

# Automating the Optimization of Catalytic Reaction Mechanism Parameters Using Basin-Hopping: A Proof of Concept

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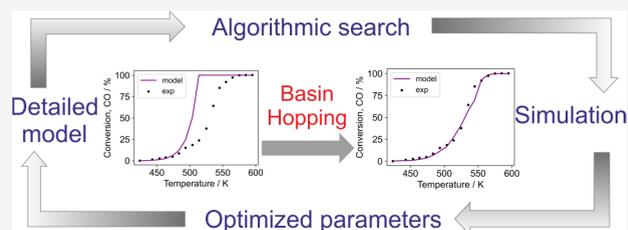
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**ABSTRACT:** Parameter estimation is a crucial step for successful microkinetic modeling in catalysis. However, the large number of parameters to be optimized in order to match the experimental data is a bottleneck. In this regard, the global optimization algorithm Basin-Hopping is utilized to automate the typically time-extensive and error-prone task of manual fitting of kinetic parameters for a heterogeneous catalytic system. The stochastic approach of the Basin-Hopping algorithm to explore the kinetic parameter solution space coupled with local search methods makes it possible to screen the high-dimensional space for an optimal set of kinetic parameters giving the least residual between the simulated and the experimentally measured catalytic performance data. Our approach also ensures that only thermodynamically consistent solution candidates are explored at each optimization step. We utilize two example case studies in heterogeneous catalysis, namely, methane oxidation over a palladium catalyst and carbon monoxide methanation over a nickel catalyst, with corresponding detailed kinetic models to illustrate the applicability of the algorithm to efficiently fine-tune detailed kinetic models.



## INTRODUCTION

Microkinetic modeling (MKM)<sup>1</sup> is widely used in the field of catalysis to better understand kinetics that controls the catalyst performance and helps in the identification of critical reaction intermediates and rate-determining reaction pathways. It involves the formulation of a detailed reaction mechanism consisting of all possible elementary reactions without making *a priori* assumptions about the rate-determining step(s), quasi-steady-state approximation, or the most abundant surface intermediates. This requires the estimation of rate constants of all such elementary steps and a numerical solution of the governing equations for surface and fluid species,<sup>2</sup> making parameter estimation a necessary step for successful microkinetic modeling. The kinetic and thermochemical values may typically be obtained from computational methods such as density functional theory (DFT) or through more empirical methods like bond-order conservation (BOC) method and Brønsted–Evans–Polanyi (BEP) relationships.<sup>3–9</sup> However, an accurate determination of the many kinetic parameters needed when choosing the MKM approach is a limiting factor.<sup>10</sup> Additionally, MKM models do not directly account for the influence of supports or promoters on the kinetic parameters, therefore, the simulation data often does not agree well with experimental data for other catalyst/support material systems, requiring further fine-tuning of the mechanism. The traditional brute-force approach to manually tune the kinetic parameters to fit the experimentally measured performance data is useful but requires considerable time and effort to find

optimal results and relies extensively on domain knowledge. A better approach is to utilize data-driven methodologies for deriving microkinetic models.<sup>11</sup> Furthermore, kinetic parameter optimization to minimize the difference between simulated and experimental macroscopic quantities such as turnover frequency (TOF) or conversion is essentially a nonlinear optimization problem, hence, an automated and digitalized approach can be beneficial given the evolution of both computing power and sophisticated techniques. Above all, an optimized set of kinetic parameters obtained through a rigorous search may reveal more information about the nature of the active sites and could have a significant impact on the understanding of the fundamental reaction mechanism.

Over the years, many have attempted to utilize optimization methods to fit kinetic parameters and to find the optimum operating conditions in both catalysis and reaction engineering.<sup>12–15</sup> These methods aim at providing a much faster and robust alternative to the manual approach to model fitting. However, most of the studies are restricted to global reaction kinetics such as Langmuir–Hinshelwood–Hougen–Watson (LHHW) type kinetic models or deal with reduced reaction

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systems with less parameters to tune.<sup>16,17</sup> Local sensitivity analysis is often used to find a subset of steps in a detailed mechanism that could be optimized to fit the experimental data to reduce computational cost.<sup>18</sup> Recently, Kreitz et al. utilized the Reaction Mechanism Generator (RMG)<sup>19–22</sup> to automate the development of a detailed microkinetic model for catalytic conversion of exhaust gases on Pt(111), wherein important chemical reactions were optimized to obtain good agreement between experimental and modeled data. The initial parameters were determined via RMG from precompiled databases and estimates for 132 reversible reactions. Out of these, parameters for five reactions, including the rate-determining step, were further fitted to match experimental data based on their uncertainty range.<sup>23</sup> Additionally, there exist several challenges in the optimization of kinetic parameters due to the nonlinearity of the models, the necessity of gradients calculation of complex objective functions, and the possibility of getting stuck in a local minimum. In order to find the global minimum, Rangarajan et al. presented a sequential optimization framework using a multistart approach to explore the solution space and showcased the framework with methanol synthesis through hydrogenation of CO and CO<sub>2</sub> on a Cu-based catalyst.<sup>24</sup> Furthermore, it is essential to obtain a solution that not only fits the experimental data well, but also maintains thermodynamic consistency.<sup>25,26</sup> Yonge et al. developed a python-based package to simulate the temporal analysis of products (TAP) reactor systems with TAP curve fitting to extract kinetic parameters using an objective function constrained to ensure thermodynamic consistency.<sup>27</sup>

The various optimization algorithms used in the literature range from gradient-based interior point methods to heuristic algorithms such as a gravitational search.<sup>28–30</sup> Global optimization methods, such as differential evolution and genetic algorithms, along with swarm intelligent algorithms, have attracted much attention in the quest for exploring the parameter search space for an optimal solution.<sup>31–35</sup> However, many of these are also limited by their high processing times and tendency to get stuck in local minima, especially in high-dimensional search spaces.<sup>36</sup> Global methods utilize exploration (a global search probing unexplored regions of the search space) and exploitation (a local search for further investigation of potentially good solutions within the search space) to possibly obtain a global minimum or maximum of a given objective function. One such method is the Basin-Hopping (BH) algorithm, a stochastic algorithm that incorporates exploration by a series of perturbations (or hops) in the variable space, followed by a local optimization step,<sup>37</sup> developed by Wales and Doye in the field of chemical physics. It is reported to also be useful for structural characterization of biological macromolecules and argued to be particularly useful for multivariable multimodal optimization problems, as it searches for the optimal solution between adjacent local minima.<sup>38</sup> Furthermore, in this work, BH is preferred over other methods, as it provides a gradient-free method for optimization of the kinetic parameters, which is necessary for such systems where the calculation of gradients is complex and computationally intensive. Additionally, BH requires only two additional parameters, namely, the number of hops and the step size (providing the range for each hop), enabling a simple design of experiments, as opposed to, for instance, genetic algorithms that require four additional parameters: crossover probability, mutation probability, population size, and number of generations.

