

How accurate is the mean-field approximation for catalytic kinetics?

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Modelling catalytic kinetics is indispensable for the design of reactors and chemical processes. Currently, the majority of kinetic models employ mean-field approximations and are formulated as ordinary differential equations, which leads to an approximate description of catalytic kinetics by omitting spatial correlations. On the other hand, kinetic Monte Carlo (KMC) approaches provide a discrete-space continuous-time stochastic formulation that enables a detailed treatment of spatial correlations in the adlayer, but at a significant computation expense. Such spatial correlations arise from slow diffusion in tandem with 2-site reactions, or from adsorbate-adsorbate lateral interactions, and have been shown to markedly affect the observed kinetics.^{1,2} It is thus well known that mean-field models are limited, as they neglect such correlations; yet, due to their computational efficiency, such approaches are ideal in multiscale modelling frameworks (for instance as chemistry modules in computational fluid dynamics). However, it is possible to develop higher order approximations that systematically increase the accuracy of kinetic models by treating spatial correlations at a progressively higher level of detail but at the cost of higher computational effort.³⁻⁵

In this study, we assess the error and computational efficiency of mean-field and higher order approximations for kinetics in catalytic systems with strongly interacting adsorbates. We thus focus on a model for NO oxidation incorporating first nearest neighbor lateral interactions and construct a sequence of approximate models of progressively higher accuracy, starting from the mean-field treatment and continuing with a sequence of Bethe-Peierls models with increasing cluster sizes. By comparing the turnover frequencies of these models with those obtained from KMC simulation, we show that the mean-field predictions deviate by several orders of magnitude from the KMC simulation results. The Bethe-Peierls model, with a cluster incorporating sites up to 2nd nearest neighbors, performs well for predicting coverages; however, due to the exponential dependence of reaction rate on activation energy, the turnover frequency predictions are still inadequate. One requires Bethe-Peierls approximations with clusters of 4th or higher nearest neighbors, in order to faithfully reproduce the KMC predictions. We show that such approximations, while more computationally intense than the mean-field treatment, still enable significant computational savings compared to a KMC simulation, thereby paving the road for employing them in multiscale modelling frameworks.

References

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