}	0	28.01
R30f	O ₂ -a + a → 2O-a	3.87×10^{22}	0.005	170.26
R30r	2O-a → O ₂ -a + a	1.72×10^{21}	-0.005	59.61
R31f	O-b + a → O-a + b	2.35×10^{22}	0.027	116.88
R31r	O-a + b → O-b + a	1.75×10^{21}	-0.005	59.61
R32f	O-a + vac-b → a + b	7.96×10^{21}	0.025	48.27
R32r	a + b → O-a + vac-b	1.40×10^{22}	-0.02	249.32
R33f	O ₂ -a + vac-b → O-a + b	1.21×10^{24}	0.025	81.95
R33r	O-a + b → O ₂ -a + vac-b	9.46×10^{22}	-0.026	172.34
R34f	H-b + a → H-a + b	5.87×10^{22}	0	150.02
R34r	H-a + b → H-b + a	9.39×10^{21}	-0.002	117.70
R35f	CHO-b + OH-a → H ₂ O-a + CO-b	3.01×10^{22}	0.001	2.12
R35r	H ₂ O-a + CO-b → CHO-b + OH-a	3.06×10^{22}	-0.001	163.57
R36f	CHO-b + a → HCOO-a + vac-b	3.69×10^{21}	0	11.74
R36r	HCOO-a + vac-b → CHO-b + a	1.19×10^{21}	0	8.82
R37f	HCOO-a + OH-a → CO ₂ -a + H ₂ O-a	2.31×10^{23}	0.011	185.32
R37r	CO ₂ -a + H ₂ O-a → HCOO-a + OH-a	4.99×10^{23}	-0.011	386.14
R38f	HCOO-a + b → CO ₂ -a + H-b	1.70×10^{23}	0.007	177.58
R38r	CO ₂ -a + H-b → HCOO-a + b	1.74×10^{24}	-0.008	374.72
R39f	H ₂ O-a + b → OH-a + H-b	3.67×10^{21}	0	13.65
R39r	OH-a + H-b → H ₂ O-a + b	1.74×10^{22}	0.008	9.97

Table 4.2: Optimized kinetic parameters for PdO supported over ZrO₂

Nr.	Reaction	s^0 or A ([cm, mol, s])	β	E_a (kJ/mol)
R1f	$\text{CH}_4 + a + b \rightarrow \text{CH}_3-a + \text{H}-b$	0.049	-0.001	32.56
R1r	$\text{CH}_3-a + \text{H}-b \rightarrow \text{CH}_4 + a + b$	1.03×10^{21}	0.003	98.26
R2f	$\text{CH}_4 + \text{OH}-a + a \rightarrow \text{CH}_3-a + \text{H}_2\text{O}-a$	0.015	0.001	28.87
R2r	$\text{CH}_3-a + \text{H}_2\text{O}-a \rightarrow \text{CH}_4 + \text{OH}-a + a$	6.66×10^{19}	-0.003	96.79
R3f	$\text{CH}_4 + \text{O}-a + a \rightarrow \text{CH}_3-a + \text{OH}-a$	0.032	0.007	25.88
R3r	$\text{CH}_3-a + \text{OH}-a \rightarrow \text{CH}_4 + \text{O}-a + a$	2.67×10^{20}	-0.029	192.12
R4f	$\text{O}_2 + a \rightarrow \text{O}_2-a$	0.059	0	0
R4r	$\text{O}_2-a \rightarrow \text{O}_2 + a$	3.91×10^{15}	0.051	52.70
R5f	$\text{O}_2 + \text{vac}-b \rightarrow \text{O}-b$	0.057	0	0
R5r	$\text{O}-b \rightarrow \text{O}_2 + \text{vac}-b$	5.73×10^{15}	0	156.69
R6f	$\text{H}_2\text{O} + \text{O}-a + a \rightarrow 2\text{OH}-a$	0.144	0	0
R6r	$2\text{OH}-a \rightarrow \text{H}_2\text{O} + \text{O}-a + a$	3.63×10^{21}	0.013	199.52
R7f	$\text{H}_2\text{O} + a \rightarrow \text{H}_2\text{O}-a$	0.140	0	0
R7r	$\text{H}_2\text{O}-a \rightarrow \text{H}_2\text{O} + a$	6.40×10^{12}	0.045	101.21
R8f	$\text{CO}_2 + a \rightarrow \text{CO}_2-a$	0.049	0	0
R8r	$\text{CO}_2-a \rightarrow \text{CO}_2 + a$	5.93×10^{14}	-0.025	72.16
R9f	$\text{CH}_3-a + b \rightarrow \text{CH}_3-b + a$	1.56×10^{22}	0	129.65
R9r	$\text{CH}_3-b + a \rightarrow \text{CH}_3-a + b$	2.43×10^{23}	-0.008	183.32
R10f	$\text{CH}_3-b + \text{O}-a \rightarrow \text{CH}_2-b + \text{OH}-a$	1.25×10^{22}	0.012	33.91
R10r	$\text{CH}_2-b + \text{OH}-a \rightarrow \text{CH}_3-b + \text{O}-a$	1.83×10^{22}	-0.006	306.61
R11f	$\text{CH}_3-b + \text{OH}-a \rightarrow \text{CH}_2-b + \text{H}_2\text{O}-a$	1.44×10^{22}	-0.007	35.24
R11r	$\text{CH}_2-b + \text{H}_2\text{O}-a \rightarrow \text{CH}_3-b + \text{OH}-a$	1.08×10^{22}	0.007	209.62
R12f	$\text{CH}_3-a + \text{O}-a \rightarrow \text{CH}_2\text{OH}-a + a$	3.55×10^{21}	0.016	30.97
R12r	$\text{CH}_2\text{OH}-a + a \rightarrow \text{CH}_3-a + \text{O}-a$	2.15×10^{23}	-0.008	347.59
R13f	$\text{CH}_3-a + \text{OH}-a \rightarrow \text{CH}_2-a + \text{H}_2\text{O}-a$	2.15×10^{21}	-0.005	80.52
R13r	$\text{CH}_2-a + \text{H}_2\text{O}-a \rightarrow \text{CH}_3-a + \text{OH}-a$	1.10×10^{22}	0.005	109.56
R14f	$\text{CH}_2-a + \text{O}-a \rightarrow \text{CH}_2\text{OH}-a + a$	3.42×10^{21}	-0.004	12.73
R14r	$\text{CH}_2\text{OH}-a + a \rightarrow \text{CH}_2-a + \text{O}-a$	1.10×10^{22}	0.005	201.99
R15f	$\text{CH}_2\text{OH}-a + b \rightarrow \text{CH}_2\text{O}-a + \text{H}-b$	1.94×10^{22}	0.012	12.44
R15r	$\text{CH}_2\text{O}-a + \text{H}-b \rightarrow \text{CH}_2\text{OH}-a + b$	3.35×10^{20}	-0.012	57.69
R16f	$\text{CH}_2\text{O}-a + \text{OH}-a \rightarrow \text{CHO}-a + \text{H}_2\text{O}-a$	5.64×10^{21}	0.012	51.51
R16r	$\text{CHO}-a + \text{H}_2\text{O}-a \rightarrow \text{CH}_2\text{O}-a + \text{OH}-a$	2.16×10^{22}	-0.012	197.16
R17f	$\text{CHO}-a + \text{OH}-a \rightarrow \text{CO}-a + \text{H}_2\text{O}-a$	6.12×10^{22}	0.008	66.50
R17r	$\text{CO}-a + \text{H}_2\text{O}-a \rightarrow \text{CHO}-a + \text{OH}-a$	8.32×10^{21}	0.01	270.80
R18f	$\text{CH}_3-a + b \rightarrow \text{CH}_2-a + \text{H}-b$	2.08×10^{21}	-0.019	139.38
R18r	$\text{CH}_2-a + \text{H}-b \rightarrow \text{CH}_3-a + b$	5.20×10^{22}	0	166.19
R19f	$\text{CH}_2-a + b \rightarrow \text{CH}_2-b + a$	1.25×10^{22}	0	13.26
R19r	$\text{CH}_2-b + a \rightarrow \text{CH}_2-a + b$	2.85×10^{22}	-0.004	212.27
R20f	$\text{CH}_2-a + b \rightarrow \text{CH}-a + \text{H}-b$	3.80×10^{22}	0.008	111.22
R20r	$\text{CH}-a + \text{H}-b \rightarrow \text{CH}_2-a + b$	2.97×10^{22}	-0.008	165.47
R21f	$\text{CH}-a + b \rightarrow \text{CHO}-a + \text{vac}-b$	2.08×10^{21}	0.008	24.81
R21r	$\text{CHO}-a + \text{vac}-b \rightarrow \text{CH}-a + b$	1.23×10^{21}	-0.008	246.47
R22f	$\text{CH}_2-b + a \rightarrow \text{CH}_2\text{O}-a + \text{vac}-b$	2.21×10^{22}	0.004	75.48
R22r	$\text{CH}_2\text{O}-a + \text{vac}-b \rightarrow \text{CH}_2-b + a$	2.41×10^{20}	-0.008	8.94
R23f	$\text{CH}_2\text{O}-a + b \rightarrow \text{CHO}-a + \text{H}-b$	3.24×10^{21}	0.008	67.11
R23r	$\text{CHO}-a + \text{H}-b \rightarrow \text{CH}_2\text{O}-a + b$	6.03×10^{22}	-0.008	210.53
R24f	$\text{CHO}-a + b \rightarrow \text{CO}-a + \text{H}-b$	1.20×10^{23}	-0.014	55.92
R24r	$\text{CO}-a + \text{H}-b \rightarrow \text{CHO}-a + b$	7.95×10^{22}	-0.004	257.99
R25f	$\text{CHO}-a + b \rightarrow \text{CHO}-b + a$	3.33×10^{22}	0	86.57
R25r	$\text{CHO}-b + a \rightarrow \text{CHO}-a + b$	6.86×10^{21}	-0.018	108.38
R26f	$\text{CHO}-b + a \rightarrow \text{CO}-b + \text{H}-a$	2.76×10^{21}	-0.002	140.68
R26r	$\text{CO}-b + \text{H}-a \rightarrow \text{CHO}-b + a$	2.17×10^{21}	0.001	269.15
R27f	$\text{CO}-a + b \rightarrow \text{CO}-b + a$	1.36×10^{21}	0.011	33.13
R27r	$\text{CO}-b + a \rightarrow \text{CO}-a + b$	2.20×10^{21}	-0.011	16.23
R28f	$\text{CO}-b + a \rightarrow \text{CO}_2-a + \text{vac}-b$	1.38×10^{21}	0.01	42.48
R28r	$\text{CO}_2-a + \text{vac}-b \rightarrow \text{CO}-b + a$	9.45×10^{20}	-0.01	76.88
R29f	$\text{H}-b + a \rightarrow \text{OH}-a + \text{vac}-b$	1.78×10^{22}	0	129.63
R29r	$\text{OH}-a + \text{vac}-b \rightarrow \text{H}-b + a$	4.24×10^{21}	0	27.59
R30f	$\text{O}_2-a + a \rightarrow 2\text{O}-a$	3.97×10^{22}	0.006	172.32
R30r	$2\text{O}-a \rightarrow \text{O}_2-a + a$	1.79×10^{21}	-0.005	58.41
R31f	$\text{O}-b + a \rightarrow \text{O}-a + b$	2.92×10^{22}	0	119.91
R31r	$\text{O}-a + b \rightarrow \text{O}-b + a$	1.47×10^{21}	0	104.59
R32f	$\text{O}-a + \text{vac}-b \rightarrow a + b$	7.97×10^{21}	0.02	46.14
R32r	$a + b \rightarrow \text{O}-a + \text{vac}-b$	1.35×10^{22}	-0.02	248.72
R33f	$\text{O}_2-a + \text{vac}-b \rightarrow \text{O}-a + b$	1.22×10^{24}	0.026	79.53
R33r	$\text{O}-a + b \rightarrow \text{O}_2-a + \text{vac}-b$	9.27×10^{22}	-0.025	168.21

Table 4.1 Optimized kinetic parameters for PdO supported over ZrO₂ (continued)

Nr.	Reaction	A ([cm, mol, s])	β	E_a (kJ/mol)
R34f	$H-b + a \rightarrow H-a + b$	6.13×10^{22}	0.002	146.69
R34r	$H-a + b \rightarrow H-b + a$	9.29×10^{21}	-0.001	111.79
R35f	$CHO-b + OH-a \rightarrow H_2O-a + CO-b$	2.97×10^{22}	0.001	2.16
R35r	$H_2O-a + CO-b \rightarrow CHO-b + OH-a$	3.17×10^{22}	-0.001	167.74
R36f	$CHO-b + a \rightarrow HCOO-a + vac-b$	3.59×10^{21}	0	11.74
R36r	$HCOO-a + vac-b \rightarrow CHO-b + a$	1.23×10^{21}	0	8.47
R37f	$HCOO-a + OH-a \rightarrow CO_2-a + H_2O-a$	2.34×10^{23}	0.011	182.15
R37r	$CO_2-a + H_2O-a \rightarrow HCOO-a + OH-a$	4.98×10^{23}	-0.011	385.41
R38f	$HCOO-a + b \rightarrow CO_2-a + H-b$	1.67×10^{23}	0.007	179.87
R38r	$CO_2-a + H-b \rightarrow HCOO-a + b$	1.73×10^{24}	-0.007	380.91
R39f	$H_2O-a + b \rightarrow OH-a + H-b$	3.62×10^{21}	0	12.49
R39r	$OH-a + H-b \rightarrow H_2O-a + b$	1.76×10^{22}	0.008	10.27

4.4.2 Surface Coverage Analysis

The spatially-resolved coverages of specific surface species as predicted by the optimized kinetic model for PdO/SnO₂ along the length of the reactor under dry and humid conditions are provided in Fig. 4.4 and 4.5, respectively. Corresponding data for the PdO/ZrO₂ catalyst are shown in Fig. 4.6 and 4.7. The species coverage behavior across the supported catalysts is similar. For both supported catalysts, the comparison between the coverages of the surface species under dry and humid conditions reveals that H₂O-a species on the a sites and H-b species on the b sites are the most abundant surface species until full methane conversion is achieved.

Under dry conditions (cf. Fig. 4.4 and 4.6), for all temperatures until T₉₀, the coverages of H₂O-a species increases along the length as methane is consumed, accompanied by a corresponding decrease in the fraction of free a sites. In contrast, under humid conditions (cf. Fig. 4.5 and 4.7), all the a sites were predominantly covered by H₂O-a species due to the adsorption of water from the gas phase, resulting in complete blockage of active sites at lower temperatures. Methane oxidation is initiated only at elevated temperatures, where enough desorption of water from the surface occurs, releasing the active sites for adsorption of CH₄. The coverages of other transient species H-a and O-a exhibit a slight decreasing trend along the length under dry conditions, which is not predicted under humid conditions below T₅₀.

Free b sites become available at higher temperatures where methane conversion is high. At low temperatures and dry feed conditions, H–b species are formed primarily through the hydrogen abstraction reactions from methane and other C-intermediates (R1f, R15, R18, R20, R23, R24), as methane gets converted, and through R39f ($\text{H}_2\text{O}-\text{a} + \text{b} \rightarrow \text{OH}-\text{a} + \text{H}-\text{b}$) from the produced water on the surface. H–b species coverages show a decreasing trend only at higher temperatures as their consumption rate through R29f where H–b species interact with free a sites resulting in formation of OH–a and vac–b species, surpasses their production rate (cf. Fig. 4.4f, 4.4h, 4.6f, and 4.6h). This is also supported by the increase in the simulated coverages of OH–a species beyond T_{90} .

The vac–b species are crucial because they are formed through the Mars-van-Krevelen mechanism by providing lattice oxygen for the formation of CO–a and CO₂–a species. Their low coverage indicates that these species quickly react with gaseous O₂ to regenerate the b sites, following their formation. Only trace amounts of vac–b species are predicted by the model at temperatures beyond T_{90} , likely originating from reaction R29f. The behavior of species associated with the b sites are similar under humid conditions. Although the model predicts an increase in H–b species at temperatures below 550 K, this does not imply methane activation, as the a sites are completely blocked by adsorbed water and no formation of vac–b species is predicted. Therefore, the initial rise in H–b species predicted by the model most likely originate from water-induced surface reactions, particularly R7 and R39.

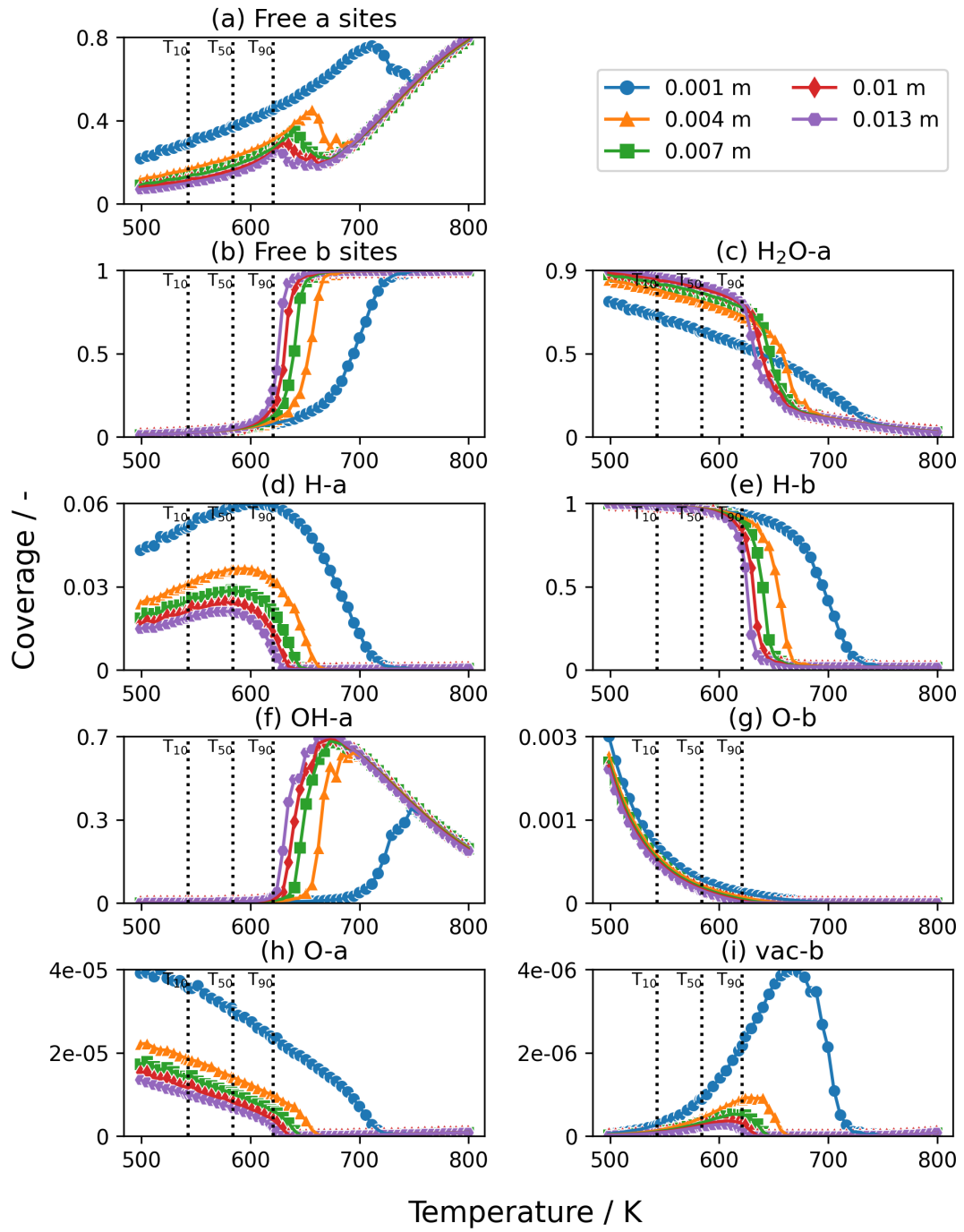


Figure 4.4: Simulated surface coverages under dry conditions of the most abundant surface species for various temperatures at different axial points along the catalyst bed containing PdO/SnO₂. Inlet conditions: 3200 ppm CH₄, 10 vol.% O₂, 0 vol.% H₂O, balance N₂. Figure reproduced from [139].