Therefore, in this work we aim to demonstrate the applicability of the Basin-Hopping algorithm in exploring the high-dimensional kinetic parameter space for parameter optimization of detailed microkinetic models for heterogeneous catalysis. The workflow is developed in such a way that only thermodynamically consistent solution candidates are explored to obtain the optimal solution. In the following sections, we present an overview of the modeling equations and the BH algorithm and showcase the automated framework to optimize the detailed mechanisms using two example case studies. The catalytic systems used in this work are CH<sub>4</sub> oxidation over Pd/ZrO<sub>2</sub> and CO methanation over Ni/Al<sub>2</sub>O<sub>3</sub>. The study of methane oxidation is useful for efficient exhaust gas abatement systems for natural gas driven engines. We aim to model the delayed lightoff and catalyst deactivation observed in the presence of water for Pd supported on ZrO<sub>2</sub> by optimizing the detailed model reported by Stotz et al.<sup>39</sup> for methane oxidation over Pd/Al<sub>2</sub>O<sub>3</sub> as an illustrative example. Similarly, catalytic methanation of CO is a crucial step in carbon oxides removal from synthesis gas in ammonia plants and production of Substitute Natural Gas (SNG) via coal gasification, with nickel being an industrially relevant catalyst.<sup>40,41</sup> With complex competing reaction pathways, the optimization of a general methanation mechanism proposed by Schmider et al.<sup>42</sup> for Ni-based catalysts is demonstrated in the second example for Ni supported over Al<sub>2</sub>O<sub>3</sub>.

## METHODS

The following section provides details about the modeling equations, the objective function, and explains the optimization workflow used in this work.

**Objective Function.** The focus of this work is to showcase a framework that optimizes the kinetic parameters of a detailed microkinetic model so as to have the least possible residual between the modeled and the measured species data at various temperatures for a given catalytic system. The objective function in this work is formulated as

$$f(\lambda_j) = \sum_{r=1}^N \sum_{i=1}^m |(X_{i,\text{sim}}^T(\lambda_j) - X_{i,\text{exp}}^T)| \quad (1)$$

where  $\lambda_j$  denotes a vector of size  $j$  corresponding to the total kinetic parameters for a given microkinetic model,  $X_{i,\text{sim}}^T$  is the simulated conversion of reactant species  $i$ , obtained by numerically solving the governing equations for the given reactor under appropriate assumptions and  $X_{i,\text{exp}}^T$  is the experimental conversion of reactant species  $i$  at temperature  $T$  in a given reactor. The objective function is calculated as a sum of absolute value of the residuals for a discrete number of temperatures based on the availability of experimental data points. It is to be noted that the choice of the objective function is dependent on the problem under consideration and should be chosen in such a way that significantly different experiments contribute in the same way to the objective function. Equation 1 is an appropriate choice for the objective function in this work since the focus is on high concentration reactant species. In other cases, a difference in logarithmic value of species or a summation of a weighted squared difference of concentrations may be possible alternatives. The weight should be chosen based on the criteria for a good solution, such as the maximum possible variation of the concentration value. For instance, in a light-off experiment, where the mass fraction could only vary between 0 and 1, a

simulated value of 0.03 could be an acceptable match for an experimental value of 0.01. However, if concentrations are considered and the value could only vary between 0 and 0.03, then it cannot be considered a good match. Therefore, dividing the difference in concentrations with 0.03 will provide a better value for the objective function.

**Modeling Details.** For this work, a packed-bed reactor model is chosen, however the framework can be extended to other reactor types by employing appropriate reactor models for simulations. All numerical simulations were performed using DETCHEM<sup>PBR</sup>, which is part of the DETCHEM program package.<sup>43</sup> DETCHEM<sup>PBR</sup> models a packed-bed reactor as a 1D heterogeneous model under the assumptions that there exists no variation in radial flow properties and any axial diffusion is negligible compared to the corresponding convective term.<sup>44</sup> The 1D heterogeneous model can then be written as a system of ordinary differential equations as

$$\frac{d(\rho u)}{dz} = a_v \sum_{i \in S_g} \dot{s}_i M_i \quad (2)$$

$$\rho u \frac{dY_i}{dz} + Y_i a_v \sum_{j \in S_g} \dot{s}_j M_j = M_i (a_v \dot{s}_i + \dot{\omega}_i \phi) \quad (3)$$

where  $S_g$  is the set of gas-phase species,  $\rho$  is the density,  $u$  is the superficial velocity,  $z$  is the axial coordinate,  $a_v$  is the area to volume ratio,  $\dot{s}_i$  is the surface production rate of species  $i$ ,  $M_i$  is the molar mass of species  $i$ ,  $Y_i$  is the mass fraction of species  $i$ ,  $\dot{\omega}_i$  is the gas-phase production rate of species  $i$ , and  $\phi$  is the bed porosity.

For a set of gas-phase reactions  $\mathcal{R}_g$  and an additional set of third-body species  $S_M$ ,

$$\dot{\omega}_i = \frac{dc_i}{dt} = \sum_{k \in \mathcal{R}_g} \nu_{ik} k_k \prod_{j \in S_g \cup S_M} c_j^{\tilde{\nu}_{jk}} \quad (4)$$

where  $c$  represents the concentration,  $k_k$  is the  $k^{\text{th}}$  reaction rate constant,  $\nu_i$  is the stoichiometric coefficient of species  $i$ ,  $\tilde{\nu}_{jk}$  is the reaction order of each species, which equals their stoichiometric coefficients in the case of elementary reactions. Analogously, for a set of surface reactions  $\mathcal{R}_s$ ,

$$\dot{s}_i = \sum_{k \in \mathcal{R}_s} \nu_{ik} k_k \prod_{j \in S_g \cup S_s} c_j^{\tilde{\nu}_{jk}} \quad (5)$$

Then, the reaction kinetics is modeled using Arrhenius-type rate expressions of the form

$$k_k = A_k T^{\beta_k} \exp\left(\frac{-E_{a,k}}{RT}\right) \prod_{i \in S_s} \exp\left(\frac{c_{i,k} \theta_i}{RT}\right) \quad (6)$$

$$\theta_i = \frac{c_i \sigma_i}{\Gamma_s^j} \quad (7)$$

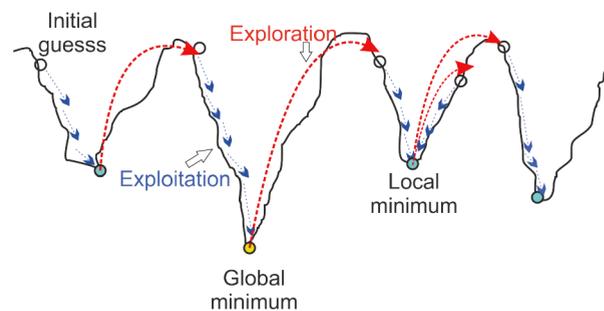
where  $A_k$  is the pre-exponential factor,  $T$  is the temperature,  $\beta_k$  is the dimensionless parameter for temperature-dependency,  $E_{a,k}$  is the activation energy,  $\theta_i$  is the surface coverage of species  $i$ ,  $c_{i,j}$  accounts for the coverage dependency of species  $i$  on the activation energy,  $R$  is the universal gas constant,  $\sigma_i$  represents the number of sites occupied by one particle of species  $i$ , and  $\Gamma_s^j$  is the surface site density of the specific surface type. Since the case studies used in this work were isothermal, the energy balance equations are not shown.

