Chemical Reaction Neural Networks for the Discovery of Microkinetic Parameters and Reaction Networks for Heterogeneously Catalyzed Reactions – A Training Strategy

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Abstract

Precisely describing dynamic reactor behavior is of increasing importance considering the future need for flexible conversion of renewable energy (e.g. for methane or ammonia synthesis). However, the determination of kinetic parameters for highly accurate transient (microscale) kinetic models is tedious and connected not only to intricate experimental design but also expensive equipment. Furthermore, even the computer aided derivation of parameters from kinetic experimental data still poses a major challenge.

Recently, physically motivated methods of capturing formalized chemical kinetics in artificial neural networks have been published. Most notably the Chemical Reaction Neural Network (CRNN) method proved to be capable of extracting kinetic information from carefully prepared transient simulation or experimental results. However, typical challenges induced by heterogeneously catalyzed reactions have not yet been addressed.

Consequently, in our current contribution we present challenges and limitations of applying CRNN-methodology to pseudo-experimental data with the aim of extracting microkinetic information and link those to the well-known concepts of rate-determining or quasi-equilibrated steps. From the identified limitations, we derive favorable reaction regimes for sampling training data and their effect on the recovered kinetics, which is the basis to design appropriate transient experiments.

Therefore, we propose an extended (heterogeneous) CRNN capable of describing reaction mechanisms catalyzed by solids. The model is trained with virtual data compiled by assuming a combination of fast and slow reactions. Finally, we conclude on the capabilities of heterogeneous CRNNs (hCRNNs).

**Keywords**: Microkinetics, Neural Networks, Kinetic Modeling, Machine Learning

* 1. Introduction

The demand for technologies capable of the flexible conversion of renewable energies and the coupling of energy and gas grids (like methanation, ammonia synthesis or Fischer-Tropsch synthesis) is rising. This drives the need for the precise description of reactor behavior in highly transient operating regimes, which in turn requires accurate microscale kinetic models for resolving transient process on catalytic surfaces. The determination of parameters for these kinds of models requires elaborate experimentation, often only enabled by prior experience, expensive analytics and supported by findings from computational chemistry methods like density functional theory (DFT). The whole model development cycle and some current applications are depicted by Motagamwala and Dumesic (2020). With the increasing computational power – already relieving some constraints on this tedious process – the field of machine learning (ML) promises even higher speedups all across the mechanism development cycle.

To help speedup of calculation and parameter identification Barwey and Raman (2021) introduced a neural network formalism for capturing chemical kinetic expressions in matrix vector notation enabling efficient handling within ML frameworks like, e.g., PyTorch. Ji and Deng (2021) used a similar construction (and coined the term Chemical Reaction Neural Network, CRNN) extended by a neural ODE solver to enable detailed kinetic discovery via temporal concentration profiles of multiple homogeneous reaction mechanisms.

Both approaches do not consider the difficulties inherent to heterogeneous reaction mechanisms, where ad- and desorption of reactants occur simultaneously to surface reactions. Specifically, to our knowledge these methods have not yet been linked to the well-established concepts of the rate-determining or quasi-equilibrated steps though from experimentation it is clearly known that the existence of extremely fast or slow reactions in a given reaction network might mask critical pathways to the desired products. Hence, the current state of CRNN models is not yet demonstrated for reaction mechanism being more realistic in heterogeneous catalysis. Consequently, we aim to investigate the influence of the rate differences on CRNN performance and thus identify suitable training strategies to obtain reliable and detailed knowledge about the investigated kinetics.

In our earlier work, we demonstrated a) the wide range applicability and generalizability of microkinetic CRNNs for heterogeneously catalyzed reaction mechanisms emerging from the physically informed network architecture and b) coupling possibilities with common reactor models. These results promise the identification of reaction networks and respective kinetic parameters from readily available transient experimental data, as obtained by periodic transient kinetics method (PTK) presented by Meyer et. al. (2021) or Gäßler et. al. (2022).

* 1. Heterogeneous CRNNs (hCRNNs)

The underlying structure of the proposed hCRNN is adapted from Ji and Deng (2021) taking advantage of the similarity between the power law and Arrhenius equation for heterogeneous reactions in log-scale and the general mathematical formulation of a single layer in multilayer aNNs (eq. (1)). We propose extending the previous structure by including a more general approach for parametrization of the reaction rate. In addition to the basic structure, our network features parametrization of surface coverage dependency of the Arrhenius expression as well as the inclusion of special kinetic expressions for the adsorption reactions typically parametrized by the initial sticking factor . In eq. (1) the rate, , of reaction depends on temperature, , via Arrhenius equation (with frequency factor, , activation energy, , and gas constant, ), on surface coverage, , of component (with coverage dependence of activation energy of reaction , ) and the surface and gas phase concentrations, , assuming elementary reactions with the order of, . Eq. (2) establishes the connection of species formation rate to all reactions in the mechanism through the stoichiometric coefficients .