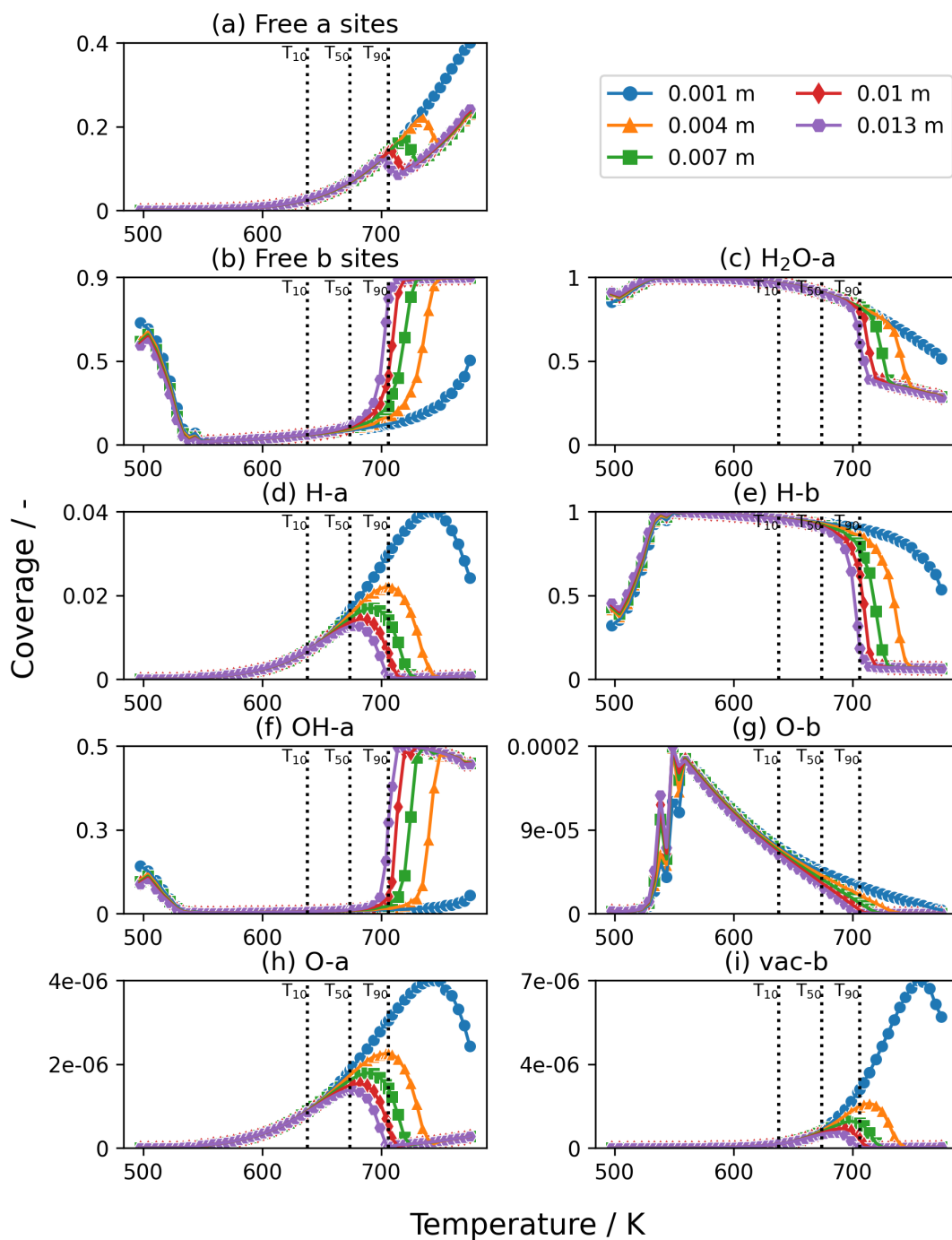


Figure 4.5: Simulated surface coverages under humid conditions of the most abundant surface species for various temperatures at different axial points along the catalyst bed containing PdO/SnO₂. Inlet conditions: 3200 ppm CH₄, 10 vol.% O₂, 12 vol.% H₂O, balance N₂. Figure reproduced from [139].

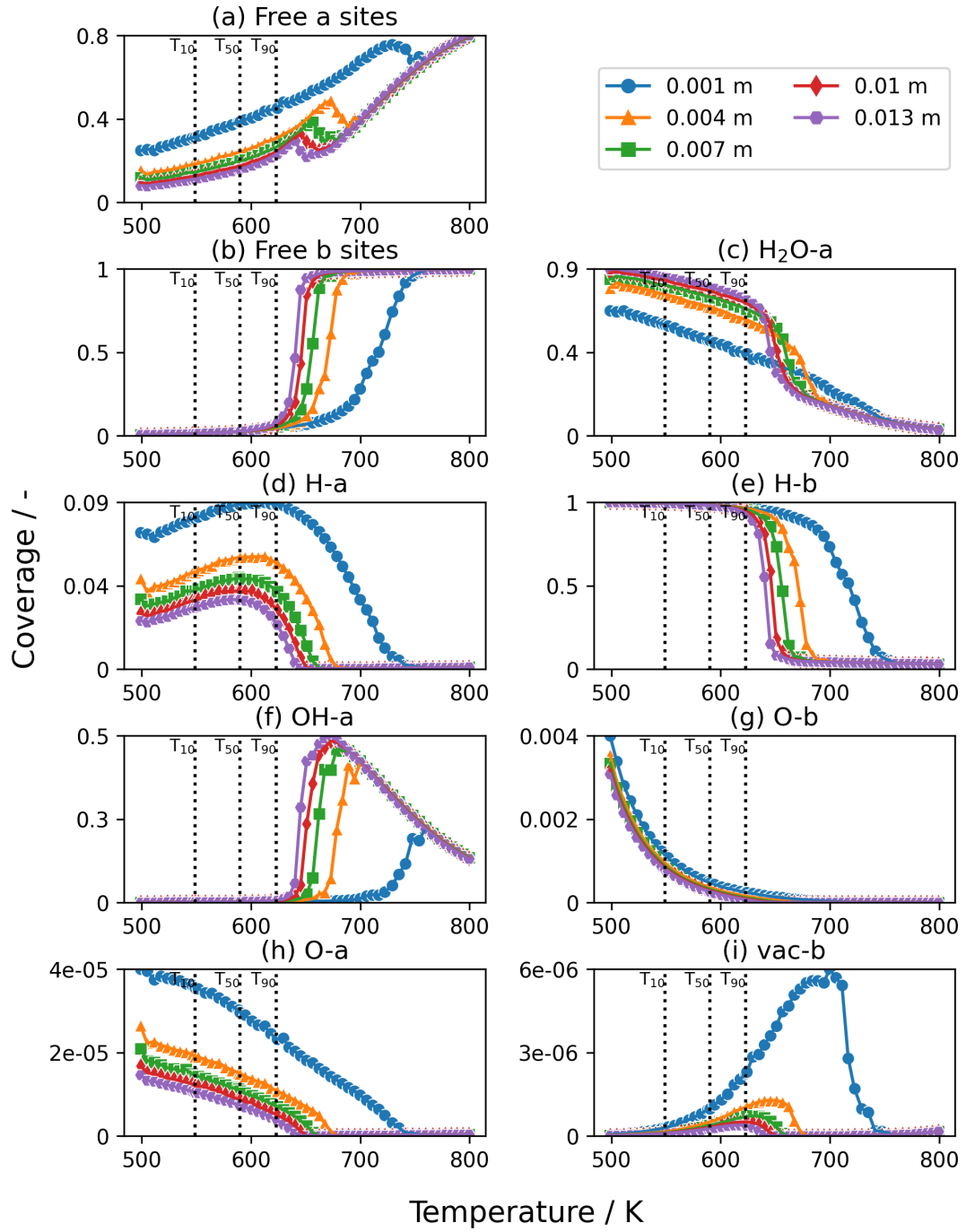


Figure 4.6: Simulated surface coverages under dry conditions of the most abundant surface species for various temperatures at different axial points along the catalyst bed containing PdO/ZrO₂. Inlet conditions: 3200 ppm CH₄, 10 vol.% O₂, 0 vol.% H₂O, balance N₂. Figure reproduced from the supporting information of [139].

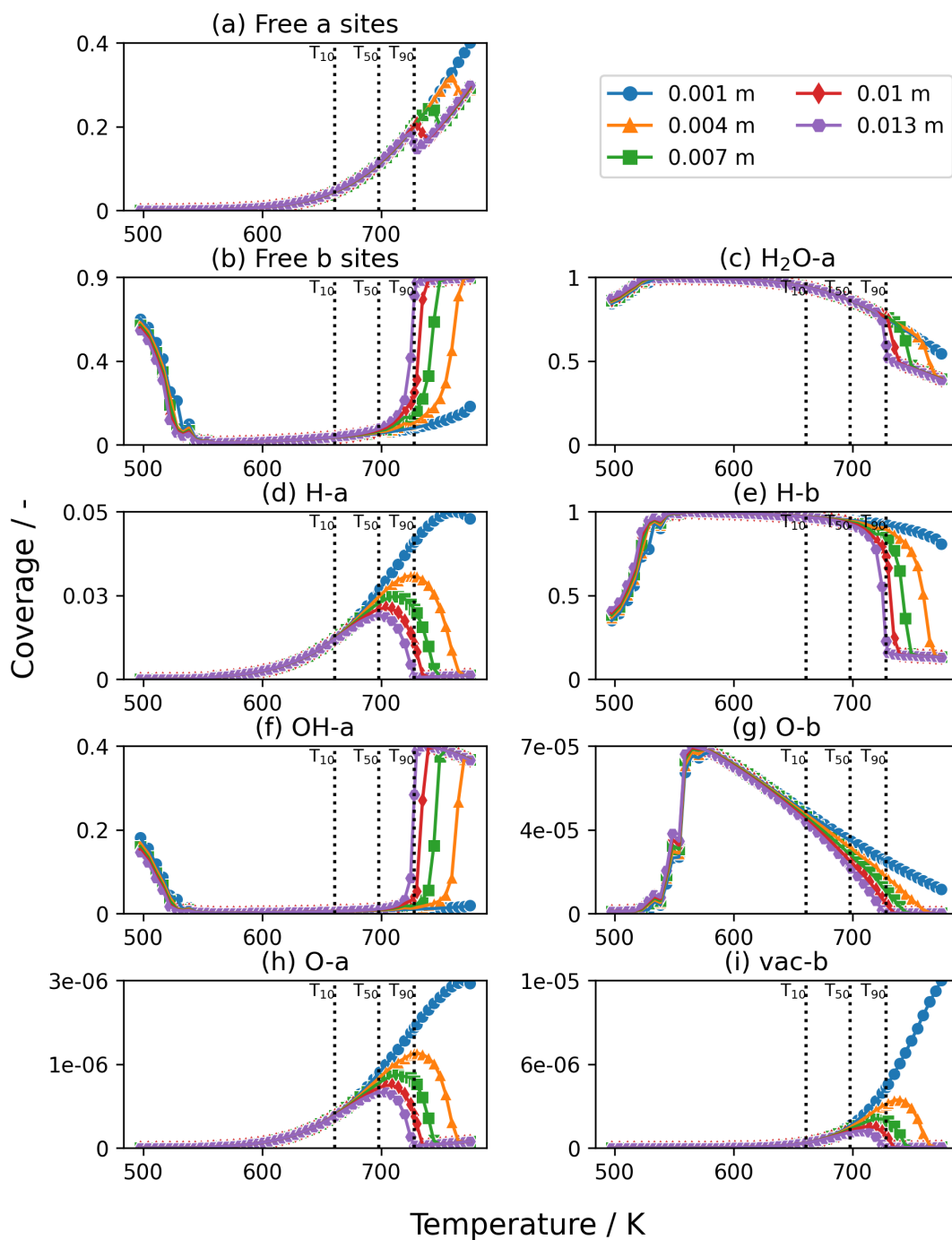


Figure 4.7: Simulated surface coverages under dry conditions of the most abundant surface species for various temperatures at different axial points along the catalyst bed containing PdO/ZrO₂. Inlet conditions: 3200 ppm CH₄, 10 vol.% O₂, 12 vol.% H₂O, balance N₂. Figure reproduced from the supporting information of [139].

4.4.3 Reaction Flow Analysis and Key Species

In order to investigate the differences in the catalytic activity across the two supports in the presence and absence of water, analysis of the integrated reaction rates at various temperatures and feed conditions were conducted. The dominant reaction pathways were identified based on the consumption and production preference of the species towards the various reaction pathways in the mechanism as outlined in Section 2.2.2. Fig. 4.8 and 4.9 illustrate the reaction flow for conversion of methane to carbon dioxide at T_{10} , T_{50} , and T_{90} for SnO_2 -supported and ZrO_2 -supported catalyst, respectively.

The dominant reaction pathways under the different reaction conditions match the findings from Stotz et al. [168], where they identified two main reaction pathways for oxidation of methane, namely the oxygen-assisted pathway and the hydroxyl-assisted pathway. In case of $\text{PdO}/\text{Al}_2\text{O}_3$ catalyst, Stotz et al. [168] showed that the oxygen-assisted pathway (i.e., $\text{CH}_4(\text{g}) \rightarrow \text{CH}_3\text{-a} \rightarrow \text{CH}_2\text{OH-a} \rightarrow \text{CH}_2\text{O-a} \rightarrow \text{CHO-a} \rightarrow \text{CO-a} \rightarrow \text{CO-b} \rightarrow \text{CO}_2\text{-a} \rightarrow \text{CO}_2(\text{g})$) is the dominant path at low temperatures and dry conditions, whereas the hydroxyl-assisted pathway (i.e., $\text{CH}_4(\text{g}) \rightarrow \text{CH}_3\text{-a} \rightarrow \text{CH}_2\text{-a} \rightarrow \text{CH}_2\text{-b} \rightarrow \text{CH}_2\text{O-a} \rightarrow \text{CHO-a} \rightarrow \text{CO-a} \rightarrow \text{CO-b} \rightarrow \text{CO}_2\text{-a} \rightarrow \text{CO}_2(\text{g})$) is the preferred path at high temperatures and humid conditions.

For the other supported catalysts investigated in this work as well, the oxidation reaction predominantly proceeds via these two key pathways; however, their relative contributions vary across the supported catalysts. Particularly for PdO/SnO_2 , the oxygen-assisted pathway was the dominant pathway under dry conditions at all temperatures (Fig. 4.8a). Whereas, under humid conditions the dominant pathway shifts to the hydroxyl-assisted pathway which becomes more prominent as the temperature increases (Fig. 4.8b). At T_{10} , under dry conditions $\text{CH}_3\text{-a}$ species has 100% preference towards reaction R12 ($\text{CH}_3\text{-a} + \text{O-a} \rightleftharpoons \text{CH}_2\text{OH-a} + \text{a}$), which reduces to 41.39% under humid conditions. Correspondingly, the preference of $\text{CH}_3\text{-a}$ towards R13 ($\text{CH}_3\text{-a} + \text{OH-a} \rightleftharpoons \text{CH}_2\text{-a} + \text{H}_2\text{O-a}$) increases from 0% at T_{10} under dry conditions to 58.47% under humid conditions, making it the dominant route. The preference for this pathway increases to 74.38% as temperature rises to T_{90} under humid conditions.

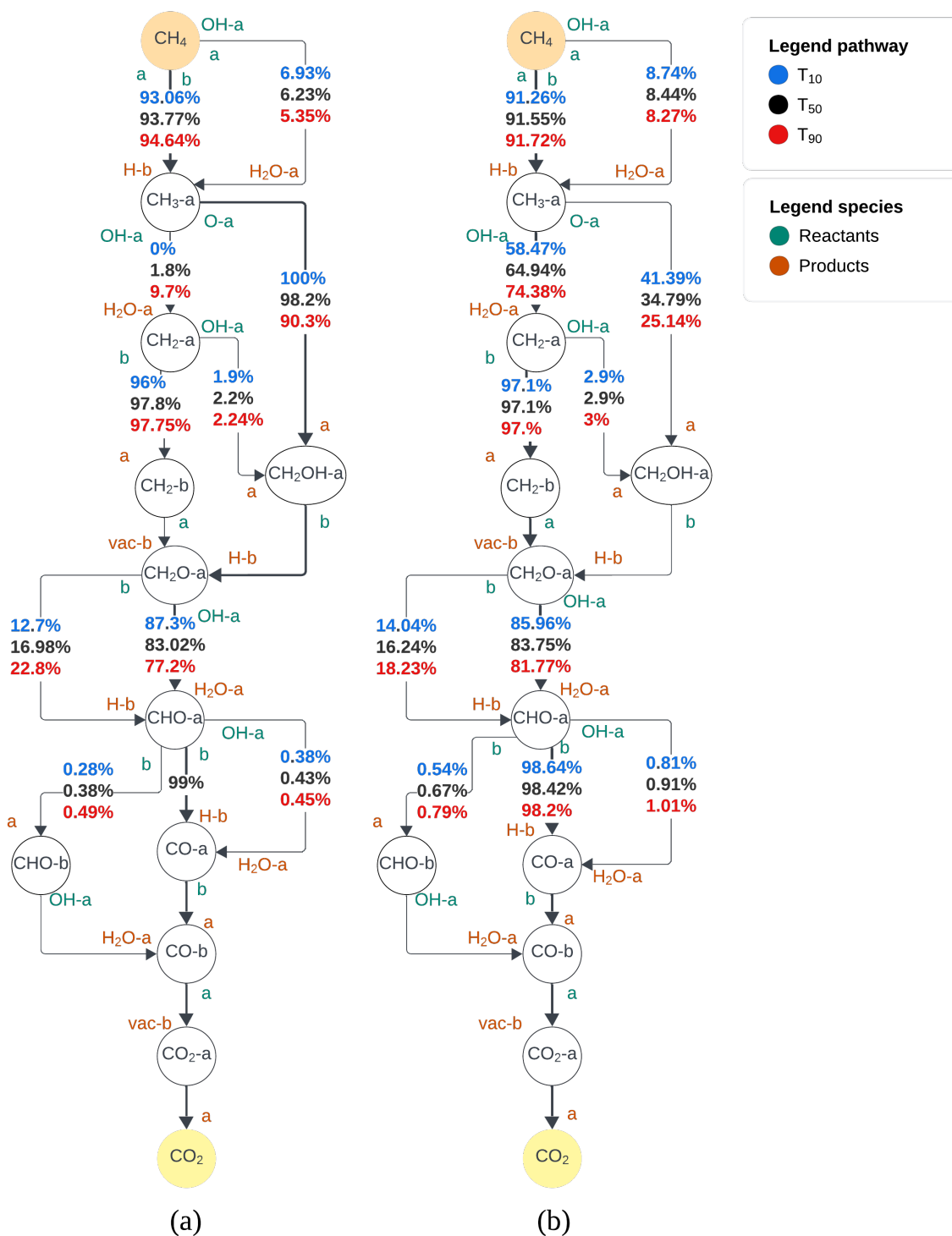


Figure 4.8: Reaction flow analysis of the mechanism optimized for PdO/SnO₂ catalyst at temperatures of 10 %, 50 %, and 90 % conversion in the (a) dry conditions and (b) humid conditions. Figure reproduced from [139].