In order to ensure that the optimized mechanism is also thermodynamically consistent, the DETCHEM<sup>ADJUST</sup> tool was utilized. In a microkinetically reversible mechanism, the rate constants for pairs of forward and backward reactions,  $k_f$  and  $k_r$  must fulfill the equation

$$\frac{k_f(T)}{k_r(T)} = \prod_i (c_i^\ominus)^{\nu_i} \exp\left(-\frac{\Delta_R G}{RT}\right) \quad (8)$$

where  $c_i^\ominus$  denotes the concentration of species  $i$  at standard conditions and  $\Delta_R G$  is the change of Gibbs free energy of the reaction. Since a reaction mechanism typically contains more pairs of reversible reactions than species, not all rate parameters may be chosen independently. For a given initial set of rate parameters, DETCHEM<sup>ADJUST</sup> calculates the minimum changes to selectable rate coefficients that are required to fulfill eq 8 for all reactions. Further details about the algorithm can be found in the works of Stotz et al.<sup>39</sup> and Herrera Delgado et al.<sup>45</sup>

**Basin-Hopping Algorithm.** In the context of the parameter optimization of catalytic reaction mechanism, Basin-Hopping (BH) can be employed to sample the parameter space and possibly obtain a global minimum for the objective function. BH, like other global optimization methods, uses a combination of exploration and exploitation to reach an optimum solution. During the exploration step, the optimizer suggests new points in the variable space where a potential solution might be found, while during the exploitation step it performs a local search to find the local minimum near the suggested point. BH performs the exploration step by hopping within the kinetic parameter space, as illustrated in the schematic in Figure 1. This



**Figure 1.** Schematic representation of the Basin-Hopping algorithm.

exploration may be stochastic, or a defined step-taking routine such as Latin hypercube (LHC) sampling may also be employed. For a stochastic sampling routine, the step size parameter of BH defines the possible range of values corresponding to each kinetic parameter for each “hop”, where the next guess for the solution could take any random value within the given range. For example, in this work the step-taking routine is defined as follows: for a user-defined step size of 0.2, a random value is sampled from a uniform distribution over  $[-0.2, 0.2]$ , which is then multiplied with the current local minimum value of the kinetic parameters, and the resulting values are then the newly suggested parameters of the same order of magnitude. The step size is therefore a crucial parameter and has to be chosen based on the problem at hand, with the value ideally close to the typical separation between the local minima of the objective function. One may also choose to modify the step-taking routine to allow for larger

Table 1. An Example of the Input Parameters Required To Simulate a Methanation Reactor in a Packed Bed Reactor

	parameter	required	value	unit
experiment	type of experiment	yes	end-of-pipe	
fixed bed	length	yes	0.0364	m
	diameter	yes	0.008	m
	catalyst + support mass	yes	0.5	g
	bed porosity	yes	38.1	%
	particle shape	yes	sphere	
	particle length			m
	particle diameter		0.00063	m
wall	wall temperature	obtained from experimental data	523	K
catalyst	active catalyst/metal	yes	Ni	
	metal loading	yes	20.0	%
surface	dispersion	any one of these	21	%
	NP diameter			
	ratio catalytic/geometric area			
flow	GHSV	any one of these		1/h
	WHSV		30000.0	mL/gh
	volumetric flow rate			slpm
	linear velocity			m/s
inlet gas	H <sub>2</sub>	may be modified based on experiment	0.6	mole fraction
	CO		0.2	
	Ar		0.2	
transport	isothermal	yes	yes	
	adiabatic	yes	no	
	external mass transfer resistance	yes	no	

changes for only certain parameters and smaller or no changes to the rest of the parameters. The number of iterations defines the number of hops BH takes during a complete fitting process. Each exploration step is then followed by an exploitation step where a local search algorithm is then utilized to obtain the local minimum (Figure 1).

Several algorithms, such as the Nelder–Mead<sup>46</sup> method and the Powell's conjugate direction method,<sup>47</sup> are possible choices and could be appropriately chosen based on the application and dimensionality of the problem at hand. The Nelder–Mead method is a popular direct search method for unconstrained optimization problems. It generates a sequence of simplices iteratively to approximate the minimum point, where a simplex is a geometric figure in  $n$  dimensions with  $n + 1$  vertices. For the reaction mechanism optimization, the original mechanism parameters act as initial guess to the objective function (eq 1), which is used as one of the vertices of the initial simplex ( $\vec{x}_1$ ) and the rest of the  $n$  vertices are then initialized at a small distance along the unit vectors of  $\vec{x}_1$

$$\vec{x}_{x+1} = \vec{x}_1 + h(\vec{x}_1, i)^* \vec{u}_i \quad (9)$$

where,  $\vec{u}_i$  is the unit vector for the  $i^{\text{th}}$  kinetic parameter and  $h(\vec{x}_1, i)$  is equal to 0.05, if the value of the  $i^{\text{th}}$  kinetic parameter in  $\vec{x}_1$  is nonzero and 0.0025 if zero. At each iteration, the vertices are sorted based on the value of the objective function such that,

$$f(\vec{x}_1) \leq f(\vec{x}_2) \leq \dots \leq f(\vec{x}_{n+1}) \quad (10)$$

a centroid is calculated  $\vec{x}_c$ , taking only the  $n$  best vertices, followed by four possible operations with associated scalar parameters to iteratively generate new simplices, replacing the worst performing vertex leading to a local minimum. The

detailed equations for the operations are available in the publications by Nelder and Mead<sup>46</sup> and Gao et al.<sup>48</sup> The Nelder–Mead algorithm was used in this work since it does not require gradient-related information and the associated scalar parameters are easily calculated as a function of the total number of kinetic parameters to be optimized, as reported by Gao and Han,<sup>48</sup> making the algorithm suitable for high-dimensional use cases without introducing additional algorithm-related parameters. The exploitation step using the Nelder–Mead algorithm is performed for a user-defined number of iterations or until the set tolerances for convergence are satisfied. The Nelder–Mead method may converge faster in the presence of gradient-related information, however, in the context of parameter optimization of MKM models, the calculation of such gradients is not trivial and would require additional computations, making the overall optimization process much slower. The obtained minimum after the exploitation step is either accepted or rejected by BH based on the Metropolis criterion of standard Monte Carlo algorithms.<sup>49</sup> The new minimum ( $\lambda_{j,\text{new}}$ ) is always accepted if the corresponding value of eq 1 is lower than the value for the minimum at the previous iteration ( $\lambda_{j,\text{old}}$ ), otherwise, it is accepted with probability  $e^{-(f(\lambda_{j,\text{new}}) - f(\lambda_{j,\text{old}}))/T}$ .  $T$  is the “temperature” parameter used in the Metropolis criterion and is set as 1.0 in this work.

**Workflow and Implementation Details.** In order to automate the workflow, a Python-based script is utilized that automatically performs packed-bed reactor simulations at each iteration to calculate the objective function for the current set of kinetic parameters for the given range of operating conditions. The software package DETCHEM is called within the script to run simulations for all operating conditions required for the objective function in parallel. The values for the reactor setup dimensions, feed composition, catalytic surface area, operating temperature, and pressure needed for

modeling the packed-bed reactor and corresponding experimental data are obtained using a simple and user-friendly spreadsheet-based input file. The file contains built-in checks for validation and completeness of the data entered by the user. Table 1 shows an example of the subset of typical input parameters users may provide for simulating, for instance, a methanation reaction. A mechanism file with a detailed kinetic model with corresponding Arrhenius parameters ( $S_0$  or  $A$ ,  $E_a$ ,  $\beta$ , and  $\epsilon$ ), with the linearly independent reactions marked by an asterisk (\*), is also provided as input. The DETCHEM<sup>ADJUST</sup> tool may be employed to find a basis set of the reactions for a given reaction system, however, a sensitivity analysis may be performed to identify the important reactions to be included in the basis set. It is necessary to mark independent reactions so that the algorithm only varies the parameters corresponding to these reactions independently, and the rest of the dependent reaction parameters are then calculated by DETCHEM<sup>ADJUST</sup> to ensure thermodynamic consistency, as given in the Modeling Details section. It is to be noted that the DETCHEM<sup>ADJUST</sup> algorithm does not intrinsically guarantee a positive activation energy for the whole temperature range, unlike the activation energy values suggested by Basin-Hopping, which are always positive due to the step-taking routine defined earlier. Therefore, it is suggested that independent reactions should be selected such that the reverse reactions with higher activation energy values are subjected to thermodynamic adjustment and reactions with nearly zero activation energy are optimized by the optimization algorithm. Since only minimum changes to the reaction parameters are calculated, the activation energy for the dependent reverse reaction from a pair of reversible reactions is not supposed to change dramatically and definitely not more than the variation in the activation energy of the corresponding independent reaction.

