



## Towards the accurate and efficient microkinetic modelling in heterogeneous catalysis

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### Abstract:

Electronic structure calculations based on density functional theory (DFT) provide valuable information on geometries, heats of reactions and reaction barrier heights, etc., for a catalytic system. To relate these atomic scale properties with the macroscopic variables of the catalytic system, however, one has to carry out reaction kinetics simulations. The central gateway to go from DFT energetics to reaction kinetics is microkinetics via kinetic Monte Carlo (KMC [1,2]) simulations in principle, but often phenomenological kinetics (PK) of the mean-field modelings [3] in practice. KMC on explicit lattices can resolve events taking place on the catalytic surfaces at the atomic level. It can explicitly account for the spatial correlations due to lateral interactions among adsorbates, which have been proved to significantly affect the surface chemical reactions. However, the disparity in time scales of various processes (e.g. adsorption/desorption, diffusion and reaction) usually makes the brute force KMC simulations impractical. The complexity can be efficiently reduced by applying the mean-field approximation to solving the reaction network with chemical rate equations. Nevertheless, the standard mean-field kinetics with chemical rate equations, though widely used, are unreliable in many circumstances of real catalytic systems.

Here we report a novel method where the reaction propensities at a given surface coverage are extracted from a diffusion-only KMC on the explicit lattices [4], while the evolutions of surface coverages are performed by an implicit lattice KMC in the PK form. The steady state is reached when the surface coverages and the corresponding reaction rates are self-consistent. This so-called eXtended PK (XPK [5]) method is shown here to provide a useful tool that complex catalytic processes can be studied efficiently and yet accurately. Case studies such as CO oxidation reactions, NH<sub>3</sub> decomposition reactions, HCOOH decomposition reactions, and CO activation in Fischer-Tropsch synthesis, etc., will be presented. Challenges and our future plans will be discussed.

### References:

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