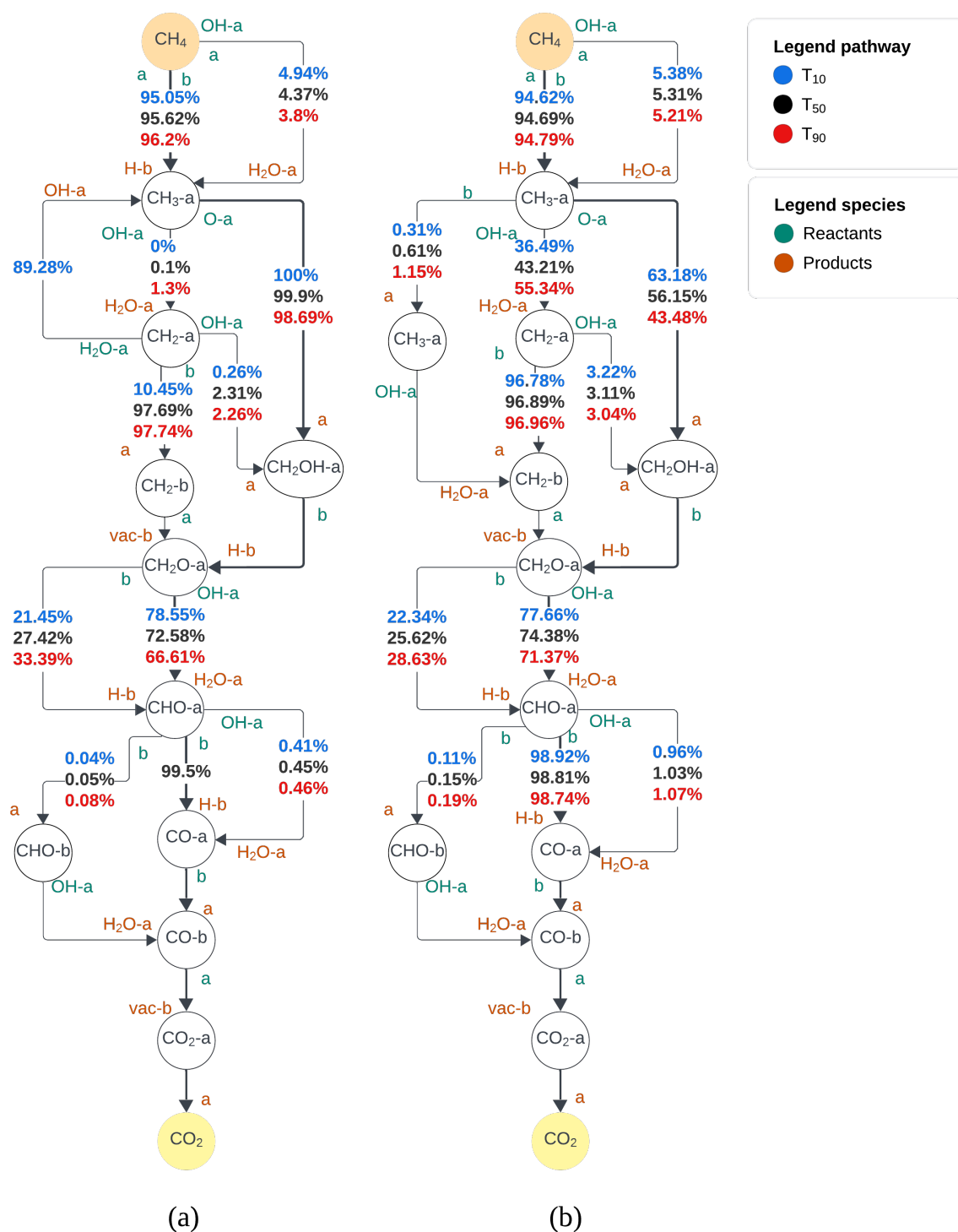


Figure 4.9: Reaction flow analysis of the mechanism optimized for PdO/ZrO₂ catalyst at temperatures of 10 %, 50 %, and 90 % conversion in the (a) dry conditions and (b) humid conditions. Figure reproduced from [139].

In contrast, for the ZrO_2 -supported catalyst, the oxygen-assisted pathway exhibits higher contribution towards formation of CO_2 under most conditions. In the absence of water in the feed, the $\text{CH}_3\text{-a}$ species show consistently high preference towards R12 (more than 98 % contribution) at all temperatures (Fig. 4.9a). In the presence of water as well, this reaction pathway is preferred as shown in Fig. 4.9b, where at T_{10} and T_{50} the consumption preference is 63.18 % and 56.15 %, respectively. Only at T_{90} , the hydroxyl-assisted pathway contributes more than the oxygen-assisted pathway. As the original model [168] was underpredicting methane conversion under dry conditions (cf. 4.2b), the parameters were algorithmically optimized in such a way that the behavior of the catalyst under dry conditions is improved while maintaining the activity under the humid conditions, resulting in higher contribution of the oxygen-assisted pathway.

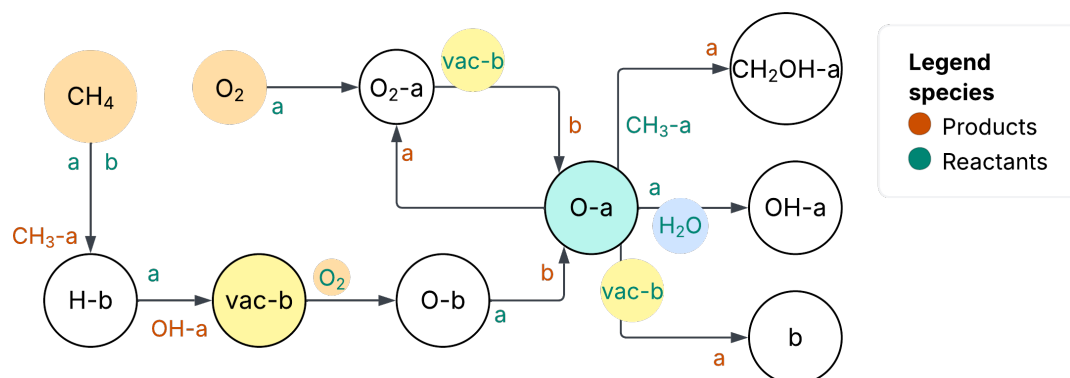


Figure 4.10: Schematic representation of the reaction pathways involving O-a and vac-b species.

As is evident from the dominant pathways under dry and humid conditions, the O-a species play a crucial role in the conversion of methane. Fig. 4.10 illustrates the reaction pathways leading to the formation and consumption of O-a species. The activation of methane leads to formation of H-b species on the surface which leads to formation of the vac-b species through the Mars-van-Krevelen mechanism. As shown in Fig. 4.10, vac-b species are the precursors for formation of O-a species which are required for the oxygen-assisted pathway leading to formation of $\text{CH}_2\text{OH-a}$. However, there are several competing pathways for the consumption of O-a species, including the water abstraction

reaction, where the O–a species react with gas-phase water to form surface hydroxyls (OH–a species).

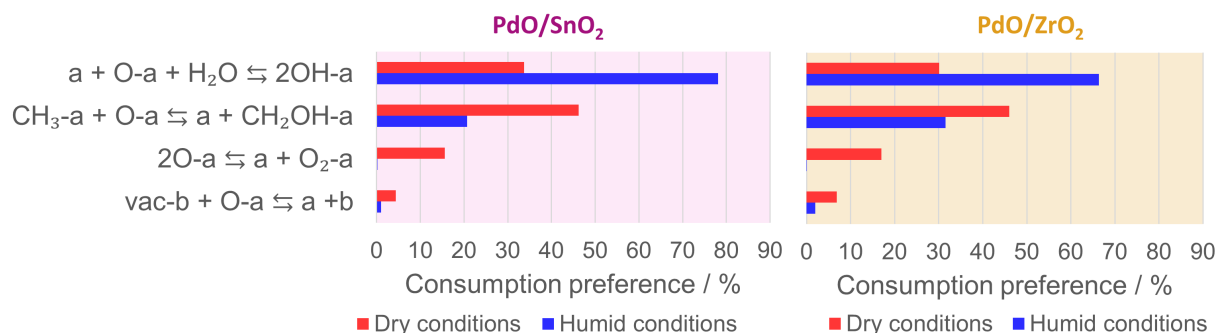
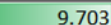
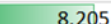
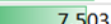
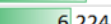


Figure 4.11: Consumption preferences of O–a species towards the various reactions for both supported catalysts at T_{10} .

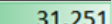
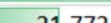
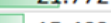
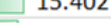
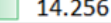
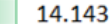
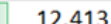
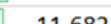
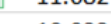
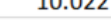
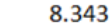
Fig. 4.11 compares the consumption preference of O–a species across the supported catalysts at T_{10} , under dry and humid conditions, among the competing reactions. A clear preference for the water abstraction reaction can be observed compared to the formation of CH_2OH-a , when the reaction conditions are humid. This behavior explains the shift towards the hydroxyl-assisted pathway, as through the water abstraction reaction more OH–a species are formed, which are the driving species for the hydroxyl-assisted pathway (cf. Fig. 4.8 and 4.9). When comparing across the supports, water abstraction reaction is still the preferred reaction under humid conditions; however, the contribution towards the formation of CH_2OH-a is higher in ZrO_2 -supported catalyst than SnO_2 -supported catalyst. Therefore, in case of PdO/ZrO_2 catalyst, the oxygen-assisted pathway remains the dominant reaction route for the conversion of methane to carbon dioxide.

4.4.4 Comparison of Kinetic Parameter Values

During the optimization process, the step size for the global search was set to 0.01 resulting in a maximum change of $\pm 10\%$ of the original kinetic parameters for both supported catalysts at each iteration, however after subsequent hops within the search space the values may reach beyond the constraints set by the step size. A comparative analysis was therefore conducted to evaluate the extent to which the newly optimized parameters deviated from their original values.

Nr.	Reaction	Dependent reaction	Energy difference between PdO/Al ₂ O ₃ and PdO/SnO ₂ , kJ/mol	
R37r	H2O-a +CO2-a >HCOO-a +OH-a	Yes		9.703
R6r	OH-a +OH-a >a +O-a +H2O	Yes		8.205
R35r	H2O-a +CO-b >CHO-b +OH-a	No		7.503
R38r	H-b +CO2-a >b +HCOO-a	Yes		6.224
R10r	CH2-b +OH-a >O-a +CH3-b	Yes		5.829
R19r	a +CH2-b >CH2-a +b	Yes		-7.242
R9r	a +CH3-b >CH3-a +b	Yes		-8.106
R21r	vac-b +CHO-a >b +CH-a	Yes		-9.061
R2r	CH3-a +H2O-a >CH4 +a +OH-a	Yes		-9.55
R1r	CH3-a +H-b >CH4 +a +b	Yes		-9.691
R25r	a +CHO-b >b +CHO-a	Yes		-11.051
R29f	a +H-b >vac-b +OH-a	No		-11.427
R12r	a +CH2OH-a >CH3-a +O-a	Yes		-13.002
R14r	a +CH2OH-a >CH2-a +OH-a	Yes		-18.998

(a)

Nr.	Reaction	Dependent reaction	Energy difference between PdO/Al ₂ O ₃ and PdO/ZrO ₂ , kJ/mol	
R21r	vac-b +CHO-a >b +CH-a	No		31.251
R14r	a +CH2OH-a >CH2-a +OH-a	Yes		21.772
R18f	CH3-a +b >CH2-a +H-b	Yes		15.402
R19r	a +CH2-b >CH2-a +b	Yes		14.256
R12r	a +CH2OH-a >CH3-a +O-a	Yes		14.143
R38r	H-b +CO2-a >b +HCOO-a	Yes		12.413
R35r	H2O-a +CO-b >CHO-b +OH-a	No		11.682
R25f	b +CHO-a >a +CHO-b	Yes		10.022
R37r	H2O-a +CO2-a >HCOO-a +OH-a	Yes		8.973
R6r	OH-a +OH-a >a +O-a +H2O	Yes		8.343
R13f	CH3-a +OH-a >CH2-a +H2O-a	Yes		7.293
R8r	CO2-a >a +CO2	Yes		7.065
R26r	CO-b +H-a >a +CHO-b	Yes		6.038
R34r	b +H-a >a +H-b	Yes		-6.038
R13r	CH2-a +H2O-a >CH3-a +OH-a	Yes		-7.293
R2r	CH3-a +H2O-a >CH4 +a +OH-a	Yes		-7.469
R1r	CH3-a +H-b >CH4 +a +b	No		-7.916
R29f	a +H-b >vac-b +OH-a	Yes		-8.167
R4r	O2-a >a +O2	Yes		-10.846
R22f	a +CH2-b >vac-b +CH2O-a	Yes		-15.742

(b)

Figure 4.12: Reactions with absolute change in the values of activation energy higher than 5 kJ mol⁻¹ in the optimized model for (a) PdO/SnO₂ and (b) PdO/ZrO₂. Figures reproduced from the supporting information of [139].

For the SnO_2 -supported catalyst, most modifications in the activation energies were less than 4 % of the original values. As demonstrated in Fig. 4.12a, 14 reactions had an absolute change of more than 5 kJ mol^{-1} , out of which only two reactions were algorithmically modified. For six elementary steps (R6r, R9r, R12r, R14r, R19r, and R21r), the pre-exponential factors deviated by about one order of magnitude. However, these reactions were part of the dependent set of reactions and were calculated by DETCHEM^{ADJUST} thus, significant deviations were necessary. In case of the optimized parameter values for the ZrO_2 -supported PdO catalyst as well, the modifications were mostly limited to less than 4 %. The activation energy values for 20 reactions were relatively higher beyond 5 kJ mol^{-1} , as demonstrated in Fig. 4.12b. The changes in pre-exponential factors were relatively small and varied by about one order of magnitude for only R6r.

Fig. 4.12a and 4.12b clearly demonstrate that most major adjustments occurred in the energies of the dependent set of reactions to ensure thermodynamic consistency. The reactions that were independently modified and had larger modifications, specifically R35r and R29f for SnO_2 , and R21r and R35r for ZrO_2 , were not significantly sensitive reactions and were not part of the dominant pathways. Moreover, the magnitude of the larger energy changes in the optimized model is consistent with the inherent uncertainties of parameters obtained from DFT calculations, which may be as high as 30 kJ mol^{-1} [178–180].

The differences in energies for steps involved in the dominant reaction pathways is illustrated in Fig. 4.13. The values are color-coded based on the extent of modification, with red color indicating larger decrease in the energy compared to the original model and green color denotes larger increase in the energies. Most steps within the dominant pathway were modified algorithmically and had relatively small changes, while the larger changes were primarily observed in the dependent reactions.

When comparing the optimized parameters across the two supported catalysts i.e., PdO/ SnO_2 and PdO/ ZrO_2 , only 9 reactions (R4r, R8r, R9r, R12r, R18f, R19r, R21r, R22f and R25r) exhibited significant differences in energies. However, these reactions were not significantly sensitive, and the larger adjustments did not significantly affect

Nr.	Reaction	Dependent reaction for PdO/SnO ₂	Energy difference between PdO/Al ₂ O ₃ and PdO/SnO ₂ , kJ/mol	Dependent reaction for PdO/ZrO ₂	Energy difference between PdO/Al ₂ O ₃ and PdO/ZrO ₂ , kJ/mol
R1f	CH ₄ +a +b >CH ₃ -a +H-b	No	1.074	No	-0.593
R1r	CH ₃ -a +H-b >CH ₄ +a +b	Yes	-9.691	No	-7.916
R12f	CH ₃ -a +O-a >a +CH ₂ OH-a	No	0.327	No	0.02
R12r	a +CH ₂ OH-a >CH ₃ -a +O-a	Yes	-13.002	Yes	14.143
R13f	CH ₃ -a +OH-a >CH ₂ -a +H ₂ O-a	No	-0.023	Yes	7.293
R13r	CH ₂ -a +H ₂ O-a >CH ₃ -a +OH-a	No	-1.977	Yes	-7.293
R15f	b +CH ₂ OH-a >CH ₂ O-a +H-b	No	0.002	No	-0.218
R15r	CH ₂ O-a +H-b >b +CH ₂ OH-a	No	-0.406	No	0.048
R16f	CH ₂ O-a +OH-a >H ₂ O-a +CHO-a	No	-0.111	No	-0.064
R16r	H ₂ O-a +CHO-a >CH ₂ O-a +OH-a	Yes	2.265	No	4.928
R19f	CH ₂ -a +b >a +CH ₂ -b	No	0.217	No	0.153
R19r	a +CH ₂ -b >CH ₂ -a +b	Yes	-7.242	Yes	14.256
R22f	a +CH ₂ -b >vac-b +CH ₂ O-a	No	0.536	Yes	-15.742
R22r	vac-b +CH ₂ O-a >a +CH ₂ -b	No	-0.019	No	-0.096
R24f	b +CHO-a >CO-a +H-b	No	-0.278	Yes	0.309
R24r	CO-a +H-b >b +CHO-a	No	-4.086	No	3.189
R27f	CO-a +b >a +CO-b	No	0.107	No	-0.739
R27r	a +CO-b >CO-a +b	No	-0.365	No	-0.029
R28f	a +CO-b >vac-b +CO ₂ -a	No	0.716	No	0.457
R28r	vac-b +CO ₂ -a >a +CO-b	No	0.719	No	-1.594
R8f	a +CO ₂ >CO ₂ -a	No	0	No	0
R8r	CO ₂ -a >a +CO ₂	No	0.63	Yes	7.065

Figure 4.13: Changes in the optimized activation energies in the dominant reaction pathways for both supported catalysts. Figure reproduced from the supporting information of [168].

simulation outputs. Overall, for this application only small adjustments in almost all reactions were required, yet the cumulative effect of these smaller adjustments was evident in the reactor outputs. This highlights the necessity of using algorithmic optimization over manual tuning, as it enables more precise and effective parameter refinement.

4.4.5 Limitations

As discussed in Chapter 3, the optimization approach performs best when the initial mechanism provides a complete and accurate representation of the reactions occurring on the surface, with no missing reaction pathways. Here, the impact of using different support materials with the active PdO catalyst could be modeled without introducing new reaction pathways, as the supports primarily influence the size and stability of PdO nanoparticles. This makes it appropriate to apply the optimization approach by refining only the kinetic parameters. However, for systems where the support may play a more

active role in the surface reactions, or where formation of new products require additional elementary steps, this approach has not yet been explored and remains a topic for future investigations.

4.5 Conclusions

This chapter showcased yet another example of using the global optimization algorithm Basin-Hopping to obtain tailored microkinetic models for describing the experimental trends in heterogeneous catalysis, specifically to study the catalytic activity of palladium-based catalysts for methane oxidation. Initial simulations with an existing microkinetic model for PdO/Al₂O₃ considering Pd_{cus} and O_{cus} sites as active sites, indicated that the microkinetic model needs refinement, to account for the influence of the support material on the catalytic performance.

With the optimized parameter sets, the experimental trends were more closely captured compared to the original model, even for experimental data that were not used for fitting. Consequently, the optimized mechanisms were employed to identify key surface species and dominant pathways to gain a better understanding of the reactions happening on the surface. It was shown that for both supported catalysts, when water is fed at the inlet with the reacting gas mixture, the catalytic active sites are blocked by adsorbed water on the surface. Since methane and water compete for the same active site, this suppresses methane activation at low temperatures, shifting catalytic activity towards higher temperatures where water desorption becomes sufficiently fast to allow dissociative adsorption of methane and subsequent reactions. Therefore, at low temperatures, H₂O on Pd_{cus} sites and hydrogen on O_{cus} were the most abundant species on the surface. Under dry conditions, water on Pd_{cus} sites originates from the oxidation reaction, whereas under humid conditions, it primarily results from water adsorption from the gas phase. At higher temperatures as conversion increases beyond 90 %, the coverage of hydroxyl species increases on the Pd_{cus} sites. Correspondingly, hydrogen coverage on O_{cus} sites reduces thereby, freeing more O_{cus} sites on the surface.

The analysis of the rates of the various mechanistic steps showed that across both SnO_2 - and ZrO_2 -supported catalysts two dominant pathways exist for methane oxidation, similar to those observed for alumina-supported PdO. The key distinction between the supported catalysts studied in this work lies in the relative contribution of these pathways towards formation of CO_2 . For PdO/ SnO_2 , oxygen-assisted pathway dominates under dry conditions. However, as water is introduced at the inlet, the hydroxyl-assisted pathway becomes increasingly dominant. This shift is attributed to the preference of O-Pd_{cus} species to react with gaseous water, forming surface hydroxyls, rather than partaking in the reaction with methyl species in the oxygen-assisted pathway. In contrast, for PdO/ ZrO_2 the oxygen-assisted pathway remains the dominant pathway under both dry and humid conditions. Although the water abstraction reaction is still favored over methyl oxidation for PdO/ ZrO_2 , the relative preference for the reaction of O-Pd_{cus} species with methyl species is higher compared to PdO/ SnO_2 .

This chapter demonstrated how algorithmic optimization of microkinetic models can accelerate the development of tailored reaction mechanisms. These mechanisms can help advance the understanding of the surface chemistry, when these models are well-validated. A key requirement for the success of this approach is availability of a robust initial model, which in this case was the model for PdO/ Al_2O_3 originating from DFT, requiring minimal modification to its original parameters and no addition of new elementary steps to the microkinetic model. Only a subset of the experimental dataset was used for model fitting, while the remaining data was used for validation, ensuring that the model generalized well across relevant operating conditions. Overall, this study highlighted how numerical methods, combined with automation, simulation tools, and systematic analysis of species coverages and reaction rates, can significantly accelerate model development, help understand the reaction mechanism, and facilitate its future application in scale-up studies and reaction engineering.

5 Surrogate Modeling using Deep Learning Architectures and its Application

This chapter presents the development and application of a surrogate model for methane oxidation over PdO/Al₂O₃ in a packed bed reactor. The objective of this work was to numerically study the deactivation behavior of PdO/Al₂O₃ catalysts in the presence of water. The existing microkinetic model [168] is unable to accurately predict the experimental light-off behavior [149] of the alumina supported PdO catalyst under all reaction conditions. In order to better understand the phenomenon governing the behavior of these catalysts under lean and humid conditions, the numerical model considering a constant value of dispersion is insufficient, and therefore in this work, a neural network-based surrogate model is proposed to help understand the light-off behavior. The chapter describes the various steps of data generation, the employed model architectures, the methodology followed for the surrogate model training, and demonstrates its application in understanding the dynamic nature of the active sites during light-offs. Simulated data were generated for a variety of operating conditions and were used to train a neural network architecture which acted as a surrogate to the original simulation model to enable gradient-based optimization of the catalyst properties.