The BH algorithm is implemented using the Python library *Scipy*,<sup>50</sup> and the *multiprocessing* library is used to achieve parallelization of the simulations. The overall workflow is shown in Figure 2, which starts with the user providing the path to the input files, including the spreadsheet for reactor setup details and the mechanism. The number of local and global search iterations and the step size are initialized, and an appropriate objective function is provided. During each iteration, simulations at various temperatures are run automatically based on the given user input to obtain conversion of the reactant species, which are then compared with the experimental data to calculate the objective function. Multiple spreadsheets may be included to obtain a function considering different feed compositions or reactor setups. The optimization process begins by first obtaining the local minimum near the initial mechanism using the Nelder–Mead algorithm. During each of the global and local search iterations, the independent kinetic parameters are suggested by the corresponding algorithm and the dependent parameters are calculated considering thermodynamic consistency. With the current kinetic parameters at hand, the packed bed simulations are run and the procedure is repeated for the subsequent exploitation and exploration steps. The users may also specify an early stopping of the BH iterations, in the event of the global minimum candidate not changing for a user-defined number of iterations.

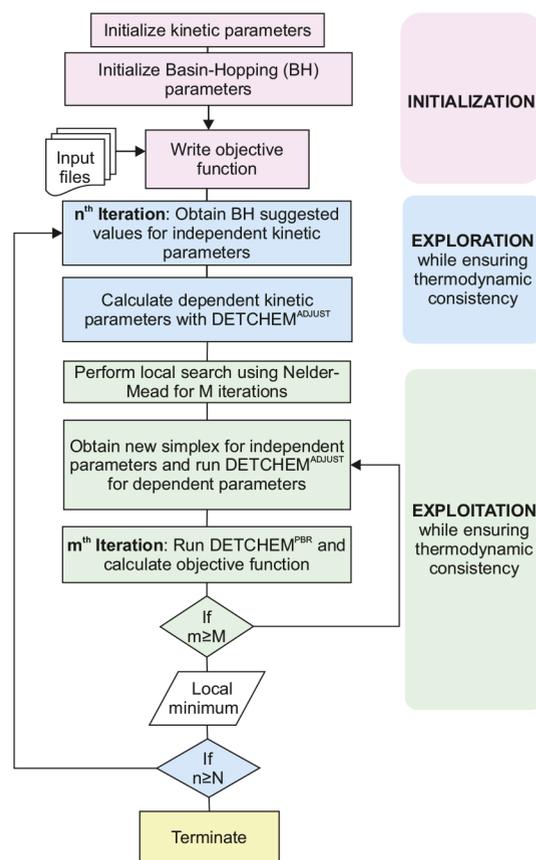
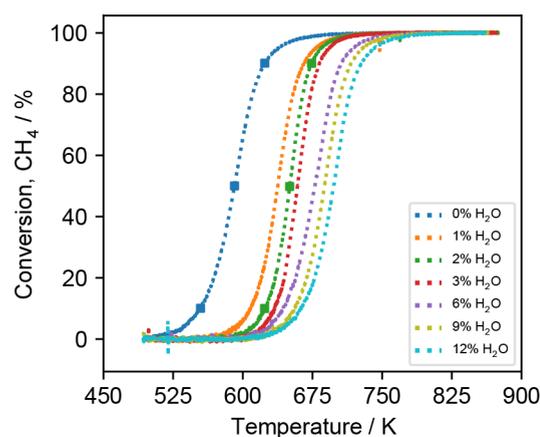


Figure 2. Parameter estimation workflow.

## RESULTS AND DISCUSSION

In this section, the application of the BH algorithm for optimizing kinetic parameters of detailed microkinetic models is showcased using two example case studies, namely, CH<sub>4</sub> oxidation over a PdO catalyst under lean conditions, and CO methanation using a Ni catalyst in a packed bed reactor. While the most relevant information on the experimental setup and parameters is summarized in brief, details may be found in the published works of Keller et al.<sup>51</sup> and Hu et al.,<sup>52</sup> respectively.

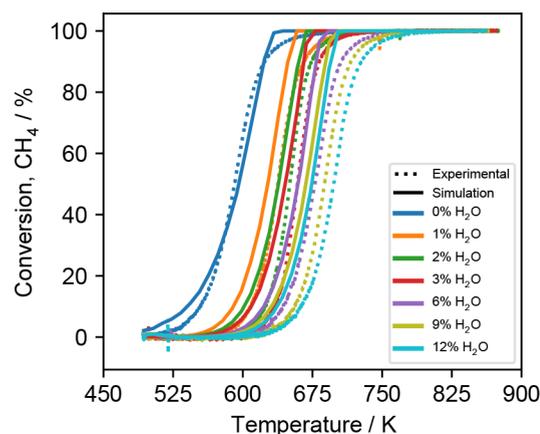
**Illustrative Example I: Methane Oxidation over a Palladium Oxide Catalyst.** The experimental data spans the temperature range of 500 to 800 K at atmospheric pressure for mixtures of CH<sub>4</sub> (3200 ppm) and O<sub>2</sub> (10 vol.%) with varying amounts of H<sub>2</sub>O (0–12 vol.%) over 2.3% PdO/ZrO<sub>2</sub> (Figure 3). Analogous to earlier studies by our group,<sup>51,53</sup> the PdO/ZrO<sub>2</sub> catalyst was prepared by incipient wetness impregnation using an aqueous solution of (NH<sub>3</sub>)<sub>4</sub>Pd(NO<sub>3</sub>)<sub>2</sub> (ChemPUR GmbH) as noble metal precursor and an aqueous solution of ZrO<sub>2</sub> (Alfa Aesar) as support material. After pressing and sieving, 300 mg of the catalyst granulate with a particle size of 125–250 μm was diluted with 700 mg of SiO<sub>2</sub> and was subject to kinetic tests (light-off) that were conducted in a quartz-glass tubular reactor (inner diameter: 8 mm) using an in-house designed catalyst testing setup. The chemical model for CH<sub>4</sub> oxidation was originally developed by Stotz et al.<sup>39</sup> for a PdO/Al<sub>2</sub>O<sub>3</sub> catalyst as a two-site mean field extended microkinetic model, based on DFT data.<sup>54</sup> The model consists of 78 (including forward and reverse) reactions with a total of 234 kinetic parameters. Out of the total 78 reactions, 58 formed the basis set of independent reactions and the rest were dependent. Note that for a given mechanism the basis set itself is not



**Figure 3.** Experimental data for  $\text{CH}_4$  oxidation over  $\text{PdO}/\text{ZrO}_2$  with 3200 ppm of  $\text{CH}_4$ , 10 vol.% of  $\text{O}_2$ , 0–12 vol.%  $\text{H}_2\text{O}$ , and the balance  $\text{N}_2$ , and GHSV 80000  $\text{h}^{-1}$ . The square markers represent the data points used in the objective function.

unique, but the size of the basis set is unique, hence, the users may choose sensitive reactions to be included during the optimization process as long as the total number of independent reactions remains the same.

