Chemical Reaction Neural Networks for Discovery of Microkinetic Parameters for Heterogeneous Reaction Networks – A Training Strategy

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Highlights
- A formulation of CRNNs for heterogeneous catalysis is presented (hCRNNS).
- hCRNNs can identify kinetic parameters from highly transient data.
- Reaction conditions and regime have a critical impact on identified parameters.
- Sophisticated dataset design enables kinetic discovery for difficult heterogeneous systems.

1. Introduction

Precisely describing dynamic reactor behavior is of increasing importance considering the future need for flexible conversion of renewable energy (e.g. in methanation plants). However, the determination of kinetic parameters for highly accurate dynamic (microscale) kinetic models is tedious and connected not only to intricate experiment 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 [1,2]. Most notably the Chemical Reaction Neural Network (CRNN) method proved to be capable of extracting kinetic information from carefully prepared simulation [3] or experimental transient results – e.g. obtained by PTK experiments [4,5]. However, it has not yet been demonstrated for heterogeneous catalysis and its inherent problems like different time scales for sorption processes and reactions or the presence of many short-lived or hard to measure intermediates [6].

2. Methods

We make use of a refined and extended CRNN architecture based on Ji & Deng [3] and a training dataset derived from pseudo experimental data. The data is sampled in a highly transient mode by calculating species formation rates at given arbitrary reaction conditions. As an exemplary system, we examine a generic but universal Langmuir-Hinshelwood (LH) type mechanism containing four elementary reaction steps (see fig. 1 a)). Optimal network hyperparameters have been identified in preliminary experiments. One remaining hyperparameter – the number of elementary reaction steps in the sought mechanism, n – remains to be determined for every individual case. However, this parameter caries physical meaning and is systematically varied in our contribution. Finally, training success is judged based on error measures between test data and prediction as well as interpretation and comparison of the determined kinetic parameters.
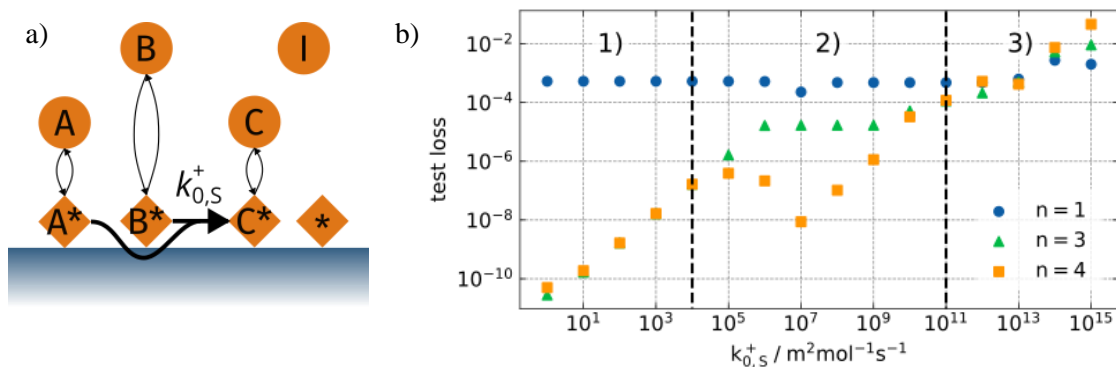

Figure 1. a) Generic LH Mechanism with $n = 4$ partly reversible elementary reaction steps and b) training result for varying number of presumed elementary reaction steps at a given surface reaction rate constant $k_{0,S}^+$. Notice the three distinct regimes (denoted by 1), 2) and 3)) and the bifurcation and reunification of the branches for $n = 3$ and $n = 4$ presumed reactions.

To investigate the CRNN training success under varying reaction rates regimes, the rate constant $k_{0,S}^+$ of the single surface reaction is deliberately varied. This change in surface reaction rate provokes regimes in which the surface reaction acts as either rate limiting or quasi-equilibrated (and some discrete states in between). Variation of temperature reveals additional kinetic information, so does variation of gas phase pressures. However, kinetic discovery is not guaranteed under all imaginable reaction conditions, as our contribution will show. We propose to put these results into context with well-established concepts of rate-limiting and quasi-equilibrated steps in classical kinetics.

3. Results and Discussion

Fig. 1 b) shows the dependence of the obtained loss (the deviation between CRNN prediction and ground truth) on the underlying mechanism (specifically the rate of the surface reaction as indicated by $k_{0,S}^+$). It is apparent, that for slow surface reactions (low $k_{0,S}^+$, 1) three reactions are enough to recover kinetic behavior while for very fast surface reaction (high $k_{0,S}^+$, 3) recovering this single one is enough. Only the intermediate regime (2) shows lower errors for $n = 4$. Further investigation reveals that discovery of kinetic parameters by hCRNNs is not necessarily possible on all reaction regimes but limited to the fastest observable reactions (indicated by the bifurcation of curves notable in fig. 1). This implies, a purely highly dynamic dataset might not be suited for kinetic discovery of certain reactions in a given reaction network. By knowing these limitations, one can derive suitable training strategies combating these difficulties. This contribution shows that training success (and thereby accuracy of the obtained mechanism) can be improved by combining data sampled at various regimes.

For example, it seems promising to combine steady-state and highly dynamic numerical and experimental data. In this combined dataset, dynamic data might illuminate the fast processes while steady-state data shows the effect of only the rate-limiting (slow) steps (an approach often described in classical experimentation [6]).

4. Conclusions

This contribution demonstrates that CRNNs 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 CRNN. Identification of the underlying mechanism is possible in the 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 CRNNs and present tailored training strategies making use of different data acquisition strategies with the goal of gaining detailed mechanistic knowledge. Thereby, we establish yet another step towards enabling kinetic discovery from experimental PTK data.

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