5.1 Motivation

PdO/Al₂O₃ oxidation catalysts are prone to deactivation, especially under wet conditions. As illustrated in Fig. 5.1, this deactivation is of two types: first, an immediate and reversible inhibition caused by hydroxyl formation or water accumulation on the surface [147, 148, 160, 162, 176, 181, 182]; and second, a gradual and irreversible loss of active sites over a period of time [183–185]. Notably, this slow deactivation can be rapidly reversed by exposure to reducing conditions [157, 158]. Therefore, this slow deactivation due to water is considered irreversible only when the reaction conditions are oxidizing.

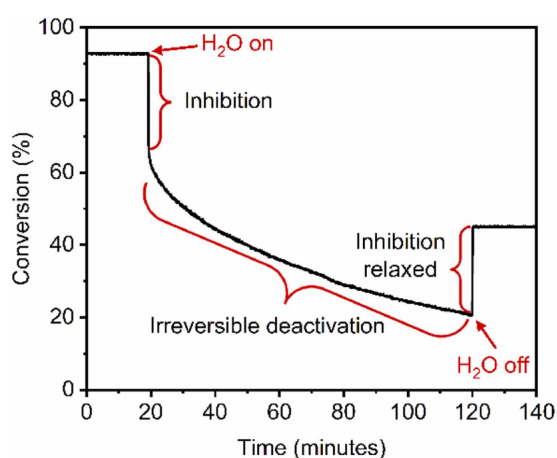


Figure 5.1: Deactivation trend of PdO/Al₂O₃ due to presence of 10 vol.% water during oxidation of methane (500 ppm CH₄, 10 vol.% O₂, balance N₂, Temperature = 713.15 K). Figure reprinted from [183], licensed under CC BY 4.0.

The deactivation behavior was also observed in the experimental observations from Keller et al. [149] for PdO/Al₂O₃ catalyst. The DFT-based microkinetic model from Stotz et al. [168], described in Chapter 4 Section 4.2, models the loss in catalytic performance as a blocking of active sites due to the presence of water in the reaction environment. Consequently, as demonstrated in Fig. 5.2 the simulation of the light-off behavior of oxidation of methane over PdO/Al₂O₃ under varying concentrations of water, using the microkinetic model [168], qualitatively predicts the shift in activity to higher temperatures when water is present in the feed. However, it does not accurately match the experimental observations as temperature is increased. Specifically, the experimental light-offs exhibit a distinct change in slope with increasing temperature and inlet water concentrations, which are not captured in the simulated data. This discrepancy likely stems from the as-

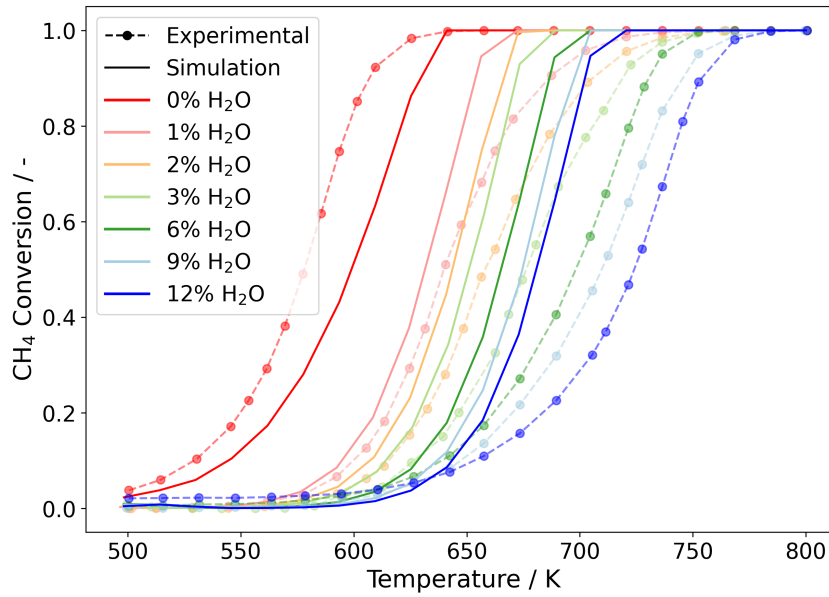


Figure 5.2: Comparison of the experimental [149] and the simulated catalytic performance of PdO supported on Al_2O_3 using the kinetic model by Stotz et al. [168] (conditions: 3200 ppm CH_4 , 10 vol.% O_2 , 0-12 vol.% H_2O , balance N_2 , GHSV = 140 000 h^{-1})

sumption of a constant catalytic surface area throughout the light-off process, which does not account for the irreversible deactivation occurring under reaction conditions. Given that the kinetic model has been validated under lean conditions [149, 168] and successfully reproduces the shift in activity to higher temperatures in the presence of water, and considering that the experiments were designed to minimize mass transfer limitations, the most plausible explanation for the mismatch is the model's failure to incorporate a dynamic active area. Stotz et al. [168] also reported that the deviations in the simulated values at elevated temperatures, are likely due to the consideration of a constant catalytically-active surface area during the light-off simulations. The experimental observations in Fig. 5.2 are taken from the study by Keller et al. [149]. The experimental conditions are briefly described in Section 5.2.

Studies indicate that during methane oxidation under dry conditions, catalyst deactivation is less pronounced than under humid conditions [147, 183, 184, 186]. At temperatures above 350 °C, significant deactivation is observed only after several hours of operation [145, 147, 183]. The experimental data measured under dry conditions in Fig. 5.2 do not show a noticeable change in slope with increasing temperature, in contrast to experiments where

additional water is present. The underprediction of methane conversion in the simulation likely arises from underestimation of the catalytically active area and/or possible hot-spots in the catalytic bed, particularly at temperatures of high conversion. Moreover, because the time-on-stream during light-off experiments at lower temperatures is relatively short, substantial deactivation due to the produced water during the reaction is not expected. Therefore, this work focuses on the deactivation behavior observed in the experimental data when additional water was dosed in the feed.

A variety of factors have been suggested to explain the deactivation phenomenon during humid reaction conditions. These include, formation of $\text{Pd}(\text{OH})_2$ due to the presence of water leading to loss of active sites [148, 160, 162, 181], or morphological changes to the active PdO particles due to the formation of smaller particles or flattening of the original spherical particles [183], or the surface reconstruction of the PdO sites from the coordinatively unsaturated sites to fully coordinated sites [187, 188]. Another reason could be sintering of the nanoparticles due to higher temperatures [148], however as reported by Stotz et al. [168], this would require that the size of the PdO nanoparticles would need to be abnormally large to exhibit the loss in activity observed in the case of $\text{PdO}/\text{Al}_2\text{O}_3$. The formation of hydroxyls is a widely recognized as the primary cause of inhibition under humid conditions. However, recent studies [183, 184] suggest that other factors such as, morphological changes in the Pd phase may also play a significant role. While the exact reason for the loss in active sites is unclear, experimental evidence indicates that there is a reduction in the number of active sites during the light-off under humid conditions [149]. It is important to highlight that the microkinetic model used in Fig. 5.2 accounts for the blocking of active sites through both the formation of surface-bound H_2O species and the adsorption of gas-phase water under humid conditions. Therefore, any further decline in the catalytic activity must stem from mechanisms beyond simple site-blocking, such as the irreversible deactivation of active Pd_{cus} sites due to formation of $\text{Pd}(\text{OH})_2$ or fully coordinated sites, which do not exhibit activity towards methane oxidation.

When numerically solving the reactor model equations with the microkinetic model in the DETCHEM simulation package [71], the overall rate of production or consumption of the species is scaled by a factor known as $F_{\text{cat}/\text{geo}}$ (Eq. 2.18), to account for the higher

surface area encountered in porous samples. For a packed bed reactor, it is defined as the ratio of the available catalytic area of the active metal to the geometrical surface area of the catalyst bed including the support particles. The value of $F_{\text{cat/geo}}$ needs to be defined in the simulation input file based on the catalyst properties. Accurate estimation of the available active metal area is difficult under the dynamic reaction conditions and would require sophisticated characterization techniques. In lieu of that, one can obtain the values of $F_{\text{cat/geo}}$ with changing reaction conditions by optimizing the values based on the comparison of the simulated data with the experimental data. It is to be noted, that in most cases the calculated value of $F_{\text{cat/geo}}$ using chemisorption or imaging techniques of the as-prepared catalyst samples is sufficient for use during the simulations. However, in the case of methane oxidation over PdO, during the additional degreening step before the light-off measurements, performed at a high temperature under dry and lean conditions, the change in dispersion of the PdO nanoparticles would likely be significant compared to the as-prepared samples. More importantly, with changing reaction conditions and in the presence of water, when the deactivation phenomenon is more pronounced, the consideration of $F_{\text{cat/geo}}$ as a fitting parameter during simulations is appropriate to obtain agreement with experimental observations, in the absence of in-situ or operando characterization [149].

The optimization of the $F_{\text{cat/geo}}$ parameter used as an input in the numerical model to reproduce the performance under the experimental conditions can be achieved by utilizing gradient-free optimization algorithms, similar to the kinetic parameter optimization demonstrated earlier in this thesis. However, since only a single parameter is being optimized in this case, gradient-based algorithms offer a more efficient approach by guiding the optimization towards the optimal solution. Additionally, this would serve as a demonstration for the potential benefits of such an approach for future applications. When employing an out-of-box software for performing simulations, such as the DETCHEM software package [71] used in this work, users generally do not need to formulate the governing equations on their own and hence, cannot directly access the gradient information needed for utilizing gradient-based optimization approaches. Additionally, in case the number of parameters for which gradient computation is required is large, unlike the cur-

rent application, then the computational effort and time involved in solving the resulting additional ODEs would be substantial. Hence, the use of machine learning-based surrogate models is often a more scalable alternative, which could easily be used to calculate the gradients during the optimization procedure. Here in this work, the development and application of a surrogate model is demonstrated for the modeling of methane oxidation on a PdO/Al₂O₃ catalyst.

5.2 Experimental Data

The experimental data used in this work are taken from the study of Keller et al. [149] for PdO/Al₂O₃, which investigated methane oxidation over PdO/Al₂O₃ in a packed bed reactor under lean conditions. The catalytic tests were conducted with varying concentrations of H₂O (0–12 vol.%) and a temperature ramp of 3 K min⁻¹ between 500 and 825 K. Prior to testing, the catalyst samples were degreened under reactive conditions (3200 ppm CH₄, 10 vol.% O₂ in N₂) at 825 K to ensure comparable catalyst properties across samples used at different conditions.

The tests were performed in a packed bed reactor containing 300 mg of PdO/Al₂O₃ with a metal loading of 2.3 %. The bed was diluted with 700 mg of quartz to prevent hot-spots within the reactor. The resulting catalytic bed had a length of 1.5 cm and the internal diameter of the channel was 8 mm, with a bed porosity of approximately 56 %. The average diameter of the bed particles was 200 µm. Transmission Electron Microscopy (TEM) measurements indicated an average PdO nanoparticle size of 1.7 nm. The experimental setup was designed to minimize mass transfer limitations.

5.3 Methodology

A schematic representation of the methodology is shown in Fig. 5.3, which is used to obtain a reliable surrogate model and its subsequent application in optimization of the $F_{\text{cat/geo}}$ parameter. The methodology involves generating a robust dataset for training the machine

learning-based surrogate model and validation of the trained model. Once a surrogate model is obtained that has comparable performance to the numerical simulation model, it is used to obtain the gradients of the relevant model outputs with the $F_{\text{cat}/\text{geo}}$ parameter which is fed to a gradient-based optimization algorithm to search for the optimum values of $F_{\text{cat}/\text{geo}}$ to minimize the error between the simulated data and the experimental data with the changing reaction conditions during the light-offs. The following subsections outline each step in detail.

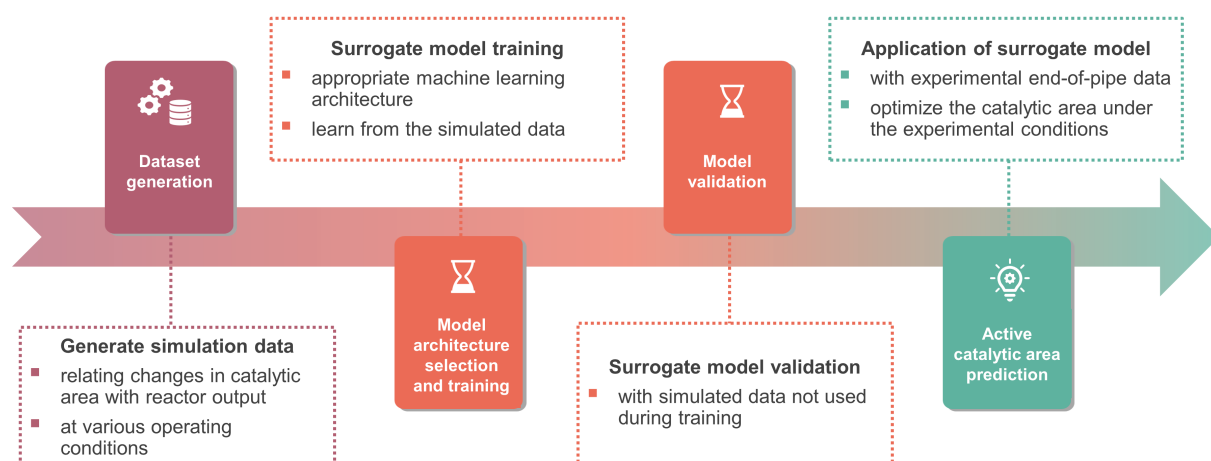


Figure 5.3: Schematic representation of the surrogate model development and application workflow.

5.3.1 Data Generation

A crucial requirement in the development of a neural network-based surrogate model is the availability of high-quality dataset for training. Based on the available literature, it is evident that the available catalytic area during the light-offs change as the experimental conditions are changed and it is likely to decrease with the increase in water concentration in the feed [149]. In this context, the decline in the catalytic performance at higher temperatures also indicates that the available catalytic area might decrease as a function of the reactor temperature. However, the extent of this decrease remains uncertain, as does the possibility of it varying along the length of the reactor. Therefore, a dataset was generated through simulations of the packed bed reactor model with variations in several input parameters, including defining sections of catalytic bed with decreasing $F_{\text{cat}/\text{geo}}$ from

one section to another. The input parameters and the range of their variation are listed in Table 5.1.

Table 5.1: Details on the variation in parameters during the data generation.

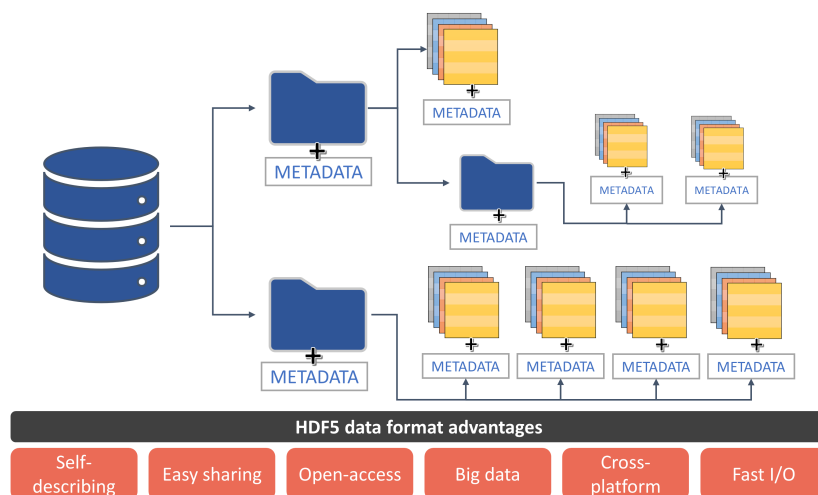
Input parameter	Range of values and units	Step
Temperature	450–900 K	5 K
H ₂ O mole fraction in the feed	0–12 vol. %	1 vol. %
Reactor length	0.01–0.02 m	0.0005 m
$F_{\text{cat/geo}}$	5–100 % of reference value	5 % or 3 %
Number of sections with different $F_{\text{cat/geo}}$	2–5	1
Section length	Uniform/Random	-

The generated data are essentially the outputs from running the simulations using the DETCHEM^{PBR} code with the kinetic model for PdO/Al₂O₃ [168] under varying inlet and reactor operating conditions. In order to reduce the complexity in the dataset and focus the surrogate model on learning the dependency of $F_{\text{cat/geo}}$ on the output, certain input parameters were kept constant. These included the input mole fraction of reactants other than H₂O, porosity of the catalytic bed, reactor diameter, particle diameter, and pressure. A Python-based script [110] was used to parallelize and automate the various steps in the generation of the dataset namely, the generation of the input files needed for DETCHEM^{PBR}, the execution of the simulations, the extraction of the relevant data from the output files, and the storage of the data in an appropriate data format (HDF5) to make them compatible for training the surrogate model and ensure adherence to FAIR principles [41]. Overall 2,739,828 simulations were performed to generate the complete dataset. The simulations were performed using an AMD Ryzen Threadripper 3990X processor, leveraging 10 cores in parallel for computations, and required approximately 58 h to generate the dataset.

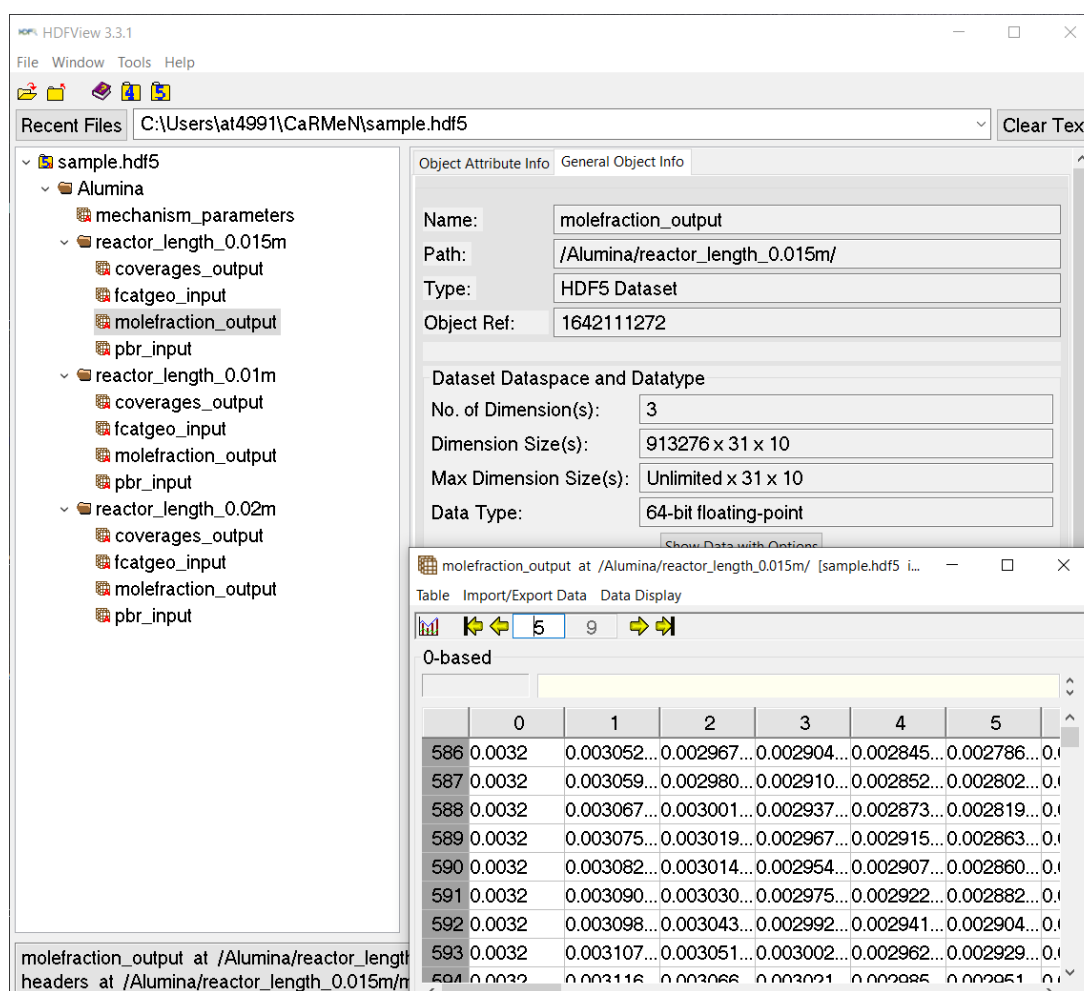
5.3.2 Data Storage

The primary outputs during the simulation of methane oxidation in a packed bed reactor with a catalytic bed of PdO supported on Al_2O_3 particles, are the mole fractions of the gas-phase species and the surface coverages of the surface species, along the length of the reactor. Hence, the data needed to be stored as three-dimensional arrays of the following shape = [Number of sample points (N), Number of length-steps (L), Number of variables (D)]. The first dimension of the array corresponds to the total number of simulations with variation in any of the input parameters. The second dimension in the dataset corresponds to the resolution of the axial coordinate. In this work data was captured at every 0.5 mm of the reactor length. The third dimension corresponds to the number of variables (or features) in the dataset including, the temperature, the mole fractions of the gas-phase species, the coverages of the surface species, pressure, velocity, residence time, and the $F_{\text{cat/geo}}$ value at each axial point within the reactor. Since, the number of simulated sample points are large, the dataset is considered to be big data and without a proper data storage architecture, it would lead to memory and performance issues during model training. Therefore, the Hierarchical Data Format version 5 (HDF5) [189] was chosen to store the dataset so as to streamline its use during training and ensure adherence to the FAIR [41] principles for data storage and reuse.