Figure 4 shows the modeled data with the original mechanism parameters reported by Stotz et al.,<sup>39</sup> with a

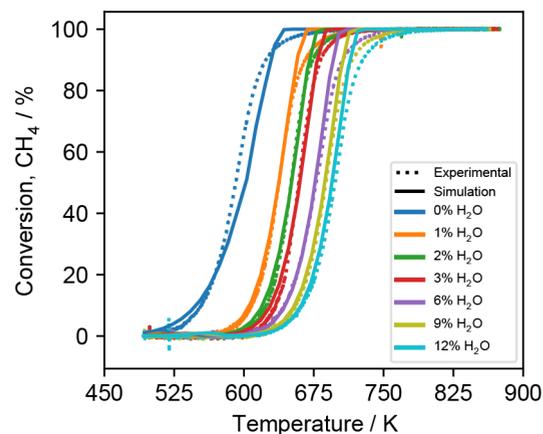


**Figure 4.** Comparison of  $\text{CH}_4$  oxidation experimental conversion over  $\text{PdO}/\text{ZrO}_2$ , with the simulated conversion using the original mechanism from Stotz et al.<sup>39</sup> developed for  $\text{PdO}/\text{Al}_2\text{O}_3$  for various water compositions in the feed.

close fit observed only for the feed with 0%  $\text{H}_2\text{O}$ . So far, a single MKM theory could not take into account what support material has been used and therefore ignores interactions between the support and the noble metal, such as spillover effects, better adsorption/desorption behavior, as well as other electronic properties that will definitely influence kinetic parameters that are included in most of the reaction steps. For this reason, the MKM of Stotz et al.<sup>39</sup> should not be directly used for systems other than  $\text{Al}_2\text{O}_3$  as support material. The objective function in this case comprised only the data corresponding to the  $\text{CH}_4/\text{O}_2$  mixture with 0% and 2%  $\text{H}_2\text{O}$  at temperatures corresponding to 10%, 50%, and 90% conversion (Figure 3, square markers). All other data with other water concentration mixtures were used for validation of the optimized mechanism. These points were considered for the objective function since the focus is primarily on the correct

prediction of the overall water-inhibition effect and since the plot of conversion vs temperature is almost linear until around 90% conversion, therefore just three points in this area of interest were selected.

Figure 5 illustrates the simulation results after the MKM model is optimized using BH, with a step size of 0.2, 5 BH



**Figure 5.** Validation of the optimized mechanism using Basin-Hopping for various feed compositions for  $\text{CH}_4$  oxidation over  $\text{PdO}/\text{ZrO}_2$ .

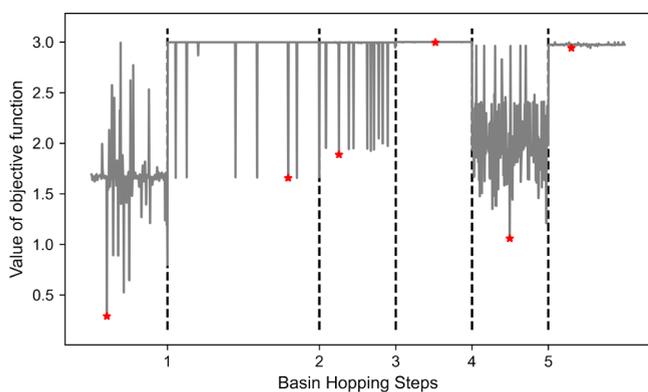
iterations, and 3 Nelder–Mead iterations. The light-off curves before and after the optimization procedure clearly demonstrate the suitability of the presented approach for fine-tuning detailed kinetic models. At higher temperatures, the kinetic reactions are quite fast; therefore, external as well as internal diffusion might limit catalytic  $\text{CH}_4$  conversion at these conditions, which needs to be considered for both the experimental and the simulation framework. However, the start and the behavior of the ignition and the overall water inhibition can be highly influenced by the kinetic parameters and are therefore the focus in the present study. The optimized model is able to simulate these effects significantly better than the original unoptimized model for the  $\text{ZrO}_2$  support. Table 2 shows the value of the kinetic parameters that were modified during the optimization process. Interestingly, in this case, the optimal solution was obtained during the first local search itself (Figure 6), which could be because of the relatively large value of the step size and lower number of iterations. Since the optimal solution in this case is actually the local minimum, only parameters corresponding to eight reactions (out of which only one is independently modified) were significantly changed to obtain an optimal fit with the experimental data, which warrants a further study into the role of these particular reactions for this support. In future works, the authors will include experimental data with different supports and study the change in the original and optimized mechanisms for each support, along with a study of the effect of step size on the optimized solution.

In addition to an optimized set of thermodynamically consistent kinetic parameters, the automated workflow provides a substantial time advantage considering the large number of parameters to be fine-tuned. For this example, the optimization procedure took approximately 5.3 h to complete on a AMD Ryzen Threadripper 3990X processor with 64-cores with a boost clock of 4.3 GHz. A manual optimization of these parameters by an iterative simulation-experiment comparison and step-by-step parameter modification usually takes several

**Table 2. Modified Parameters in the Optimized Mechanism for CH<sub>4</sub> Oxidation over PdO/ZrO<sub>2</sub>, Compared With the Original Parameters from Stotz et al.<sup>39</sup> for PdO/Al<sub>2</sub>O<sub>3</sub>; (a) Denotes a (Pd)<sub>cus</sub> and (b) Represents a (O)<sub>cus</sub> Site**

reaction	optimized parameters			original parameters		
	S <sub>0</sub> or A (cm, mol, s)	E <sub>a</sub> (kJ mol <sup>-1</sup> )	β	S <sub>0</sub> or A (cm, mol, s)	E <sub>a</sub> (kJ mol <sup>-1</sup> )	β
CH <sub>2</sub> (b) + OH(a) → O(a) + CH <sub>3</sub> (b) <sup>a</sup>	1.86 × 10 <sup>22</sup>	318.2	-0.012	1.86 × 10 <sup>22</sup>	303.0	-0.012
(a) + CH <sub>2</sub> OH(a) → CH <sub>2</sub> (a) + OH(a)	2.19 × 10 <sup>22</sup>	165.1	0.004	2.19 × 10 <sup>22</sup>	180.2	0.004
vac(b) + OH(a) → (a) + H(b)	4.22 × 10 <sup>21</sup>	43.0	0	4.22 × 10 <sup>21</sup>	27.9	0
(b) + O(a) → vac(b) + O <sub>2</sub> (a)	9.46 × 10 <sup>22</sup>	169.1	-0.025	9.47 × 10 <sup>22</sup>	169.1	-0.025
CH <sub>3</sub> (a) + H <sub>2</sub> O(a) → CH <sub>4</sub> + (a) + OH(a)	7.07 × 10 <sup>19</sup>	104.2	-0.003	7.07 × 10 <sup>19</sup>	104.2	-0.004
CH <sub>3</sub> (a) + OH(a) → (a) + O(a) + CH <sub>4</sub>	2.69 × 10 <sup>20</sup>	208.0	-0.029	2.70 × 10 <sup>20</sup>	192.9	-0.029
2OH(a) → (a) + O(a) + H <sub>2</sub> O	8.39 × 10 <sup>21</sup>	222.0	-0.113	3.31 × 10 <sup>21</sup>	191.2	0.013
H <sub>2</sub> O(a) → (a) + H <sub>2</sub> O	1.60 × 10 <sup>13</sup>	115.6	-0.081	6.29 × 10 <sup>12</sup>	99.9	0.045

<sup>a</sup>Reaction parameters independently modified by Basin-Hopping.