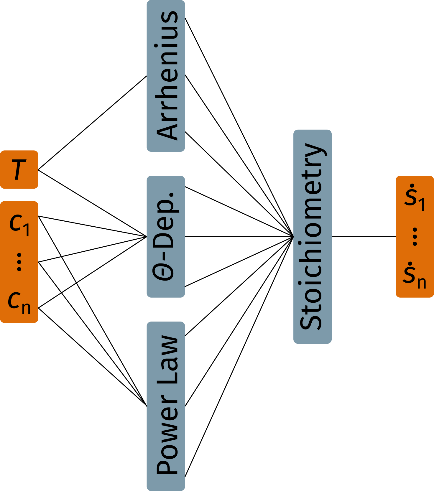


Figure 1: Proposed network architecture. Each box represents a fully connected linear layer. Power law, Arrhenius and coverage dependence layers are further separated into forward and backward sub-layers acting on their own set of trainable parameters.

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| --- | --- |
|  | (1) |
|  | (2) |

Here, we construct a more strongly separated network in the open-source deep learning framework PyTorch. Our architecture aims to make use of clearly interpretable parameter groups for different parts of the microkinetic model such as stoichiometric coefficients, reaction orders, Arrhenius-type parameters, and surface coverage dependency parameters grouping them into their own dedicated layers. Hence, the architecture clearly reflects the structure of eq. (1). An overview of the proposed network architecture is depicted in fig. 1. The main and most physically interpretable hyperparameter to influence learning success is the number of suspected reactions involved in the mechanism. We make extensive use of this hyperparameter and evaluate its influence on the accuracy of the determined kinetic parameters.

* 1. The influence of rate determining steps in the mechanism

To investigate the influence of reaction rates on training and performance of the hCRNN, a generic but universal Langmuir-Hinshelwood (LH) type microkinetic model consisting of four elementary reactions is constructed, parametrized and used as a benchmark in the depicted experiments. As a building block of more complex reaction networks, the LH-mechanism encapsulates reactant adsorption (eqs. (R1) and (R2)) and product desorption (eq. (R4)) as well as a single surface reaction (eq. (R3)), which – depending on their rate constant – can act either as the rate-determining or a quasi-equilibrated step.

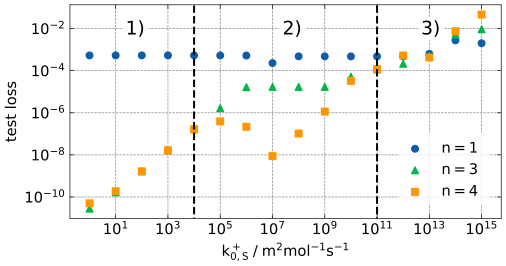


Figure 2: Training result for varying number of presumed elementary reaction steps and surface reaction rate constant . Notice the three distinct regimes (denoted by 1), 2) and 3)) and the bifurcation and reunification of the branches for and presumed reactions.

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| --- | --- |
|  | (R1) |
|  | (R2) |
|  | (R3) |
|  | (R4) |

Reaction conditions for training data preparation are sampled at constant temperature and random gas- and surface-phase compositions for *all* involved species according to a flat Dirichlet distribution. The so generated dataset consists of 10000 samples at different reaction conditions sampled uniformly from the composition space. To generate the needed composition () – temperature () – formation rate () pairs, the latter are calculated according to the presumed LH mechanism at the sampled conditions. Therefore, the rate constant of the surface reaction, , is varied with fixed ad- and desorption reaction rate constants. This way, we create multiple versions of the dataset corresponding to different surface reaction rates in the mechanism. These cover the dynamic range of the surface reaction being rate determining (slow) up to quasi-equilibrated (fast). This approach represents a highly transient mode of reactor operation far from equilibrium. It should be noted that variation of results in differing values for the formation rates in the dataset but does not influence the sampled reaction conditions.

Training of the hCRNN is then conducted using the Adam-optimizer with a custom learning-rate decay schedule by minimizing the L2-Norm as a measure for the error between network formation rate prediction and ground-truth mechanistic knowledge. The number of presumed reactions is varied between 1, 3 and 4. Prior knowledge tells us to expect best results at four presumed reactions matching the number in the ground truth mechanism. As can be observed from fig. 2 the obtained loss (the error between hCRNN prediction and ground truth) behaves differently depending on the order of magnitude of the reaction rate constant of the surface reaction. Three regimes can be identified:

*1) Very slow reaction*: The surface reaction is too slow to have meaningful impact on overall kinetic behavior; three reactions explain the observed data equally well.

*2) Medium fast reaction*: The surface reaction is fast enough for the overall behavior to not be explained by only three reactions (see the bifurcation of the branches for and reactions) but requires four.

*3) Very fast reaction*: The surface reaction dominates the reaction network, in the limit for even higher one reaction is enough to describe the kinetic behavior.

These results tie in with the known theory of the rate determining step, although they somewhat contradict the experimentalists intuition. As opposed to steady-state kinetic experiments in which quasi-equilibrated steps are virtually invisible to the observer, in the presented transient regime these *fast* steps dominate the dynamics and are therefore easy to identify. Carrying over these results into the design of suitable training regimes hints at the advantages that arise from combining data from both highly transient and steady-state experimental results.

* 1. Conclusions

This contribution demonstrates that hCRNNs are capable of identifying the number of reactions and determining kinetic parameters for complex mechanisms in heterogeneous catalysis. It is apparent that the reaction regime has a critical impact on the performance of the hCRNN. Identification of all reactions is possible in the isothermal transient regime with no rate limiting or quasi-equilibrated steps, while the significant reaction steps are identified in any case. In our contribution we further investigate this behavior of hCRNNs and present tailored training strategies making use of different data acquisition strategies with the goal of gaining detailed mechanistic knowledge.

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