The HDF5 data format is commonly used in training deep learning models with big data and offers several advantages (Fig. 5.4a). HDF5 data format is an open data format, useful for storing large and heterogeneous data, which can be organized hierarchically in groups. The format is self-describing meaning all elements of an HDF5 file may have an associated metadata needed for understanding the data contained within the element. HDF5 supports data slicing, enabling the extraction of subsets of data for processing without requiring the entire file to be loaded into memory. This attribute is especially useful during the surrogate model training where batches of data are sampled and processed. Fig. 5.4 demonstrates the data organization and the screenshot of the data as viewed using the HDFView software [190], a visual tool for viewing and editing HDF5 files.



(a)



(b)

Figure 5.4: (a) Illustration of Hierarchical Data Format version (HDF5) structure and (b) screenshot of the dataset visualized in HDFView.

5.3.3 Surrogate Model Architecture Selection

Given the sequential nature of the generated dataset containing reactor outputs along the length of the reactor, neural network architectures that are capable of learning dependencies across the various dimensions in the dataset and output the spatially-resolved data are required. Such architectures are commonly used in the field of natural language processing (NLP) and have also been showcased to be useful in multi-variable forecasting tasks such as weather prediction [191, 192]. Several deep learning architectures were explored in this work which are briefly summarized in Table 5.2.

Table 5.2: The various deep learning architectures used in this work.

Architecture	Long Short-Term Memory (LSTM)	Crossformer	Mamba2
Type	Recurrent neural network	Transformer	State-space model
Advantages	Effective in learning long-term dependencies in sequential data	Able to learn dependencies across features in sequential data	Learns the state of the system over time with reduced computational complexity

The Long Short-Term Memory (LSTM) [193] networks are a type of recurrent neural network (RNN) [194], designed for learning long-term dependencies across sequential datasets. In general, an RNN incorporates a looping mechanism, which allows operation over a sequence of vectors. This looping mechanism is analogous to an unrolled neural network which re-uses the network parameters (i.e. the weights and the biases of the layers in the network) across each step to propagate information through the sequence. Therefore, the output of an RNN is influenced by the “history” of the inputs that were fed to it. RNNs try to learn this history by updating a hidden state vector every time information from a new step is given as inputs to it, and pass this updated hidden state to the next step. However, vanilla RNNs (i.e., the most simplest form of RNN, with a single hidden state) tend to lose information from earlier steps in larger sequences, a limitation known as the vanishing gradient problem.

To overcome this challenge, LSTM networks [193] were developed which had a more sophisticated gating mechanism in its cell to update its memory, to retain information over large sequences. The long-term memory of an LSTM cell is termed as its cell state. At each step, first the current input at that step and the hidden state of the previous step is used to calculate the candidate memory cell. This is then used to update the cell state via the gating mechanism. A typical LSTM cell consists of three gates: input gate, forget gate and output gate. The input gate determines how much of the new information from the current step should be stored in the memory, while the forget gate controls how much of the information already stored in the memory from the previous steps need to be retained. The output gate is then used to determine how much of the stored memory is allowed to be passed on to the next step as the new hidden state. Given the relatively short sequence lengths in the dataset, the LSTM architecture was selected as one of the surrogate models for its simplicity and fast training time.

Unlike RNN-type networks, which handle sequential data step-by-step in a progressive manner, transformer-based neural networks process them all at the same time using a self-attention mechanism, making them significantly faster and efficient in handling large sequences compared to RNNs. Through the self-attention mechanism, the transformer networks learn to weigh the importance of all the steps in an input sequence for generating the output, enabling them to retain information over very large sequences. Since, all steps in the sequence are processed at the same time, they lose the order-information which is explicitly present in the RNNs through their recurrent connections. Therefore, transformers utilize embedding layers with positional encoding to capture this information. With these capabilities, transformers become particularly powerful for tasks requiring fast computation and contextual understanding of large sequences of data, such as machine translation and text summarization.

While transformers excel at learning long-term dependencies within a sequence, they can only implicitly capture cross-channel dependencies (i.e., relationships between various features of the sequential data) through their embedding layers. This is where the Crossformer [195] architecture is more useful. Crossformer builds upon transformers, by explicitly modeling the cross-channel dependencies across sequences, enabling them to handle

multivariate time-series datasets more efficiently. These datasets comprise multiple sequences of data over time, and are commonly found in domains such as finance, weather forecasting, and energy analytics, requiring understanding of the inherent patterns within the dataset not only across time but also across multiple variables. Hence, Crossformer was selected to be one of the architectures for training the surrogate model, since in order to efficiently model the reactor outputs, the model needs to learn the complex relationships across different variables of the spatially-resolved data such as the temperature, the velocity and the reaction environment at a particular point in the reactor.

The self-attention mechanism used in transformer-based networks introduces significant computational complexity ($\mathcal{O}(L^2)$) during training, as it requires calculating the attention values for each step in relation to all the steps in the sequence. In the domain of NLP, where the number of steps (commonly known as tokens) can reach up to millions, this quadratic scaling can lead to slow training. To address this challenge, the Mamba model [196], a selective structured state-space model (SSM), has shown superior performance by achieving linear scaling with sequence length. State-space models strive to learn the state of the system as it evolves over time. The state of the system refers to the variables which when combined with input variables, determine the behavior of the system in future. Essentially, the state of a system is a compressed version of the history of a system. The concept of state in SSMs is similar to the hidden state vector used in RNNs, however, they differ in how the state is computed. SSMs are capable of maintaining a dynamic state of the system and learn dependencies for much larger sequences, by employing a selective mechanism, which allows the model to determine how much of the new input is relevant for the desired output. Moreover, the updated Mamba code (Mamba2) [197] allows simultaneous update of the state across multiple features, bridging the gap between state-space models and transformers, while offering improved scalability without the burden of quadratic complexity. Therefore, given its computational advantages and architectural alignment with the current application, Mamba was also selected for exploration as a potential surrogate model.

5.3.4 Surrogate Model Training

All the three architectures detailed above, i.e., LSTM, Crossformer and Mamba, were used for surrogate model training to find the best performing architecture. The following procedure was followed for all architectures involving the steps related to data preprocessing, model training, and validation. The models were built and trained using the Pytorch library [198] for the Python programming language [110]. In the data preprocessing step, a **Dataset** class is created that is used to prepare the dataset for training. In this **Dataset** class, the HDF5 file containing the dataset is read and converted into tensors of spatial data for each feature. These are thereafter standardized using Eq. 5.1 in order to scale the data to have a mean value of 0 and a standard deviation of 1. This step helps ensure that all features are on the same scale during the model training. Therefore, the outputs of the surrogate model need to be de-normalized to obtain the original values during inference (i.e., when the trained model parameters are used for prediction without further update).

$$X_{std} = \frac{X - \mu}{\sigma} \quad (5.1)$$

In Eq. 5.1, X_{std} is the standardized value, X is the original value of the sample point for a given feature, and μ and σ are the mean and standard deviation of all data points for that feature, respectively. Before training, the dataset was split in an 80:20 ratio to obtain training data and validation data, respectively. The validation data was further split in a 50:50 ratio to obtain a test dataset, reserved as the unseen samples on which the final model performance is tested. The validation set excluding the test set is used to evaluate the model after each training loop. The test set is used to estimate the generalization error of the model, as described in Section 2.4. Pytorch's **Dataloader** class is used to load and shuffle batches of data for efficient processing. Since the dataset is sequential in nature with variable reactor lengths and spatial points in the reactor (cf. Table 5.1), padding operation [199] was also performed to obtain the same size for the number of length-steps for each batch.

During a typical deep learning training procedure, data is processed in mini-batches for multiple number of epochs, where each epoch means that the model has seen the complete

training data once. In this work, all models were trained for at least 50 epochs. Each mini-batch consists of small subsets of the full sequences for all features, on which the model learns iteratively. After each epoch the batches are shuffled again to avoid overfitting. During each epoch, the model makes predictions (known as the forward pass), which are compared with the true output values (also known as the ground truth value) through a predefined loss function. Typical loss function include, mean squared error, root mean squared error, and cross-entropy loss, among others, based on the type of the task. During the forward pass, Pytorch stores a computational graph for all the operations performed as the input is passed through the surrogate model architecture to obtain the final model output and the loss value. After the calculation of the loss, the gradients of the loss function with respect to the model parameters are calculated, using the computational graph via backpropagation (known as the backward pass), and based on the gradients, the model parameters are updated using an optimizer.

In this work, the mean squared error was used as the loss function to compare the model predictions with the ground truth, and the Adam optimizer [102] was used to perform parameter update after each epoch. The loss function for the spatially-resolved data is calculated through Eq. 5.2 as mean squared error (MSE) between the predicted ($\hat{y}_{n,l,d}$) and the ground truth value ($y_{n,l,d}$) for all N samples, L length-steps, and D features,

$$\mathcal{L} = \frac{1}{N \cdot L \cdot D} \sum_{n,l,d} (\hat{y}_{n,l,d} - y_{n,l,d})^2. \quad (5.2)$$

The model weights are saved as checkpoints after each epoch, and as the best model whenever the loss is improved, ensuring that progress was not lost in case model training was interrupted.

As the dataset contains spatially-resolved data where the input data is known only at the inlet at $z = 0$, the reactor output at any given point in the reactor is to be calculated based on the previous points, hence the complete training of all the three architectures is performed in an autoregressive manner. During an autoregressive training, the model predictions at one step (here, point in the reactor) is used as input for the next step, instead of using the ground truth values. Therefore, during each epoch, for each mini-

batch of sequences with total length-steps L , predictions are made in a loop as one length-step at a time. The inlet data at $z = 0$ is first fed to the model, which then predicts for the next step, $z = 1$, and continues iteratively until predictions are made for $z = L$. Within this loop at each length-step $z = l$, the loss function is calculated between the predicted values and the ground truth value. After the final length-step loss calculation, the total loss averaged over the full sequence in the mini-batch is used for the backward pass, followed by the update step. Due to autoregressive training, the errors accumulate with each length-step and hence, the models are harder and slower to train in comparison with the typical training approach where ground truth values are used.

After each training loop, the model performance is evaluated on the validation dataset in the `eval` mode, where gradient calculations are not performed and only the model performance is tested on samples not seen during training. As the model trains, the difference between the training and validation loss reduces. Once the losses are converged, model training is complete and the saved model weights are used for inference on unseen data. The model performance is examined on the unseen data and compared with other models to obtain the best performing surrogate model.

The surrogate model training was performed on the high-performance computing cluster “Helmholtz AI computing resources (HAICORE)@KIT”. The deep learning models were built using the libraries `Pytorch` 2.3.1 [198], `mambapy` 1.2.0, and `mamba-ssm` 2.2.2 in Python [110]. Other additional Python packages such as `matplotlib` 3.7.5 [200], `NumPy` 1.24.4 [201], `pandas` 2.0.3 [202], and `h5py` 3.11.0 [189] were used for processing of data and plotting. The Distributed Data Parallel (DDP) in `Pytorch` was used to parallelize model training on multiple Graphics Processing Units (GPUs) to improve the performance.

Reduction of training data

It was initially considered that it was possible that the catalyst properties may be changing along the length of the reactor and therefore, using spatial variations in the value of $F_{\text{cat/geo}}$ in the catalytic bed during the simulation of light-offs might help obtain a better

agreement with the experimental data. Therefore, the generated dataset consisted of variable sections of catalytic zones in the reactor with decreasing value of $F_{\text{cat/geo}}$. However, during the surrogate model training with the various architectures, it was observed that the surrogate model did not learn the spatial variation of the $F_{\text{cat/geo}}$ parameter accurately. The model also struggled to learn the constant temperature trend along the length, even though the simulated data were for isothermal reactor temperatures. To ensure that this was not because of the accumulated errors at each length-step during autoregressive training, the ground truth values of temperature and $F_{\text{cat/geo}}$ at each length-step were given during the model training for comparison. Such an approach where the ground truth values are given to the model for prediction of the next step is known as teacher forcing.

In both approaches, the model training remained unaffected, and the model outputs were the same. This indicated that the spatial variation of $F_{\text{cat/geo}}$ used during dataset generation did not significantly influence the simulation results. The comparison between the autoregressively-trained outputs and the teacher-forced outputs suggested that only the temperature value and the $F_{\text{cat/geo}}$ value given as inputs i.e., at $z = 0$ was important for the surrogate model predictions, as the model outputs remained consistent across both approaches. Therefore, it was decided to reduce the dataset size by using only one reactor length with a constant value of $F_{\text{cat/geo}}$ throughout the reactor length.

The reduction in the dataset to constant $F_{\text{cat/geo}}$ and one reactor length i.e., $L = 0.015$ m significantly reduced the complexity and the time required to train the various surrogate model architectures. Using a single reactor length also helped minimize information leakage between the training and validation datasets, as full conversion is achieved near the reactor's inlet at higher temperatures. Consequently, data from longer reactor lengths would inherently include information from shorter lengths. Therefore, with the reduced dataset, the values of reactor temperature and $F_{\text{cat/geo}}$ were considered as inputs to the surrogate model and not predicted at the next length-steps, except in the case of the Crossformer architecture, which does not support different feature size in the input and the output sequences. Hence, the final surrogate models used in this work were trained with the reduced data containing overall 68,614 samples which resulted in the total number of data points considering the length-steps in the sequences to be 2,058,420.

5.3.5 Optimization of Active Catalyst Area

Once the surrogate model is trained and is validated well on unseen data, then the best performing model can be used in place of the simulation model (here, DETCHEM^{PBR}) for the optimization of the $F_{\text{cat/geo}}$ parameter under the dynamic reaction conditions during the light-offs. The optimization process is similar to the training of a neural network architecture, where the optimizer learns to update the input parameters whose values are unknown, instead of the model parameters as done during a typical model training. In this scenario, the loss function acts as an objective function for minimization of error between the surrogate predictions and actual experimental outputs. Therefore, during the optimization process, the surrogate model weights are kept constant and the input $F_{\text{cat/geo}}$ parameter is defined as a trainable parameter, which would be updated using an appropriate optimizer. The experimental data measured at the end of the reactor i.e., at $z = 0.015$ m for a given reactor temperature is used as the ground truth and used to calculate the loss function as expressed in Eq. 5.3, where $X_{\text{CH}_4, \text{surr}}$ is the value of CH_4 mole fraction predicted autoregressively by the surrogate model based on the inlet data provided as inputs, and $X_{\text{CH}_4, \text{exp}}$ is the experimentally measured mole fraction of CH_4 at the end of the reactor.

$$\mathcal{L} = (X_{\text{CH}_4, \text{surr}} - X_{\text{CH}_4, \text{exp}})^2 \quad (5.3)$$

The Adam optimizer, used during the surrogate training, was also used here for updating the $F_{\text{cat/geo}}$ value after each iteration. The total number of iterations for the optimization were kept to be 2000. The optimization process was performed for every temperature and inlet feed condition from 0–12 vol.% H_2O . For each feed condition, at least 20 temperature points were considered for optimization between 500 K and 800 K. The optimization process was stopped either when the set number of total iterations are exceeded or when the loss value is lower than a given threshold value (in this work, threshold = 10^{-5} with the scaled data).

For gradient-based optimization methods, it is imperative to start from a good initial point to avoid converging to a sub-optimal solution, especially when the objective function has multiple local minima or a noisy landscape. Therefore, for the optimization of how the

ratio of catalytically active area to geometrical area changes under the dynamic reaction conditions during the light-off at a given water concentration, it is essential to start from a good value of the initial ratio for the catalyst. As during the light-off, the catalyst properties change over time, i.e., with the temperature ramp and the conversion of CH_4 , the initial value of the catalyst surface area to be used for simulation would also need to change with change in the operating conditions. The initial active area at any given temperature T in the light-off would depend on how much of the active surface area was lost at the earlier temperatures because of the loss of active sites, either due to the presence of water or due to the conversion of CH_4 . The initial $F_{\text{cat}/\text{geo}}$ value for the temperature at the beginning of the experimental light-off for a given concentration of water were approximated from the characterization data of the as-prepared samples. Once an optimal value is obtained by the optimizer with help of the gradients from the surrogate model under the given reaction conditions (i.e., the reactor temperature and the inlet feed condition), the obtained optimal $F_{\text{cat}/\text{geo}}$ value then served as the initial $F_{\text{cat}/\text{geo}}$ value for the next temperature point and so on. This way the dynamic change in the catalyst properties during the experimental light-offs could be closely simulated.

5.4 Results and Discussion

5.4.1 Surrogate Model Performance across Various Architectures

In this section, the performance of the various deep learning architectures is compared on unseen samples of data that were not used in the model training and validation loops. Each architecture has a different set of hyperparameters, that are fixed before training is started. However, the optimal values for these hyperparameters are not known beforehand, hence multiple combinations of these hyperparameters need to be tested to find the optimal set, a process known as hyperparameter tuning. In this work, the study of several distinct architectures with multiple hyperparameters made a complete grid search for hyperparameter tuning computationally impractical. Instead, a manual search was performed within a predefined range of values of hyperparameters, by iteratively refining

hyperparameter combinations based on model performance. Table 5.3 shows the range of hyperparameters tested for each architecture. The following subsections discuss the various hyperparameters for each architecture and the results obtained with the optimal set of hyperparameters.

Table 5.3: The range of values of various hyperparameters used during the hyperparameter tuning.

Architecture	Number of hyperparameters	Hyperparameter name	Range	Best value
Crossformer	5	e_layers	2, 3	2
		factor	5, 10	10
		d_model	64 – 256	64
		n_heads	4, 6, 8	8
		d_ff	64 – 512	64
Mamba	4	n_layers	2	2
		d_state	64 – 256	64
		d_model	64 – 512	256
		d_head	8 – 64	64
LSTM	2	n_layers	1 – 4	2
		d_model	64 – 512	256

Crossformer

The crossformer architecture contains five hyperparameters that need to be tuned to obtain the best performing model. The hyperparameter **e_layers** corresponds to the number of encoder-decoder layers used in the architecture. Encoders and decoders are typical building blocks in transformer-based architectures. The encoder layers take the multi-variate sequences as input and generate a context vector to serve as a dense representation of the input data. The decoder layers on the other hand take these context vectors as inputs and learn to decode the output multi-variate sequences based on the information contained in the context vectors. In this work, the total number of encoder-decoder layers were kept small to keep the number of learnable parameters in the model

comparable to the number of training data points. If the number of learnable parameters are much larger than the data points, then the model would tend to memorize all data points rather than learning the inherent patterns.

As mentioned in Section 5.3.3, crossformer architecture aims to effectively capture both cross-time dependencies and cross-channel dependencies. This is achieved primarily through its Two-Stage-Attention (TSA) layer. The first stage in the TSA layer is the “cross-time stage” where multi-head self-attention (MSA) is applied to all time steps (here, length-steps) for each feature. The output from the cross-time stage becomes the input for the second “cross-dimension stage” in the TSA layer, where MSA is applied to all dimensions (or features) at each time step, to capture the cross-channel dependencies. In the process of applying MSA in transformer-based networks, every element in the input determines the attention values (referring to how important the element is for the output) for every other element including itself. Each head in MSA computes its own attention scores, enabling the model to learn various kinds of dependencies from the data. To reduce the high computational cost of attention calculation ($\mathcal{O}(D^2L)$) when the feature dimension D is large, crossformer introduces a fixed set of learnable router vectors that aggregate and redistribute attention values, lowering complexity to $\mathcal{O}(DL)$. The hyperparameter **factor** is the number of such routers in the crossformer model. The hyperparameter **n_heads** represents the number of heads in the MSA mechanism. The hyperparameter **d_model** represents the number of features in the embedding vector for each length-step. The value of **d_model** also determines the size the attention vectors computed in the TSA layer. The hyperparameter **d_ff** represents the size of the **Linear** layers used in the TSA mechanism.