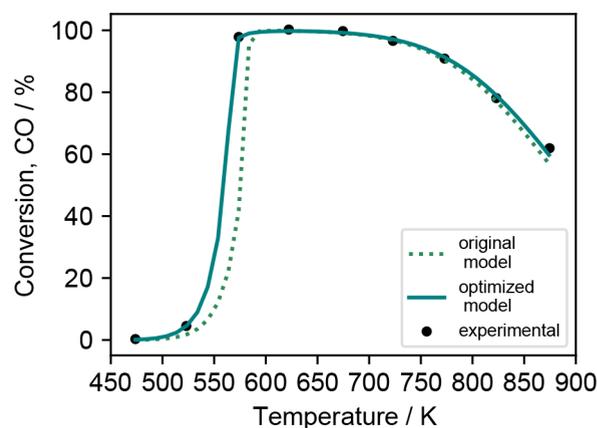


**Figure 6.** Change in the value of the objective function during the local minimum search with the Nelder–Mead method, and the best obtained value before the next iteration of Basin-Hopping (marked in red, star marker) for methane oxidation over PdO/ZrO<sub>2</sub>.

weeks to months. The time taken for the complete workflow is, however, dependent on the individual simulation time of the packed bed reactor and the total number of tunable parameters in the kinetic model.

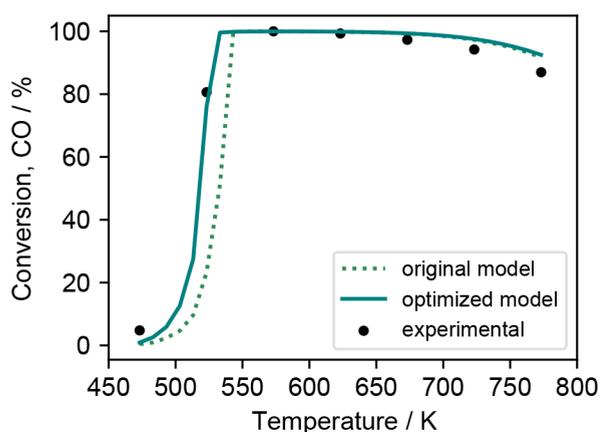
**Illustrative Example II: Carbon Monoxide Methanation over a Nickel Catalyst.** Schmider et al.<sup>42</sup> presented a thermodynamically consistent mechanism for methanation reactions of CO and CO<sub>2</sub> over Ni-based catalysts comprising 42 reactions (including forward and reverse) with a total of 136 kinetic parameters. The algorithm was used to tune 109 parameters corresponding to the 34 independent reactions, while the rest of the parameters for the dependent reactions were calculated by the DETCHEM<sup>ADJUST</sup> package, to ensure that the overall MKM model remains thermodynamically consistent at each step. The experimental data<sup>52</sup> used for the objective function corresponded to a mixture of CO, H<sub>2</sub>, and N<sub>2</sub> in the mole ratio of 3:1:1 over 20% Ni/Al<sub>2</sub>O<sub>3</sub> with an average particle size of 630 μm. Figure 7 shows that the modeled data with the original Schmider et al.<sup>42</sup> mechanism parameters agreed well with the experimental points except at 573 K. Since the mechanism was developed considering various catalyst/support systems, the model parameters fine-tuned for Ni over Al<sub>2</sub>O<sub>3</sub> as support could provide a better match with the experimental data.

After the BH optimization routine with a step size of 0.1, 25 BH iterations, and 50 Nelder–mead iterations, a much closer fit with the experimental data is obtained. For this example, all the data points were used in the objective function, as the gradient of the conversion vs temperature plot is changing continuously

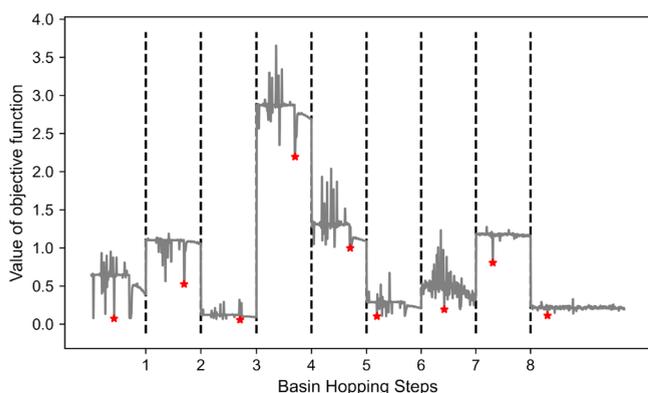


**Figure 7.** Experimental data of CO methanation over Ni/Al<sub>2</sub>O<sub>3</sub> compared with simulated data using the original kinetic parameters from Schmider et al.<sup>42</sup> and using the optimized parameters from Basin-Hopping.

in the whole temperature range, and since the original model is close to the experimental data, a small value of step size is kept. Additionally, the optimal solution did not change after 6 consecutive iterations, hence the procedure was terminated to reduce computational effort. The optimized mechanism is then also used to model the experimental data by Rahamani et al.<sup>55</sup> with a CO:H<sub>2</sub> (1:3 mol ratio) reaction mixture over 20% Ni/Al<sub>2</sub>O<sub>3</sub> in order to validate the optimized mechanism parameters. Figure 8 shows the experimental and the simulated conversion of CO, demonstrating a better agreement between the simulated and the measured data using the optimized model. In this case, certain values used for simulation such as dispersion of metal nanoparticles over the support surface had to be approximated, which could explain the deviations from the experimentally measured conversions. The change in the value of objective function during each BH step and the corresponding Nelder–Mead search is shown in Figure 9. In this work, the parameters with the best value of objective function are reported (Table 3), however, it can be seen that there exist several local minima, including the initial local minimum with the objective function value quite close to the best value obtained after the second hop. This could be due to the initial parameters showing a close agreement earlier on with the experimental data and the small value of step size. The several close local minima may be considered as a pool of possible solutions for the kinetic parameters to minimize overfitting, which will be considered in our future works.



**Figure 8.** Modeled and experimental data from Rahmani et al.<sup>55</sup> for CO methanation over Ni/Al<sub>2</sub>O<sub>3</sub> using kinetic parameters from Schmider et al.<sup>42</sup> and using the optimized parameters.



**Figure 9.** Change in the value of the objective function during the local minimum search with the Nelder–Mead method and the best obtained value before the next iteration of Basin-Hopping (marked in red, star marker) for CO methanation over Ni/Al<sub>2</sub>O<sub>3</sub>.

Table 3 compares the kinetic parameters before and after the optimization procedure (graphical comparison in Figure S1). It is observed that, after optimization, the order of the pre-exponential factors remains largely the same, while the activation energies and the temperature dependency parameters are altered to achieve a better fit with the experimental data. The algorithmic changes to the parameters are observed to be in the range of a 0.1–12% increase or decrease from the original value, while some parameters showed large changes that were deterministically calculated by the DETCHEM<sup>ADJUST</sup> program for maintaining thermodynamic consistency. It is also interesting to see that even though the original mechanism parameters have a good agreement with the experimental values at all other temperatures except between 523 and 580 K, almost all the parameters had to be optimized to match the experimental data in that range, as opposed to the previous example where few parameter changes led to a close fit for a variety of operating conditions. Furthermore, the new parameters continue to demonstrate a close fit to the other data points. This is also observed in Figure 8, where the modeled data with the optimized mechanism significantly affected the data points in the range 480–530 K. These observations strongly suggest a complex relationship between competing reaction pathways and the operating temperature range, which cannot be easily realized when using a manual

fine-tuning approach. Additionally, with relatively lesser parameters to tune and faster simulations in comparison to the methane oxidation example, the optimization procedure for this system took only 52.5 min to complete, thus making the approach particularly efficient for such systems.

