

Investigating rate-limiting steps in heterogeneous catalysis using Cramér–von Mises distance

Sina Dortaj – WS19 batch
Supervisor: Dr. Sebastian Matera (FHI)

The kinetic Monte Carlo (kMC) method is, without question, the physically most sound approach for simulating chemical kinetics on heterogeneous catalysts. Unlike prevalent approaches which employ some kind of physical approximation, it essentially is a numerical method and allows estimating turnover frequencies or coverages with a tunable accuracy, given a reaction mechanism and corresponding rate constants.

This advantage comes at much higher computational costs compared to classical kinetic approaches and stochastic noise on the simulation results. Both make the determination of rate-limiting steps very cumbersome, which requires a local sensitivity analysis. Not only in kMC, but another problem is also that rate constants often carry some sizeable uncertainty and the use of just local methods is questionable. These uncertainties might reflect the potential error in reaction barriers, e.g. due to the intrinsic approximations in quantum chemical methods or the noise in experimental data used to determine reaction barriers. Another source might result from the field of catalyst screening, where the uncertainty reflects the variability of the rate constants in a class of catalyst materials.

We address both problems, high costs, and parameter uncertainty, by a novel global sensitivity analysis based on the Cramér–von Mises distance and a Quasi-Monte Carlo sampling of the space of rate constants. While applicable to any kind of model, our approach is particularly suited for the use of kMC and other Monte Carlo models. This manifests in the relatively small number of required kMC simulations to achieve reasonably accurate sensitivity index estimates. Moreover, the method is robust against the noise in the kMC estimates and every kMC simulation can be run with a modest computational footprint. We demonstrate the approach on the first principle Kinetic Monte Carlo models for CO oxidation on RuO₂ and for the CO₂ reduction on Cu. For these models, we investigate the influence of the commonly reported uncertainty of ~0.2 eV of the underlying Density Functional Theory derived energetics. We find that with this uncertainty, it is not possible to predict whether the two catalysts are actually active or not. However, we find that only a few barriers control this uncertainty, and it is still possible to draw meaningful conclusions on the rate-limiting steps.

- [1] K. Reuter, M. Scheffler, *Phys. Rev. B*, **2006**, 73.045433.
- [2] H. Meskine, S. Matera, M. Scheffler, *Surface Science*. **2009**, 0039-6028.
- [3] E. Plischke, E. Borgonovo, *European Journal of Operational Research*. **2013**, 0377-2217.
- [4] Y. Yang, M. G. White, P. Liu, B., *J. Phys. Chem. C* **2012**, 116, 1, 248–256.