After testing multiple values for the above mentioned hyperparameters, the best set of values for the hyperparameters were obtained (cf. Table 5.3). The best model had overall 418,883 trainable parameters and took approximately 47 h to train on 2 GPUs. Figure 5.5 demonstrates the variation in the MSE loss across all training and validation samples with each epoch. The model losses converged after 20 epochs and the MSE loss on the validation data was calculated to be 0.263. The significant difference between the training loss and the validation loss suggest that the model could not generalize well on

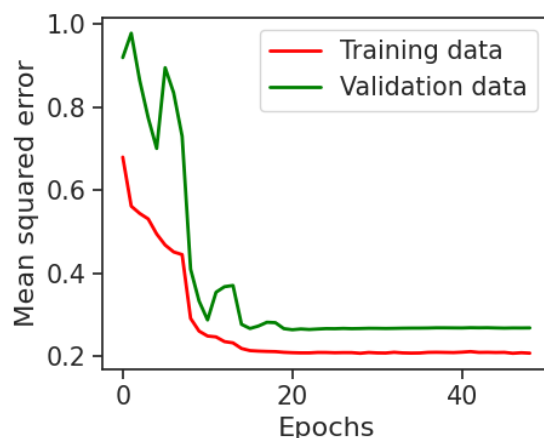


Figure 5.5: Training history of crossformer model with best set of hyperparameters.

unseen data. This is more clearly seen in Fig. 5.6, which shows the crossformer model predictions compared to the ground truth simulated values for a subset of features, for a randomly selected set of samples not used during training or validation. To reiterate from Chapter 4, in the nomenclature of the surface species, “a” represents the Pd_{cus} sites and “b” represents the O_{cus} sites of the supported PdO catalyst. The comparison between the numerically simulated and predicted spatial curves show that the crossformer model struggles to learn the complex reaction kinetics in the packed bed reactor. Since the crossformer model does not support using input and output sequences of different sizes, it was necessary to predict all features in the output including the parameters used as input in the simulations i.e., the reactor temperature and the $F_{\text{cat/geo}}$ parameter. As can be observed in the Fig. 5.6, the model does not accurately predict the isothermal behavior and the constant $F_{\text{cat/geo}}$ values. The crossformer model was able to predict the methane mole fractions under the conditions of full conversion quite well but performed poorly at low conversion temperatures. Additionally, it was unable to capture the water production trends, leading to the conclusion that the crossformer architecture was unsuitable as a surrogate to the numerical simulation model. It is possible that the model lacked sufficient complexity to capture the underlying trends in the data, or that the architecture itself was not well-suited for regression tasks of this nature. Furthermore, the significant training time in spite of parallel training on multiple GPUs, constrained the exploration of deeper network configurations.

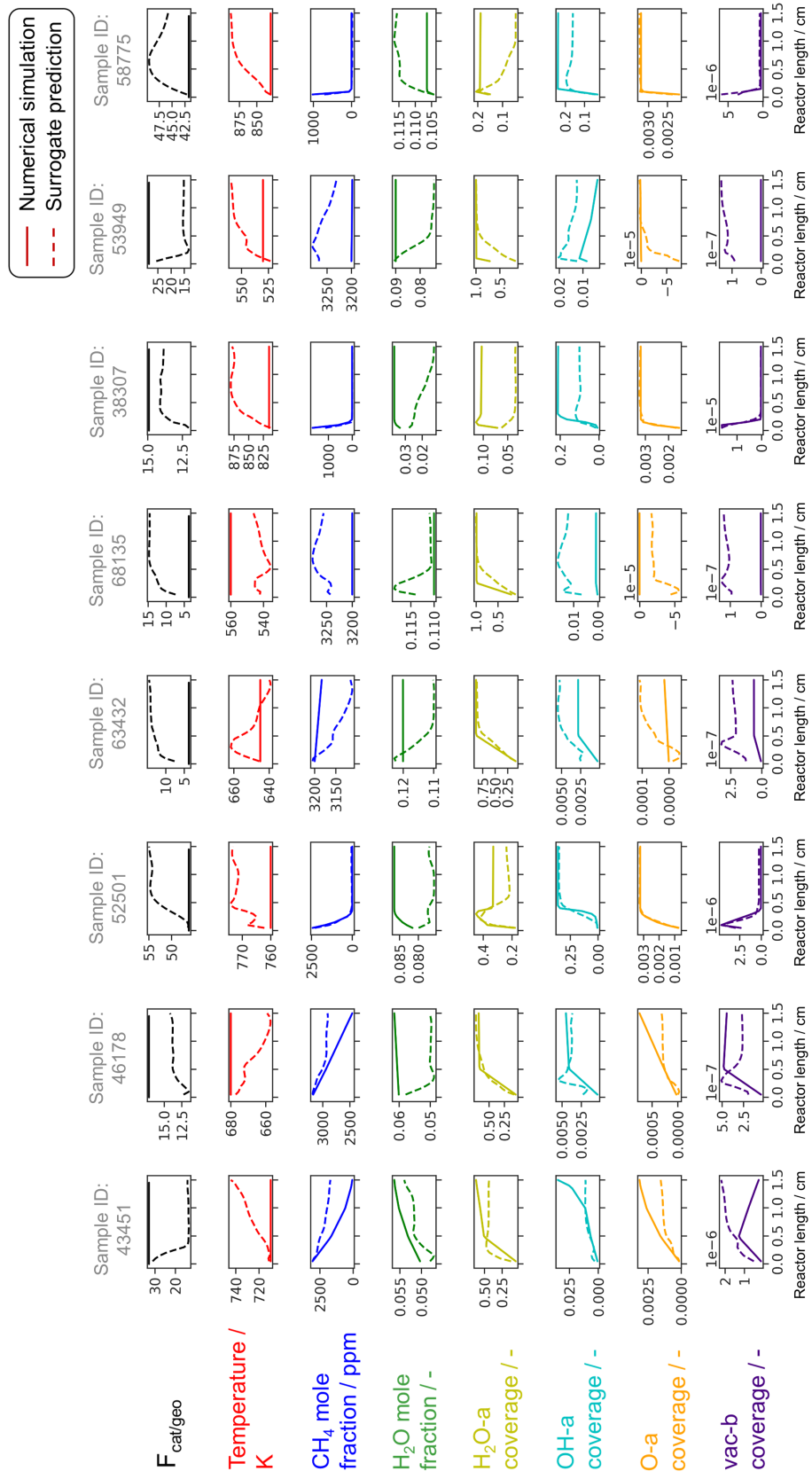


Figure 5.6: Comparison of the ground truth with the predictions from the crossformer model on unseen data.

Mamba

The Mamba architecture consists of four hyperparameters. The `n_layers` hyperparameter determines the number of Mamba blocks in the overall architecture. Each Mamba block implements a multi-head selective state-space model. The `d_state` hyperparameter specifies the size of the state vector used in the state-space computations within each head of a Mamba block. The `d_model` hyperparameter determines the dimensionality of the input and output vectors passed between the various Mamba blocks, similar to the embedding size in Transformer models. The `d_head` hyperparameter specifies the dimensionality of each head used in a Mamba block. The heads in Mamba are analogous to the heads in multi-head attention, except that here they are used to divide the input vectors of size `d_model` into smaller subsets of size `d_head`, enabling parallel application of the state-space models.

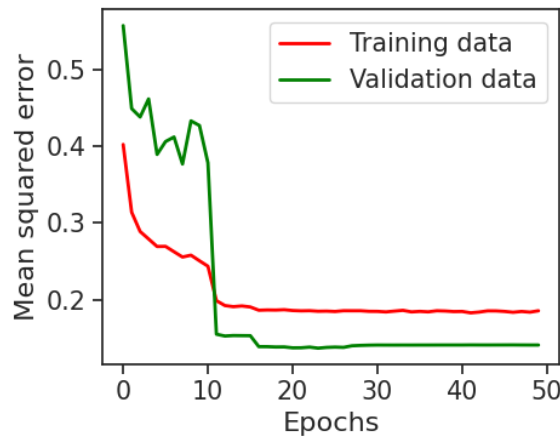


Figure 5.7: Training history of Mamba model with the best set of hyperparameters.

Fig. 5.7 shows the progression of the loss values with the training and validation datasets during the model training with best set of hyperparameters (Table 5.3). The validation loss at the beginning of the training was noisy likely due to the autoregressive training approach. However, both the training and validation loss converged after around 30 epochs. The minimum validation loss associated with the best model was 0.1366. The validation dataset in this case showed lower loss value compared to the crossformer architecture. The total number of trainable parameters in the best model were 880,719 and

the model took approximately 17 h to train on a single GPU. The time taken for training the Mamba model was significantly less compared to the crossformer architecture, since it does not depend on attention calculation for learning long term dependencies. Additionally, its hardware-aware implementation makes its training on GPUs significantly faster than transformer based architectures. The performance of the best model on the testing set samples are shown in Fig. 5.8. Since, Mamba could be configured to have different sizes for the input and the output sequences, the features namely the reactor temperature and the $F_{\text{cat/geo}}$ parameter were used only as inputs and not predicted with the outputs. The results show that, similar to the crossformer model, the Mamba model struggles to capture the water production trends, particularly at low conversion temperatures. However, the coverages of certain surface species, such as O-a and H₂O-a, were predicted reasonably well. Interestingly, while the model correctly captured the overall trend of methane conversion, it underpredicted the outlet concentrations. Therefore, the Mamba model was also deemed unsuitable to be used as a surrogate for DETCHEM^{PBR}. The reasons for the inadequate performance remain unclear, given the inherently black-box nature of the model and its limited interpretability.

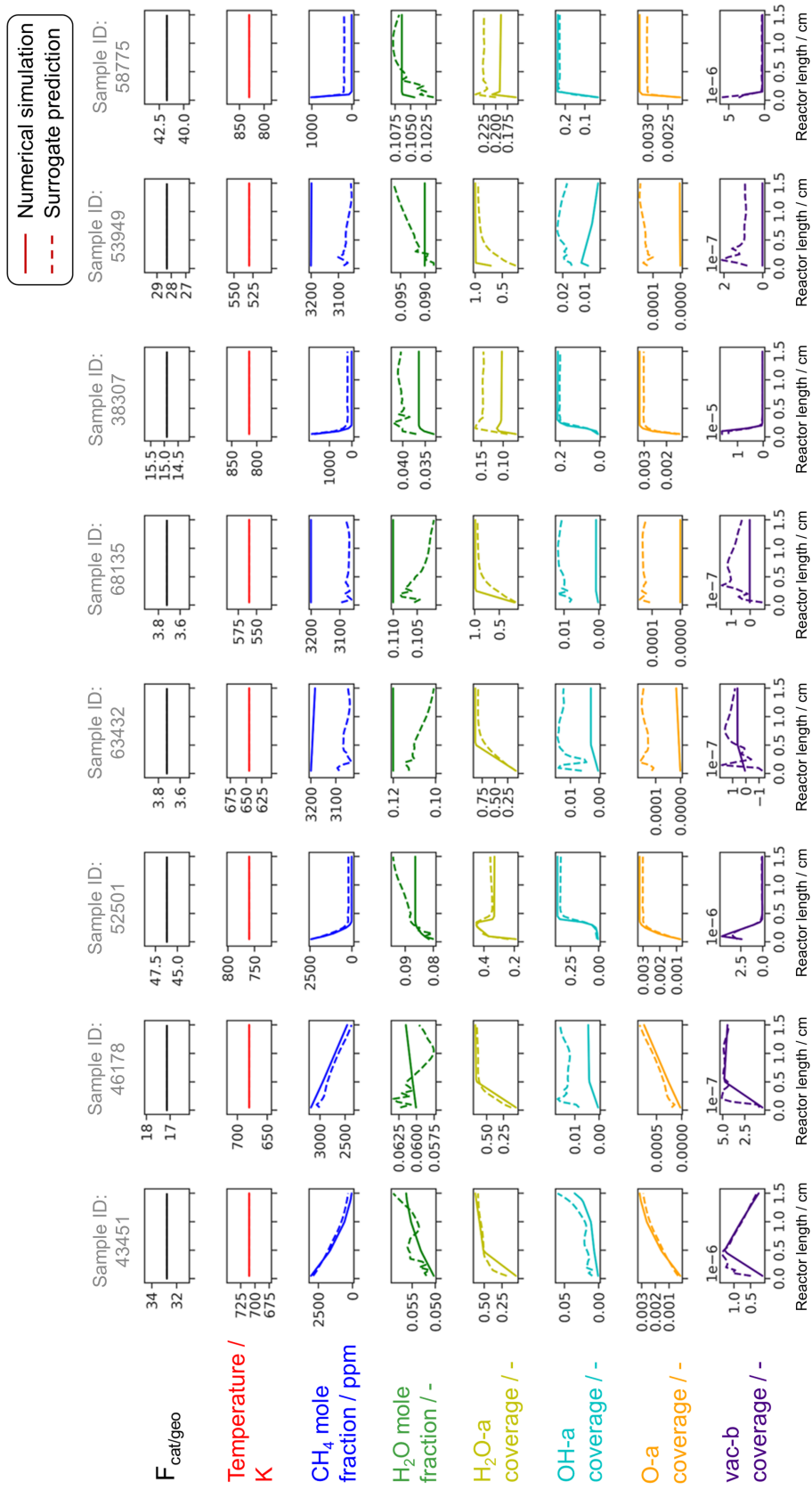


Figure 5.8: Comparison of the ground truth with the predictions from the Mamba model on unseen data.

LSTM

In comparison to the other models, the LSTM architecture has the lowest number of hyperparameters, namely `n_layers` relating to the number of LSTM layers and `d_model` relating to the dimensionality of the hidden state. During LSTM training, reactor temperature and $F_{\text{cat/geo}}$ were only considered as inputs to the model and not predicted. In order to improve performance of the model, a penalty was also imposed during training on the error in prediction of the mole fractions of methane and water, hence the loss function for LSTM model training had an additional penalty term as expressed in equation 5.4, where $\lambda = 10$, is the penalty weight,

$$\mathcal{L} = \frac{1}{N \cdot L \cdot D} \sum_{n,l,d} (\hat{y}_{n,l,d} - y_{n,l,d})^2 + \lambda \cdot \frac{1}{N \cdot L} \sum_{n,l} [(\hat{y}_{n,l,CH_4} - y_{n,l,CH_4})^2 + (\hat{y}_{n,l,H_2O} - y_{n,l,H_2O})^2] \quad (5.4)$$

Fig. 5.9 compares the penalized training and validation loss values after each epoch during the model training with the best set of hyperparameter values, as tabulated in Table 5.3. The best model had 832,287 trainable parameters and took approximately 6.5 h to train on a single GPU. The model converged after 25 epochs with a minimum validation loss of 0.155. The train and validation losses showed similar trend and converged values suggesting that the trained model generalized well.

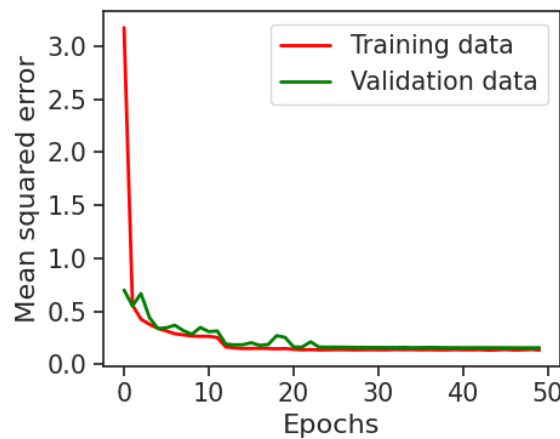


Figure 5.9: Training history of LSTM model with the best set of hyperparameters.

The LSTM model performed the best on unseen data samples compared to the crossformer and Mamba models as shown in Fig. 5.10. The additional penalty term contributed to more accurate predictions of methane and water mole fractions. Overall, the LSTM model was able to reproduce the general spatial trends across most conditions. Although the model exhibited slightly reduced accuracy at low conversion temperatures, the associated errors between the prediction and the ground truth were minimal. It is important to note that the comparison plots in this work are scaled to emphasize discrepancies, making even small differences appear more pronounced. Based on the performance on the unseen samples, the LSTM architecture with 2 layers and hidden state of size 256 was shown to be the best candidate for a surrogate model, among all the studied architectures. In order to compare the performance of the LSTM-based surrogate model to the DETCHEM^{PBR} simulation model at relevant experimental conditions, predictions were made at several temperatures between 500 K and 800 K for various water concentrations in the feed. Fig. 5.11 compares the predicted end-of-pipe conversion of methane by the surrogate model, the numerically simulated conversion using DETCHEM^{PBR}, and the measured experimental data under varying conditions. For the simulations and the surrogate predictions, a reference value of $F_{cat/geo} = 74.48$ was used, calculated based on the nanoparticle diameter of the as-prepared catalyst samples. The comparison shows that the surrogate model closely follows the simulated conversions using DETCHEM^{PBR} under all conditions and therefore, can be used for the optimization of the $F_{cat/geo}$ values based on the experimental data.

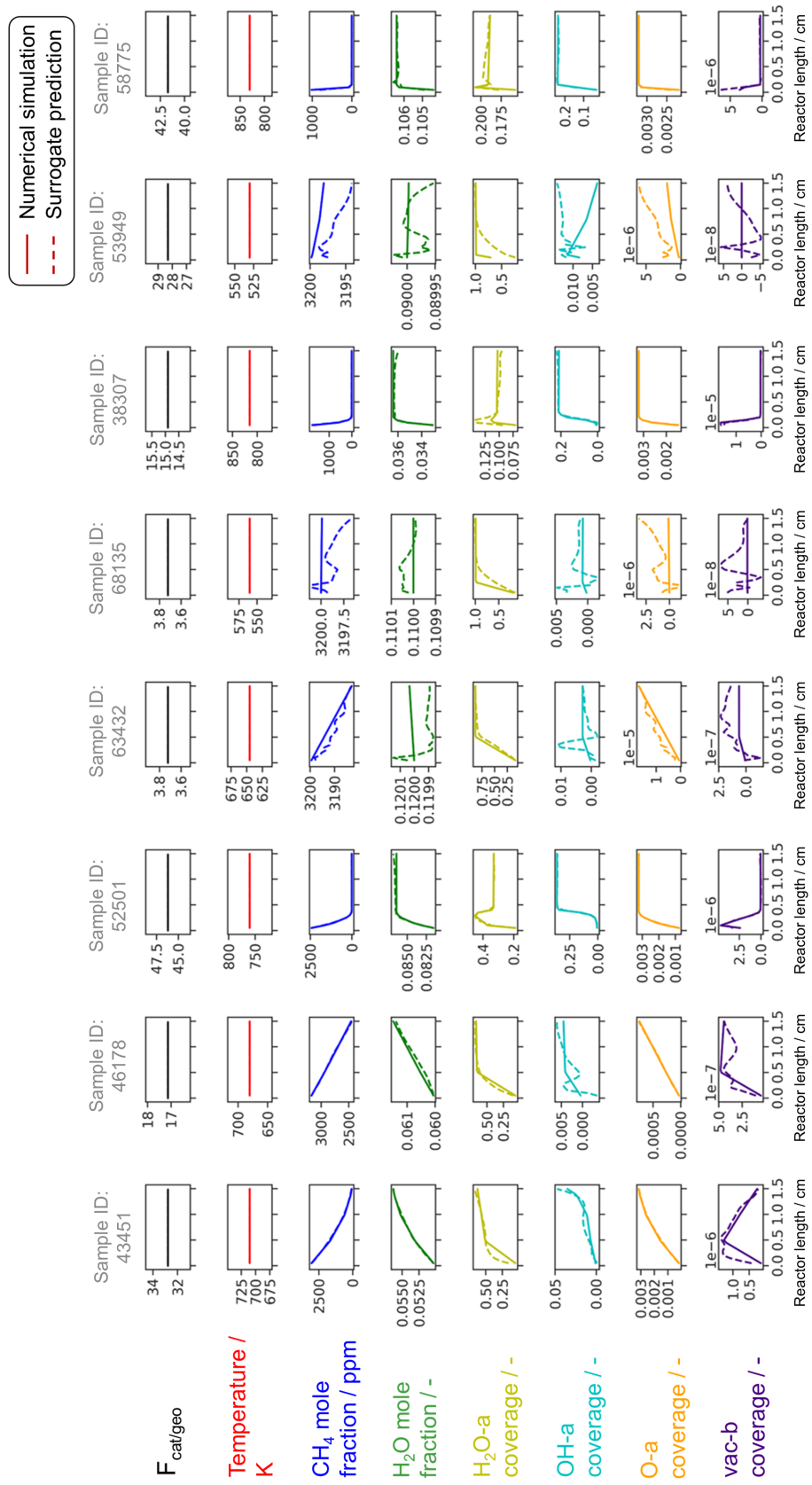


Figure 5.10: Comparison of the ground truth with the predictions from the LSTM model on unseen data.