It is important to also note that BH does not guarantee reaching a global minimum and, due to its stochasticity, may provide different optimal solutions during different runs. It is also possible that when the algorithm is run for a higher number of iterations to possibly reach a global minimum, the proposed kinetic parameters may lead to solver errors or have significantly slower simulations, which would lead to an overall slow optimization procedure. This is showcased in Table 4 when the algorithm was run twice for 300 BH hops, wherein during the first run, the procedure had to be terminated prematurely due to solver errors leading to failed simulations. As can also be seen from the data summarized in Table 4, the value obtained in all cases is much better than for the unoptimized parameters, and an increase in the number of hops results in only minor differences. Since the gain in accuracy of the simulated model with higher iterations is limited, a choice needs to be made between the accuracy and the computational time and costs involved with higher iterations. It also suggests that with higher iterations, though not studied in this work, appropriate bounds for the kinetic parameters may be considered.

## CONCLUSIONS

This work demonstrates the applicability of the Basin-Hopping algorithm for the optimization of kinetic parameters using two example case studies in heterogeneous catalysis. In both the examples, Basin-Hopping combined with the Nelder–Mead method for a local search was able to provide modeled data with a significantly better fit compared to the one simulated using the original parameters, in a fast and robust manner. The utilization of a Python-based script to obtain input data needed for simulations and subsequently run multiple simulations at various operating conditions during the optimization procedure through the simulation software suite DETCHEM allows for an automated and efficient workflow. The inclusion of DETCHEM<sup>ADJUST</sup> ensures that only thermodynamically consistent solutions are explored, which also reduces the number of parameters that need to be independently optimized during the procedure. An appropriate choice of step sizes may be made based on the uncertainty of the original kinetic parameters, with the number of iterations being the only parameter that needs to be chosen based on trial and error. The choice of objective function, the data points to be included in the objective function, and the step size should overall be based on the species of interest, the criterion for a good solution, and the initial agreement between the simulated and experimental data points. Furthermore, BH does not guarantee reaching a global minimum even with a large number of hops, but in many cases a solution is reached within lesser hops, which performs significantly better than the initial parameters, as showcased in both examples in this work. It is evident from the validation results that the optimized parameters fit well not only to the data used in the objective function, but also for data corresponding to other feed compositions and operating conditions using the same catalyst/support material. However, it has to be noted that the fitted parameters may or may not reflect the true parameters, in spite of the optimized model being closer to

**Table 3. Optimized Kinetic Parameters for CO Methanation over Ni/Al<sub>2</sub>O<sub>3</sub> and the Generalized Original Parameters Reported by Schmider et al.<sup>42</sup> for Ni-Based Catalysts<sup>a</sup>**

reaction	independently modified	optimized parameters			original parameters		
		S <sub>0</sub> or A (cm, mol, s)	E <sub>a</sub> (kJ mol <sup>-1</sup> )	β	S <sub>0</sub> or A (cm, mol, s)	E <sub>a</sub> (kJ mol <sup>-1</sup> )	β
H <sub>2</sub> + 2(s) → 2H(s)	yes	1.22 × 10 <sup>-2</sup>	0	0	1.46 × 10 <sup>-2</sup>	0	0
2H(s) → H <sub>2</sub> + 2(s)	yes	5.05 × 10 <sup>21</sup>	101.6	-0.149	4.54 × 10 <sup>21</sup>	96.1	-0.138
CH <sub>4</sub> + (s) → CH <sub>4</sub> (s)	yes	0.039	0	0	1.06 × 10 <sup>-2</sup>	0	0
CH <sub>4</sub> (s) → CH <sub>4</sub> + (s)	yes	2.76 × 10 <sup>15</sup>	39.6	0.085	2.79 × 10 <sup>15</sup>	37.0	0.085
H <sub>2</sub> O + (s) → H <sub>2</sub> O(s)	yes	0.116	0	0	0.116	0	0
H <sub>2</sub> O(s) → H <sub>2</sub> O + (s)	yes	1.75 × 10 <sup>12</sup>	63.0	-0.029	2.04 × 10 <sup>12</sup>	61.0	-0.031
CO <sub>2</sub> + (s) → CO <sub>2</sub> (s)	yes	5.97 × 10 <sup>-5</sup>	0	0	6.29 × 10 <sup>-5</sup>	0	0
CO <sub>2</sub> (s) → CO <sub>2</sub> + (s)	yes	4.99 × 10 <sup>7</sup>	28.0	0.021	4.99 × 10 <sup>7</sup>	25.8	0.018
CO + (s) → CO(s)	yes	0.381	0	0	0.374	0	0
CO(s) → CO + (s) <sup>b</sup>	yes	1.05 × 10 <sup>12</sup>	111.9	-0.114	1.14 × 10 <sup>12</sup>	112.0	-0.103
CO <sub>2</sub> (s) + (s) → CO(s) + O(s)	yes	1.55 × 10 <sup>23</sup>	79.0	-0.947	1.6 × 10 <sup>23</sup>	89.3	-1.001
CO(s) + O(s) → CO <sub>2</sub> (s) + (s) <sup>b</sup>	yes	5.99 × 10 <sup>19</sup>	127.4	0	5.81 × 10 <sup>19</sup>	123.6	0
CO(s) + (s) → C(s) + O(s) <sup>b</sup>	yes	2.67 × 10 <sup>14</sup>	113.4	0	2.36 × 10 <sup>14</sup>	116.2	0
C(s) + O(s) → CO(s) + (s) <sup>c</sup>	yes	2.60 × 10 <sup>18</sup>	150.3	0	2.54 × 10 <sup>18</sup>	148.1	0
CO(s) + H(s) → C(s) + OH(s) <sup>b</sup>	yes	2.66 × 10 <sup>18</sup>	111.9	-0.228	3.05 × 10 <sup>18</sup>	105.3	-0.223
C(s) + OH(s) → CO(s) + H(s) <sup>c</sup>	yes	2.18 × 10 <sup>18</sup>	63.0	0.143	2.18 × 10 <sup>18</sup>	62.8	0.128
CO(s) + H(s) → HCO(s) + (s)	yes	6.50 × 10 <sup>21</sup>	135.0	-0.911	6.82 × 10 <sup>21</sup>	132.1	-0.979
HCO(s) + (s) → CO(s) + H(s) <sup>b</sup>	yes	2.19 × 10 <sup>20</sup>	0.16	-0.022	2.18 × 10 <sup>20</sup>	0.15	-0.021
HCO(s) + (s) → CH(s) + O(s)	yes	5.84 × 10 <sup>15</sup>	72.5	0.026	5.10 × 10 <sup>15</sup>	81.7	0.023
CH(s) + O(s) → HCO(s) + (s)	yes	3.54 × 10 <sup>19</sup>	117.7	-0.022	3.42 × 10 <sup>19</sup>	110.2	-0.023
C(s) + H(s) → CH(s) + (s) <sup>c</sup>	yes	1.50 × 10 <sup>24</sup>	154.6	-0.437	1.33 × 10 <sup>24</sup>	157.7	-0.456
CH(s) + (s) → C(s) + H(s)	no	3.15 × 10 <sup>22</sup>	28.1	0.403	2.63 × 10 <sup>22</sup>	22.3	0.456
CH(s) + H(s) → CH <sub>2</sub> (s) + (s)	yes	3.17 × 10 <sup>25</sup>	90.0	-0.09	3.21 × 10 <sup>25</sup>	81.1	-0.084
CH <sub>2</sub> (s) + (s) → CH(s) + H(s)	yes	6.14 × 10 <sup>24</sup>	83.8	0.087	6.16 × 10 <sup>24</sup>	95.2	0.084
CH <sub>2</sub> (s) + H(s) → CH <sub>3</sub> (s) + (s)	yes	8.62 × 10 <sup>22</sup>	55.6	-0.051	7.78 × 10 <sup>22</sup>	59.5	-0.048
CH <sub>3</sub> (s) + (s) → CH <sub>2</sub> (s) + H(s)	yes	5.84 × 10 <sup>24</sup>	99.1	0.046	6.16 × 10 <sup>24</sup>	95.9	0.048
CH <sub>3</sub> (s) + H(s) → CH <sub>4</sub> (s) + (s)	yes	3.78 × 10 <sup>21</sup>	70.5	-0.049	3.63 × 10 <sup>21</sup>	65.7	-0.048
CH <sub>4</sub> (s) + (s) → CH <sub>3</sub> (s) + H(s)	no	3.79 × 10 <sup>17</sup>	57.4	1.333	6.16 × 10 <sup>21</sup>	53.6	0.048
H(s) + O(s) → OH(s) + (s)	yes	1.02 × 10 <sup>24</sup>	102.0	-0.187	1.16 × 10 <sup>24</sup>	104.2	-0.176
OH(s) + (s) → H(s) + O(s)	no	8.55 × 10 <sup>19</sup>	16.3	0.184	7.70 × 10 <sup>19</sup>	29.8	0.176
H(s) + OH(s) → H <sub>2</sub> O(s) + (s)	yes	2.58 × 10 <sup>20</sup>	45.0	0.074	2.34 × 10 <sup>20</sup>	44.1	0.075
H <sub>2</sub> O(s) + (s) → H(s) + OH(s)	no	1.91 × 10 <sup>21</sup>	83.1	-0.11	2.91 × 10 <sup>21</sup>	90.4	-0.075
2OH(s) → H <sub>2</sub> O(s) + O(s)	yes	1.13 × 10 <sup>20</sup>	84.5	0.241	1.01 × 10 <sup>20</sup>	95.1	0.251
H <sub>2</sub> O(s) + O(s) → 2OH(s)	no	9.95 × 10 <sup>24</sup>	208.4	-0.314	1.89 × 10 <sup>25</sup>	215.8	-0.251
H(s) + CO <sub>2</sub> (s) → COOH(s) + (s)	yes	1.32 × 10 <sup>25</sup>	110.1	-0.387	1.29 × 10 <sup>25</sup>	117.2	-0.46
COOH(s) + (s) → H(s) + CO <sub>2</sub> (s)	yes	1.29 × 10 <sup>20</sup>	34.4	0.499	1.29 × 10 <sup>20</sup>	33.8	0.46
COOH(s) + (s) → CO(s) + OH(s)	yes	6.70 × 10 <sup>23</sup>	50.0	-0.209	6.03 × 10 <sup>23</sup>	54.4	-0.216
CO(s) + OH(s) → COOH(s) + (s) <sup>b</sup>	no	2.23 × 10 <sup>21</sup>	88.3	0.223	1.45 × 10 <sup>21</sup>	97.6	0.216
COOH(s) + H(s) → HCO(s) + OH(s)	yes	4.01 × 10 <sup>23</sup>	107.4	-1.256	4.22 × 10 <sup>23</sup>	104.7	-1.145
HCO(s) + OH(s) → COOH(s) + H(s)	no	4.50 × 10 <sup>19</sup>	10.9	0.065	3.25 × 10 <sup>19</sup>	16.1	0.245
2CO(s) → CO <sub>2</sub> (s) + C(s) <sup>b</sup>	yes	6.78 × 10 <sup>13</sup>	262.9	0.523	6.31 × 10 <sup>13</sup>	241.7	0.5
CO <sub>2</sub> (s) + C(s) → 2CO(s) <sup>c</sup>	no	1.70 × 10 <sup>21</sup>	251.4	-0.424	1.88 × 10 <sup>21</sup>	239.3	-0.5

<sup>a</sup>Note: (s) represents an empty surface site. <sup>b</sup>represents coverage dependency of 51.9 kJ/mol on CO(s). <sup>c</sup>represents coverage dependency of 98.7 kJ/mol on C(s).

**Table 4. Summary of Several Runs of the Basin-Hopping Algorithm for Optimization of Kinetic Parameters for the Methanation Reaction over Ni**

algorithm parameters	successful hops	hop at which best solution is obtained	initial objective function value	best objective function value
25 hops, step size 0.1, Nelder–Mead iterations 50	8 (based on the early stopping criterion)	2	0.64	0.058
300 hops, step size 0.1, Nelder–Mead iterations 50	267 (due to solver errors at higher iterations)	58	0.64	0.055
300 hops, step size 0.1, Nelder–Mead iterations 50	300	95	0.64	0.062

the experiment. Since MKM models may not directly account for the effect of support materials such as spillover effects,

metal–support interactions, better adsorption/desorption behavior, and electronic properties that may influence the

kinetic parameters, the majority of published mechanisms are applicable to specific catalytic systems and must be fine-tuned for other supports. As demonstrated in both the examples in this work, with the Stotz et al.<sup>39</sup> mechanism specifically developed for the PdO/Al<sub>2</sub>O<sub>3</sub> catalyst system and the Schmider et al.<sup>42</sup> mechanism representing a generalized MKM model for methanation, both mechanisms needed to be fine-tuned when different support materials are used in experiments to obtain more accurate models. The CO methanation case is a good example of mechanisms consisting of complex reaction pathways, with the kinetic performance dependent on the operating temperature, which therefore required extensive modification of the kinetic parameters to obtain a good fit with the experimental data. The optimized mechanism for the methane oxidation case correctly predicted the water inhibition effect with minimal modifications to the original mechanism parameters. These examples clearly demonstrate the complexity of different kinetic models and showcase the necessity of using computational algorithms over the manual approach to fine-tune the model parameters. The utilization of Basin-Hopping coupled with the Nelder–Mead method allows for an efficient exploration of the high dimensional parameter space to obtain the optimal kinetic parameters for microkinetic models without the need for gradient information. It may also be useful to look at the pool of solutions obtained as the local minima to quantify the uncertainty in the optimized parameters. Furthermore, an automated approach accomplishes the optimization task within a time frame that is not possible with a manual approach considering the high dimensional parameter space of detailed microkinetic models for heterogeneous catalysis. It should be noted that with a higher number of hops the overall optimization process may become slower due to longer computational time needed for calculation of the objective function, which would nevertheless be lesser when compared to manual tuning. This approach can thus be used to conveniently fine-tune existing detailed microkinetic models and also to facilitate the derivation of new mechanisms, including new supports and for bimetallic catalysts where one metal serves as the active site and the other only enhances the novel properties of the active metal.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.2c08179>.

Table S1: Complete mechanism for methane oxidation over Pd/ZrO<sub>2</sub>. Figure S1: Graphical comparison of kinetic parameters before and after optimization for CO methanation over Ni/Al<sub>2</sub>O<sub>3</sub> (PDF)

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## Notes

The authors declare no competing financial interest.

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