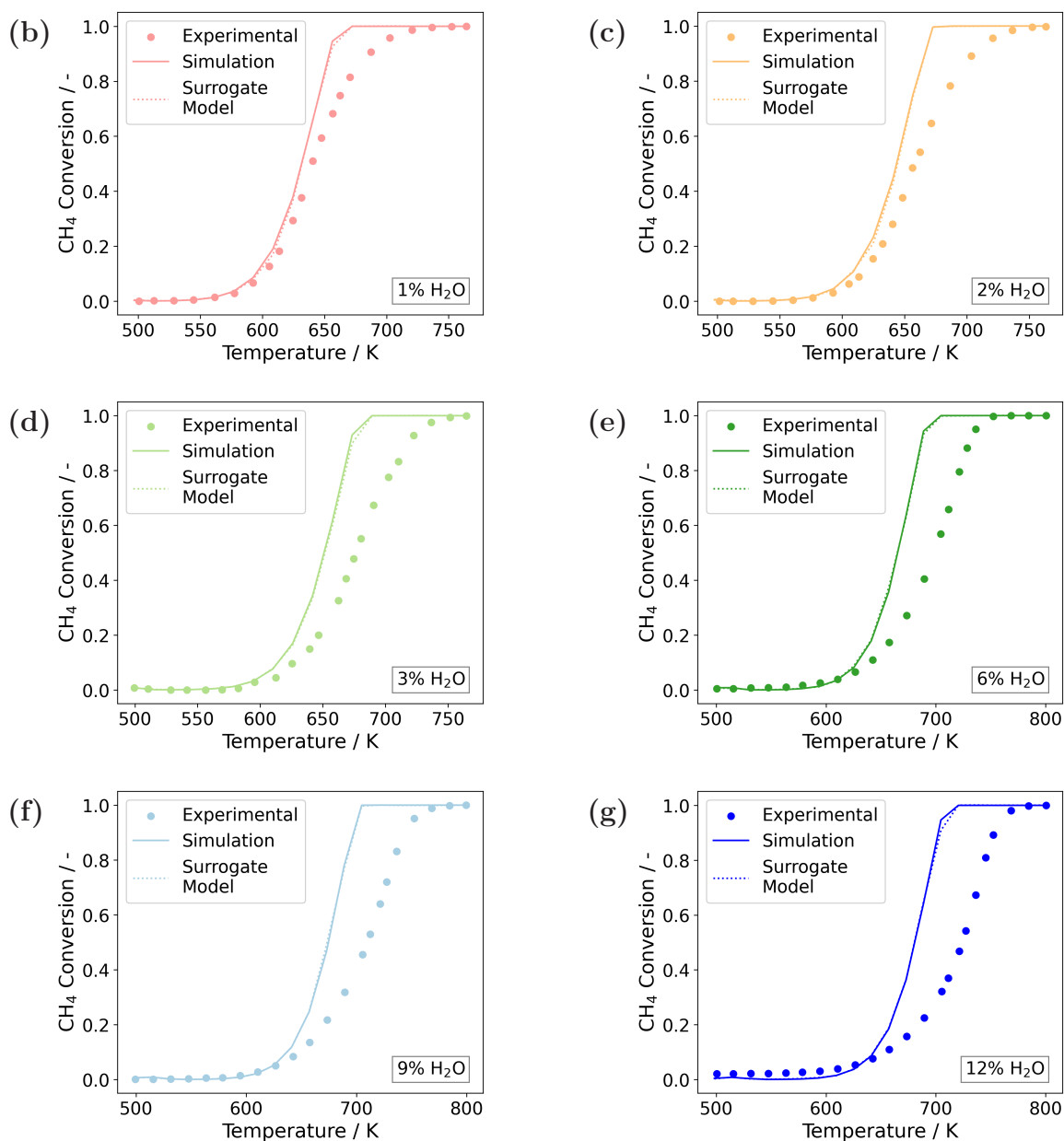


Figure 5.11: End-of-pipe performance of the surrogate under experimental conditions.

5.4.2 Simulation Results with Optimized Active Area

Keller et al. [149] in their study, suggested a correlation between the variation of $F_{\text{cat}/\text{geo}}$ and the water concentration in the feed. They reported that the catalytic performance under wet conditions may be predicted well if the loss in catalytic area due to the presence of water at the inlet is accounted for during the simulations. This loss can be incorporated

by scaling the $F_{\text{cat/geo}}$ parameter with a factor representing the percentage of active area remaining under wet conditions. This factor was obtained in the study [149] by fitting the simulated data at T_{50} (i.e., at 50 % conversion temperature). Fig. 5.12 compares the simulations and the surrogate model predictions of the conversion of methane at the reactor outlet under wet conditions based on the modified $F_{\text{cat/geo}}$ values suggested by Keller et al. [149] for various inlet water conditions, with the experimental values. The comparison shows that although the modified $F_{\text{cat/geo}}$ values do have a favorable impact on the simulation (and the surrogate predictions), but they also lead to significant deviations in the conversion values for higher concentrations of water. This indicates that the correlation considering only the loss of active sites due to presence of more water in the feed is not sufficient to accurately simulate the behavior during the light-offs. Moreover, the shift in the catalytic activity due to presence of water is predicted accurately by the kinetic model (Fig. 5.11). This modification of $F_{\text{cat/geo}}$ considering the loss in active sites only as a function of water concentration results in further shift of the activity to higher temperatures as evident in the Figures 5.12d, 5.12e and 5.12f. Specifically, the T_{10} values (i.e., the temperature at which 10 % conversion of CH_4 is achieved) for the feed with 9 vol.% water shifted to 675 K from the experimental value of 648 K. Therefore, to truly simulate the inhibition effect on PdO catalyst supported over alumina, it is necessary to incorporate also the dynamic change in the active sites as the catalyst is exposed to changing reaction conditions during the light-offs.

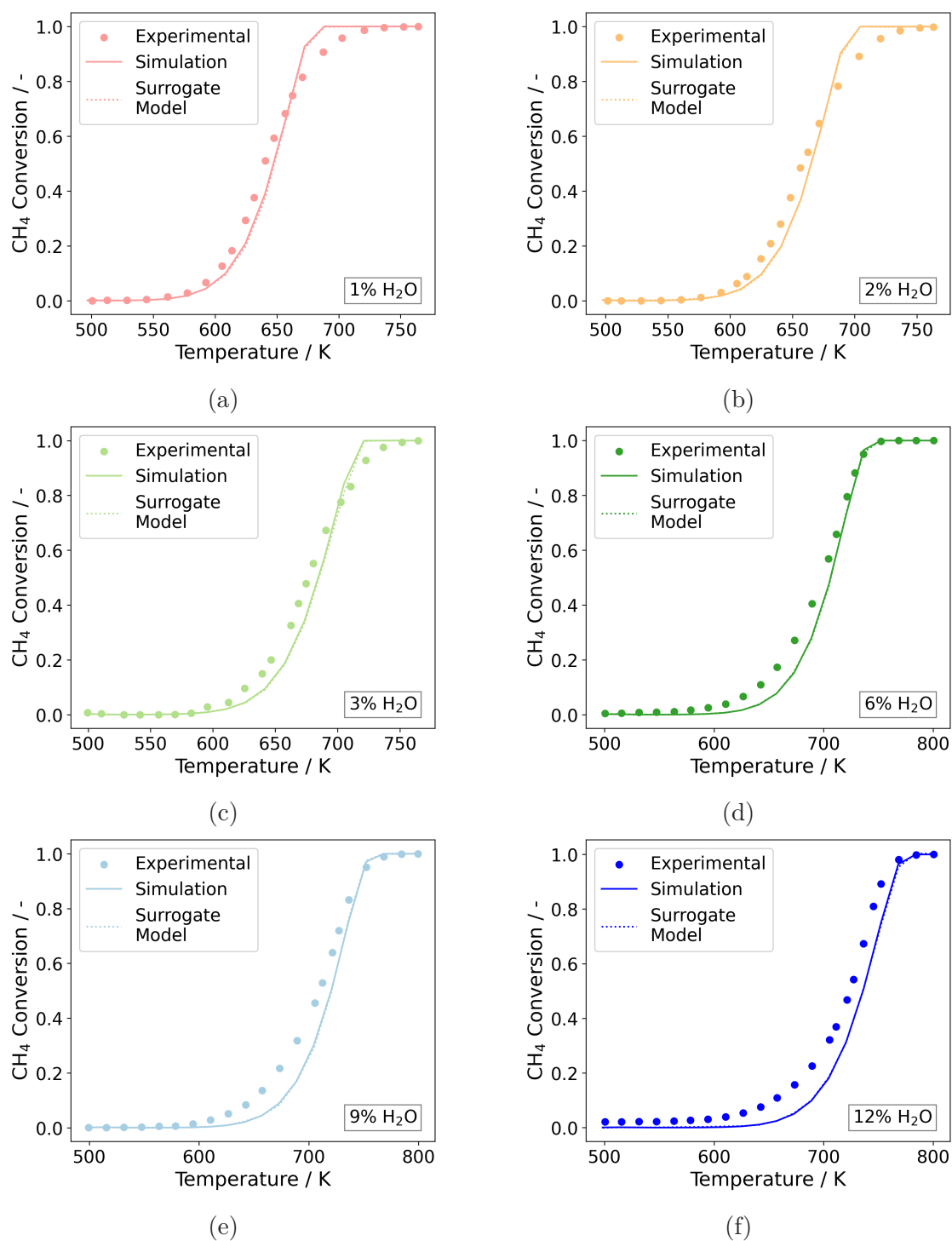


Figure 5.12: End-of-pipe simulated data under experimental conditions using the modified $F_{\text{cat/geo}}$ values based on the inlet water concentration (denoted in vol.%).

The $F_{\text{cat/geo}}$ values were optimized by minimizing the difference between the experimental end-of-pipe methane mole fractions and the predictions from the surrogate model. The optimization was performed for at least 20 temperature points for each feed condition. The resulting trends in the optimized $F_{\text{cat/geo}}$ values during light-off for various wet feed conditions, based on the experimental data, are illustrated in Fig. 5.13. In the figure, the light blue background highlights the temperature range where a variation in $F_{\text{cat/geo}}$ has an influence on the reactor outputs. The areas shaded in gray correspond to temperature regions where either the rates are too low to have any conversion or so high that the inhibition effects become negligible, therefore the $F_{\text{cat/geo}}$ values under these conditions are irrelevant. As shown in Fig. 5.13, the use of optimized $F_{\text{cat/geo}}$ values leads to a much closer agreement between the experimental light-off data and the simulations using DETCHEM^{PBR}, compared to simulations assuming a constant $F_{\text{cat/geo}}$ throughout the light-off. The optimized $F_{\text{cat/geo}}$ values generally decrease with increasing temperature, and the rate of this decrease depends on the inlet water concentration. Notably, at higher temperatures, the optimized $F_{\text{cat/geo}}$ values converge to approximately 10 across all water concentrations, indicating that inhibition effects are minimal in this regime, consistent with the findings of Mortensen et al. [183]. The discrepancies observed in simulations using a constant $F_{\text{cat/geo}}$ at high temperatures (Fig. 5.11) may also stem from internal mass transfer limitations not accounted for in the model, leading to overestimated reaction rates. The reduction in $F_{\text{cat/geo}}$ in the optimized case effectively lowers the predicted rates, aligning them more closely with experimental observations. Given that inhibition is negligible at elevated temperatures [145], the analysis of $F_{\text{cat/geo}}$ trends should primarily focus on the lower temperature range, where its impact is more pronounced. The Weisz-Prater number [177] calculated for these conditions showed values lower than 0.2 at all conditions except at T_{90} for both dry and humid conditions. At T_{90} , the values were estimated to be 0.29 and 0.32 for 0 vol.% and 12 vol.%, respectively. These values imply that internal mass transfer is not limiting under the studied conditions.

A comparison of the $F_{\text{cat/geo}}$ trends across different water concentrations in Fig. 5.13 reveals that the rate at which $F_{\text{cat/geo}}$ changes with reactor temperature is strongly influenced by the water content in the feed. With 1 vol.% water in the feed, $F_{\text{cat/geo}}$ ini-

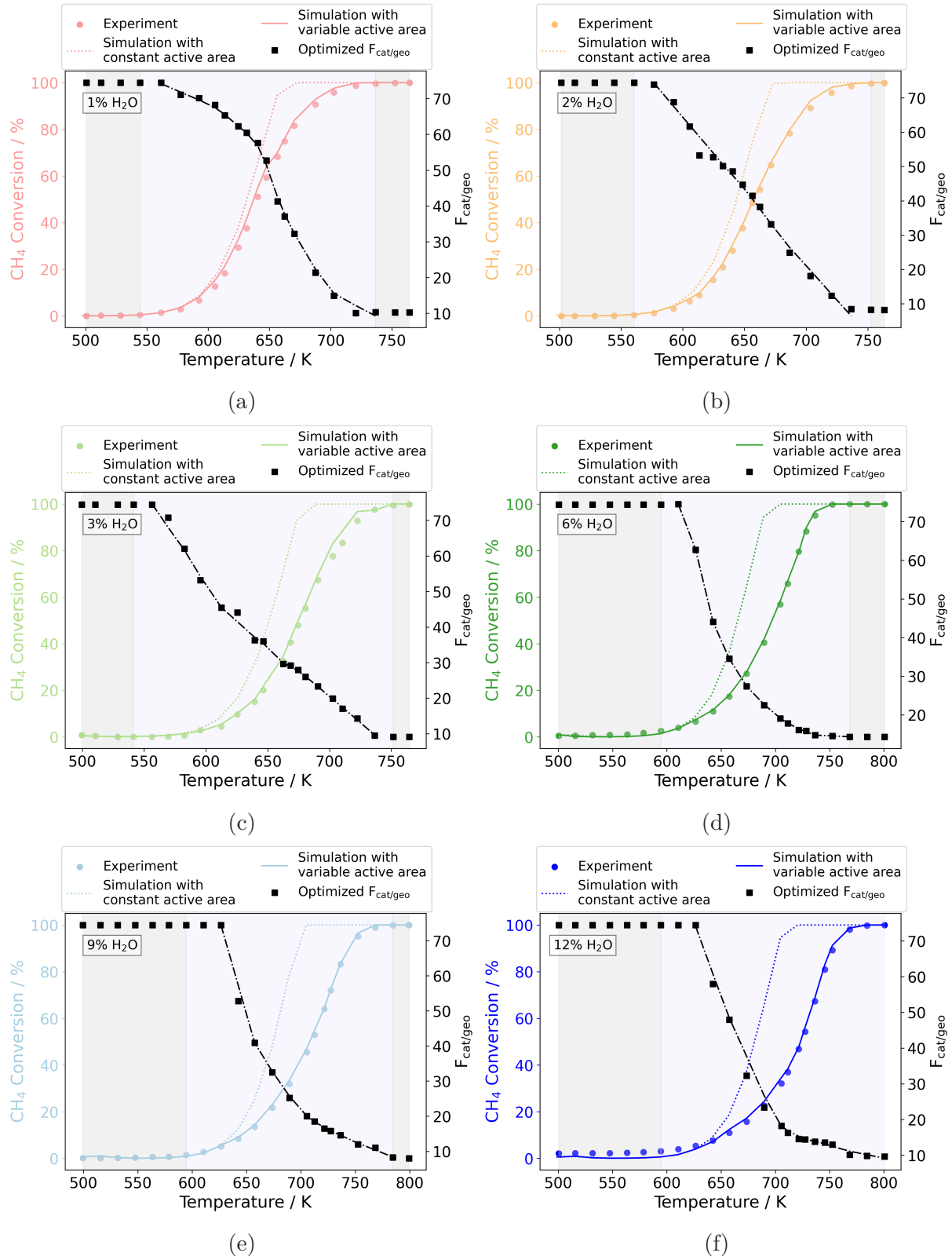


Figure 5.13: End-of-pipe simulated data with DETCHEM^{PBR} under experimental conditions using the optimized $F_{cat/geo}$ values through the surrogate model.

tially decreases gradually up to the temperature corresponding to approximately 60 % methane conversion. Beyond this point, the decline becomes steeper until full conversion is achieved. For feeds containing 2 vol.% and 3 vol.% H_2O , the decrease in $F_{\text{cat}/\text{geo}}$ follows an almost linear trend throughout the temperature range. However, at higher water concentrations, the behavior becomes distinctly non-linear. In these cases, $F_{\text{cat}/\text{geo}}$ exhibits a sharp initial drop followed by a more gradual decline as conversion increases. This effect is particularly pronounced at 12 vol.% water, where $F_{\text{cat}/\text{geo}}$ drops dramatically from an initial value of 74.48 to around 15 at temperatures corresponding to only 25 % conversion. This suggests that higher water content in the feed intensifies the inhibition effect at lower temperatures, leading to a more significant early reduction in $F_{\text{cat}/\text{geo}}$ value.

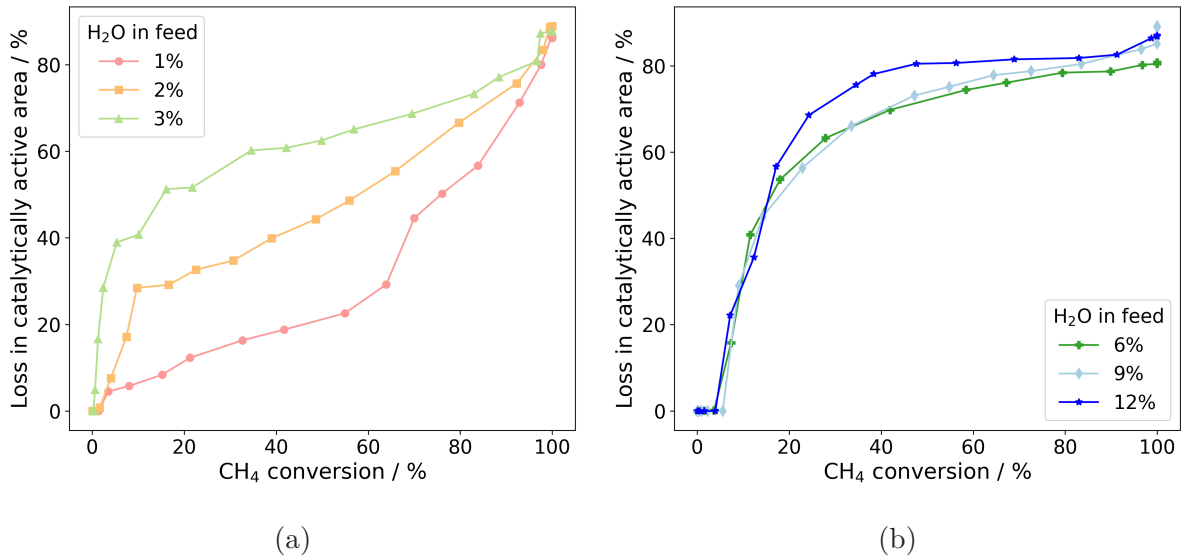


Figure 5.14: Loss in catalytically active area with respect to conversion for various feed conditions.

Compared to the optimized $F_{\text{cat}/\text{geo}}$ values, the loss in active area reported by Keller et al. [149] was overestimated across all concentrations of water. For example, for 1 vol.% water in feed, Keller et al. suggested that nearly 50 % of the catalytically active area is lost at the very onset of light-off. In contrast, the optimized data indicate that such a significant loss occurs after more than 70 % conversion is achieved (cf. Figure 5.14a). This much loss in active area is encountered much earlier for water concentrations of 3 vol.% and above at temperatures of approximately 20 % conversion, due to the intensified inhibition effect. At lower concentrations of water, the loss in active area progresses more

gradually as more conversion takes place with increase in temperature. The overlap in the curves at higher concentrations of water (Fig. 5.14b) indicates a saturation point in the inhibition with respect to water content, similar to the findings of Keller et al. [149]. In the Fig. 5.14b, at low conversions (less than 5 %) the loss in active area is negligible. This may be attributed to the fact that the loss is calculated relative to the as-prepared catalyst, whereas the catalyst properties likely changed after the degreening step. As a result, the initial $F_{\text{cat/geo}}$ values at the start of light-off may have been underestimated, underscoring the need for accurate post-degreening characterization of catalyst samples.

Overall, the experimental observations during the light-offs are reproduced well using the modeling approach in this work. The modeling results with changing values of $F_{\text{cat/geo}}$ show that there is an irreversible loss of active sites as the samples are continuously exposed to humid conditions and increasing temperatures during the light-off measurements. Fig. 5.14 shows that this irreversible deactivation is a function of both water concentration and how much of the methane is converted at any point in the light-off. The dependency of the loss in catalytically active area on conversion values is consistent with the findings from Mortensen et al. [183], which suggested that an inactive state is a result of the migration and re-dispersion of the Pd^0 species which are formed when methane gets activated. The use of the surrogate model for gradient-based optimization enabled capturing the complex interactions of water concentration and the reaction temperature on the surface coverages and the observed end-of-pipe methane concentrations, without relying on making prior assumptions about the conditions driving the deactivation.

5.5 Conclusions and Summary

In this chapter, the use of a surrogate model to optimize the $F_{\text{cat/geo}}$ simulation parameter was explored. Several neural network architectures were trained on simulated data to capture the methane oxidation kinetics in a packed bed reactor. Among them, the Long Short-Term Memory (LSTM) network [193] delivered the best performance on test data and was selected as the surrogate model to replace the DETCHEM^{PBR} simulation model.

The LSTM model accurately predicted the spatially-resolved reactor outputs across all studied reaction conditions and was successfully applied in gradient-based optimization tasks. Surrogate models like these offer a powerful alternative when direct gradient extraction from numerical simulations is either unavailable or too costly to compute. A key factor in their success is the availability of a high-quality dataset. In this work, the dataset was generated and stored following FAIR principles [41], ensuring it is well-suited for training and future reuse. This approach is especially valuable in tasks, where multiple interacting parameters must be tuned for optimal performance.

The study investigated the deviations in simulation results in comparison with the experimental data using the microkinetic model by Stotz et al. [168] for PdO/Al₂O₃. These deviations were traced to the assumption of a constant catalytically active area during light-off. While the model correctly captured the shift in activity to higher temperatures in the presence of external water, experimental data revealed additional inhibition not explained by site blocking alone. Instead, the findings suggest an irreversible loss of active sites due to prolonged exposure to reaction conditions, in agreement with recent studies [183, 184]. Through the optimization of the $F_{\text{cat/geo}}$ parameter, the variation in the catalytically active area with water concentration could be investigated. At low water concentrations (<3 vol.%), a gradual loss of active sites was observed as temperature and conversion increased. Higher water concentrations led to a more pronounced loss, up to 50 % of the active area at 20 % conversion.

The results also showed that the inhibition effect saturates with increasing water concentration and becomes negligible at higher temperatures, aligning with literature [145]. Overall, the findings highlight the significant role of external water in irreversible catalyst deactivation. While the simulations with optimized $F_{\text{cat/geo}}$ values do not pinpoint whether this deactivation is due to Pd(OH)₂ formation, or a change in the Pd²⁺ state, or re-dispersion of the Pd particles, they underscore the need to account for the change in catalyst state for accurate simulation of catalyst performance, especially under wet conditions.

The study also highlights the importance of characterization of catalyst samples before and after measuring light-offs, in addition to as-prepared samples, as the catalyst properties may change significantly after degreening, and an accurate measurement of the catalytic area during the reaction conditions is imperative for accurate modeling. In the present investigation, the simulated dataset indicated that variation of $F_{\text{cat/geo}}$ values along the length of the reactor did not significantly influence the reactor output. However, this result is likely influenced by the coarse and poorly defined section with variable catalytic area in the bed. A more thorough investigation employing a finer and more realistic spatial variation of $F_{\text{cat/geo}}$ is therefore warranted, to draw a more reliable conclusion.

Furthermore, although the internal diffusion was found to be negligible under the conditions studied here, such effects may need to be incorporated in future work. Parameter fitting that directly affects reaction rates may inadvertently mask the influence of diffusion limitations. If present, these effects must be explicitly incorporated into the dataset and, consequently, into the surrogate modeling framework as well.

In conclusion, this chapter highlighted the effectiveness and practicality of surrogate modeling for accelerating optimization in heterogeneous catalysis. The LSTM-based surrogate model enabled accurate, efficient predictions and facilitated gradient-based optimization, offering a practical alternative to costly numerical simulations. The study also revealed the critical role of water-induced irreversible catalyst deactivation and emphasized the need to account for dynamic catalyst properties in modeling. This study highlights the value of using data-driven tools to bridge the gap between simulation and experimental catalytic performance. These data-based surrogate models are particularly useful in scenarios that require a large number of costly simulations, for example during scale-up studies or when designing setups with multiple unit operations.

6 Conclusions and Outlook

The work presented in this thesis demonstrates how numerical optimization techniques and machine learning methods can support the development and application of microkinetic models. The primary objective was the development of an automated workflow that integrates the DETCHEM simulation package for reactor modeling with the global optimization algorithm Basin-Hopping to generate tailored mechanisms for catalytic systems. The inherent uncertainty in microkinetic model parameters obtained from DFT or empirical estimates makes parameter fitting to experimental data essential, yet challenging due to the high dimensionality of microkinetic models.

The optimization approach developed in this work overcomes this challenge by employing a stochastic, gradient-free algorithm that efficiently navigates large parameter spaces, while ensuring that the mechanism is always thermodynamically consistent. The workflow enables fully automated execution of multiple simulations across various reaction conditions, allowing efficient comparison of model predictions with experimental data during the optimization procedure. The parallelized execution of the multiple simulations needed at each run together with the gradient-free approach followed in Basin-Hopping, significantly reduces the overall time needed for any iterative model development procedure.

Several examples were presented to illustrate the effectiveness of this workflow in generating tailored mechanisms for a variety of catalytic systems, spanning microkinetic models of various sizes. The approach shows great promise, producing accurate models even for large mechanisms containing more than 200 kinetic parameters within only a few hours. The resulting optimized microkinetic models were further validated against additional experimental data, enabling a deeper understanding of the surface chemistry and reliable

prediction of the catalyst behavior across a wide range of operating conditions. This is a key advantage of microkinetic models as they are valid for a wide range of operating conditions, distinguishing them from lumped kinetic models which offer limited extrapolation capacity.

Although the methodology developed in this work requires minimal user intervention during the optimization procedure, its overall success remains strongly dependent on the quality of the initial system setup. It is therefore essential that all relevant reaction pathways are accurately specified, that the assumptions employed in the simulations are consistent with the experimental conditions, and that all significant physical and chemical effects are incorporated accurately into the model formulation.

When the kinetic parameter fitting procedure fails to reasonably reproduce the experimental data, such discrepancies may provide valuable insights. They may indicate the presence of missing reaction pathways and/or intermediates, or additional transport or heat transfer effects that are not yet represented in the current simulation. In this sense, unsuccessful fits can highlight gaps in the underlying model assumptions or structure.

However, this situation also introduces a potential risk. In the absence of a complete or physically accurate model structure, the optimization algorithm may compensate for these deficiencies by adjusting the kinetic parameters in a way that improves agreement with the experimental data but lacks physical justification. Such overfitting can lead to parameter values that obscure the true surface chemistry and limit the predictive capability of the microkinetic model when applied beyond the specific conditions used for optimization. Ensuring that the modeling foundation is as complete and physically meaningful as possible prior to optimization is therefore crucial for maintaining both parameter interpretability and model reliability. This further underscores the necessity of validating the generated mechanisms with additional experimental data that were not used during the fitting.

Furthermore, the stochastic nature of the Basin-Hopping algorithm represents both an advantage and a limitation within the optimization framework developed in this work. Its reliance on random perturbations helps prevent the search process from becoming trapped

in local minima points, thereby facilitating broader exploration of the high-dimensional parameter landscape. However, this same randomness also introduces the possibility that the global minimum may be missed, particularly in systems with complex objective functions.

For this reason, careful configuration of the optimization procedure is essential. Multiple independent optimization runs, a sufficiently large number of iterations, appropriately chosen step sizes, and sufficient number of experimental data points are required to enhance the robustness and reliability of the results. Because no universally optimal parameter settings exist for these algorithmic parameters, the optimization must be conducted iteratively, guided by both performance observations and domain-specific understanding of the system under study. Adopting such a systematic and exploratory approach ensures that the search process is as exhaustive as practically achievable and increases confidence that the identified solution represents a meaningful and physically relevant model.

In addition to the global stochastic optimization strategies explored in this work, the thesis has also demonstrated the potential of machine-learning-based surrogate models to enable gradient-based optimization in catalytic reactor simulations. Surrogate models based on neural networks offer a computationally efficient means of approximating complex simulation frameworks, while providing access to gradients that are otherwise difficult or prohibitively expensive to compute directly from detailed reactor or microkinetic models. This capability creates new opportunities for incorporating derivative-based optimization methods into workflows where such information is traditionally unavailable.

A proof-of-concept implementation was presented in which a surrogate model was constructed for the DETCHEM^{PBR} simulation tool modeling the methane oxidation behavior over a Pd-based catalyst under lean conditions. This surrogate was subsequently used to predict the effective catalytic area to be used during simulations so as to accurately reproduce the experimental trends under increasing operating temperature in the presence of various concentrations of water. The easy availability of gradient information from the surrogate enabled the prediction by iteratively optimizing the available catalytic area needed to obtain the same reactor outputs as measured during the experiments.

Although this represents a relatively simple application of the surrogate model, it nevertheless demonstrates that surrogate models are capable of reproducing reactor outputs with sufficient accuracy. The results underscore the promise of surrogate-based approaches in accelerating parameter optimization and facilitating the numerical investigation of parameters that influence catalytic performance. With the rapidly growing availability of materials databases and the increasing number of literature studies publishing original experimental data in open repositories, the opportunities for leveraging machine-learning-based approaches are substantial. Such methods hold promise across a broad spectrum of applications, ranging from accelerated catalyst discovery and improved catalyst performance to enhanced reactor design and optimization.

While the application demonstrated here focused on predicting reactor-level outputs for a specific catalytic system under limited operating conditions, the overall methodology is inherently flexible. The design and training of a surrogate model, whether based on neural networks, Gaussian processes, or other machine-learning architectures, must be tailored to the specific characteristics of the underlying system. Factors such as the dimensionality of the input space, the desired accuracy, the variability in the outputs, and the computational cost of generating training data all influence the appropriate modeling strategy. As such, the development of effective surrogate models represents a problem-specific engineering challenge, requiring careful consideration of both data generation and model architecture. Overall, the inclusion of surrogate modeling in this thesis highlights a promising direction for future research.

Surrogate models may also offer significant potential for further accelerating the optimization of microkinetic models, particularly through the exploitation of gradient information. Such an approach could enable a more efficient and systematic exploration of the parameter space compared to the stochastic and heuristic-based strategies employed in the Basin-Hopping algorithm. In the present work, the optimization framework was applied primarily to parameter optimization based on the experimental data corresponding to a single reactant. Future research should therefore investigate the robustness and scalability of the proposed methodology when extended to datasets comprising multiple reaction products measured across a range of operating conditions. Additionally, the incorporation

of experimentally observed trends in the reacting gas mixture along the axial direction of the reactor remains an important aspect for further development of the optimization methodology. Ongoing efforts are focused on integrating additional DETCHEM reactor modeling codes into the optimization workflow, such as DETCHEM^{CHANNEL} modeling a 2D catalytic channel and DETCHEM^{STAG} modeling a stagnation flow reactor. The application of the optimization procedure with these reactor configurations within the proposed framework will form a central component of future work.

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List of Publications and Presentations

Journal Publications

- (1) **Chacko, R.**, Keller, K., Tischer, S., Shirsath, A. B., Lott, P., Angeli, S., Deutschmann, O.: “Automating the Optimization of Catalytic Reaction Mechanism Parameters Using Basin-Hopping: A Proof of Concept”. *J. Phys. Chem. C*, 2023, 127, 7628-7639. DOI: 10.1021/acs.jpcc.2c08179
- (2) **Chacko, R.**, Gossler, H., Angeli, S., Deutschmann, O.: “Interconnected Digital Solutions to Accelerate Modeling of the Reaction Kinetics in Catalysis”. *ChemCatChem*, 2024, 16, e202301355. DOI: 10.1002/cctc.202301355
- (3) **Chacko, R.**, Keller, K., Shirsath, A. B., Angeli, S., Lott, P., Deutschmann, O.: “Microkinetic Modeling of Support Effects in PdO-Based Methane Oxidation Catalysts”. *ACS Catalysis*, 2025, 15, 9, 6937-6952. DOI: 10.1021/acscatal.5c00516
- (4) Davari, S., **Chacko, R.**, Bastek, T., Lott, P., Dailly, J., Angeli, S., Deutschmann, O.: “Experimental and Microkinetic Investigation of Thermo-Catalytic Ammonia Decomposition over a Ba-promoted Ru/Ni-BCZY Catalyst for Use in Ammonia-fed Protonic Ceramic Cells”. *Appl. Catal., A*, 2025, 708, 120571. DOI: 10.1016/j.apcata.2025.120571
- (5) Gossler, H., Riedel, J., Daymo, E., **Chacko, R.**, Angeli, S., Deutschmann, O.: “A New Approach to Research Data Management with a Focus on Traceability: Adacta”. *Chemie Ingenieur Technik*, 2022, 94(11), 1798-1807. DOI: 10.1002/cite.202200064

Oral Presentations

- (1) **Chacko, R.**, Keller, K., Tischer, S., Shirsath, A. B., Lott, P., Deutschmann, O.: “Optimization of Catalytic Reaction Mechanism Parameters Using Basin-Hopping”. The 28th North American Catalysis Society Meeting, Providence, USA, 2023.
- (2) Keller, K., **Chacko, R.**, Lott, P., Deutschmann, O.: “Catalytic Total Oxidation of Methane – Towards a Better Understanding of the Water Inhibition Effect and the Influence of the Support Material”. International Symposia on Chemical Reaction Engineering (ISCRE 27) Québec, Canada, 2023.
- (3) **Chacko, R.**, Gossler, H., Riedel, J., Schunk, S., Deutschmann, O.: “Digitalization in Catalysis and Reaction Engineering: Automatizing Work Flow”. Conference on Research Data Infrastructure (CoRDI), Karlsruhe, Germany, 2023.
- (4) Dolcet, P., Schulte, M., Maurer, F., Jung, N., **Chacko, R.**, Deutschmann, O., Jrunwaldt, J.-D.: “LabIMotion Electronic Lab Notebook as Research Data Management tool in Catalysis”. Conference on Research Data Infrastructure (CoRDI), Karlsruhe, Germany, 2023.
- (5) **Chacko, R.**, Davari, S., Gossler, H., Angeli, S., Karakaya, C., Kee, R. J., Deutschmann, O.: “Towards Digitalization of the Microkinetic Modeling Workflow: Example NH_3 decomposition”. 57. Jahrestreffen Deutscher Katalytiker, Weimar, Germany, 2024.
- (6) **Chacko, R.**, Gossler, H., Angeli, S., Deutschmann, O.: “Digitalization in Catalysis: Accelerating the microkinetic model development by automation tools”. 17th Panhellenic Symposium on Catalysis, Paphos, Cyprus, 2024.
- (7) **Chacko, R.**, Gossler, H., Angeli, S., Deutschmann, O.: “Digitalization in Catalysis: Accelerating the microkinetic model development by automation tools”. Symposium on Chemically Reacting Flows in Low-carbon Energy Transition, Beijing, China, 2024.
- (8) **Chacko, R.**, Davari, S., Gossler, H., Angeli, S., Deutschmann, O.: “Digitalization of workflow and research data management in microkinetic modeling: H_2 production via NH_3 decomposition”. MTET Workshop, Berlin, Germany, 2025.

(9) **Chacko, R.**, Keller, K., Götz, M., Lott, P., Angeli, S.: “Leveraging Optimization Algorithms and Surrogate Modeling to Understand Methane Oxidation Kinetics”. 8th International Symposium on Modeling of Exhaust-Gas After-Treatment (MODEGAT VIII), Bad Herrenalb, Germany, 2025.

Short Presentations

(1) **Chacko, R.**, Keller, K., Tischer, S., Shirsath, A. B., Lott, P., Deutschmann, O.: “Automating the Optimization of Catalytic Reaction Mechanism Parameters using Basin-Hopping”. 56. Jahrestreffen Deutscher Katalytiker, Poster Workshop: Data Driven Catalysis, Weimar, Germany, 2023.

(2) **Chacko, R.**, Gossler, H., Angeli, S., Deutschmann, O.: “Towards digitalization of the microkinetic modeling workflow”. 18th International Congress on Catalysis (ICC), Lyon, France, 2024.

Poster Presentations

(1) Riedel, J., **Chacko, R.**, Angeli, S., Gossler, H., Daymo, E., Deutschmann, O.: “Automation of Interdisciplinary Research Data Management for Catalysis”. Annual Digital Catalysis & Catalysis-Related Sciences Conference 2022 (ADCR22), Frankfurt, Germany, 2022.

(2) **Chacko, R.**, Riedel, J., Angeli, S., Gossler, H., Sheppard, T., Studt, F., Deutschmann, O.: “Automation of Interdisciplinary Research Data Management for Catalysis”. International CataLysis Networking Conference, Kassel, Germany, 2022.

(3) **Chacko, R.**, Keller, K., Tischer, S., Shirsath, A. B., Lott, P., Deutschmann, O.: “Automating the Optimization of Catalytic Reaction Mechanism Parameters using Basin-Hopping”. 56. Jahrestreffen Deutscher Katalytiker, Weimar, Germany, 2023.

- (4) **Chacko, R.**, Riedel, J., Gossler, H., Daymo, E., Deutschmann, O.: “Interdisciplinary Research Data Management for Catalysis”, 56. Jahrestreffen Deutscher Katalytiker, Weimar, Germany, 2023.
- (5) **Chacko, R.**, Keller, K., Tischer, S., Shirsath, A. B., Lott, P., Deutschmann, O.: “Automated Kinetic Parameter Optimization of Catalytic Reactions using Basin-Hopping: CH₄ Oxidation over PdO/ZrO₂”. Annual Meeting on Reaction Engineering, Frankfurt, Germany, 2023.
- (6) Gossler, H., Riedel, J., Jägerfeld, J., Kuhn, C., **Chacko, R.**, Angeli, S., Deutschmann, O.: “Catalysis-related Research Data Management Software”. Annual Digital Catalysis & Catalysis-Related Sciences Conference 2023 (ADCR23), Frankfurt, Germany, 2023.
- (7) Keller, K., **Chacko, R.**, Shirsath, A. B., Lott, P., Angeli, S., Deutschmann, O.: “Mechanistic Insights into Pd-based Methane Oxidation Catalysts: Accounting for Support Effects in Microkinetic Modeling”. Annual Meeting on Reaction Engineering and Electrochemical Processes, Würzburg, Germany, 2024.
- (8) **Chacko, R.**, Götz, M., Deutschmann, O., Angeli, S.: “Elucidating the effect of in-situ reaction environment on the catalytic performance using machine learning models”. FuturEMission, Karlsruhe, Germany, 2024.
- (9) **Chacko, R.**, Davari, S., Gossler, H., Cardenas Munoz, C., Lott, P., Angeli, S., Deutschmann, O.: “Digitalization of Workflow and Research Data Management in Microkinetic Modeling: NH₃ decomposition”. Energy Symposium 2025: Powering the Future - Accelerating the Energy Transition, Karlsruhe, Germany, 2025.
- (10) Davari, S., **Chacko, R.**, Häber, T., Cardenas, C., Lott, P., Angeli, S., Deutschmann, O.: “Kinetic Modeling of Ammonia Oxidation Based on Multi-scale Experiment Data”. 8th International Symposium on Modeling of Exhaust-Gas After-Treatment (MODEGAT VIII), Bad Herrenalb, Germany, 2025.

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Professional Experience

04/2021 – Present	Research Assistant , Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry
09/2018 – 10/2020	Researcher , Material Informatics, Tata Research Development and Design Centre, Pune, India
07/2015 – 07/2016	Graduate Engineer Trainee , Reliance Industries Limited, Vadodara, India

Education and Academic Degrees

04/2021 – Present	Doctoral Researcher , Karlsruhe Institute of Technology, Thesis: Development and application of microkinetic models leveraging optimization algorithms and surrogate models.
08/2016 – 05/2018	Master of Technology in Chemical Engineering , Indian Institute of Technology Madras, Chennai, India
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