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Scrutinizing concepts in chemical kinetics: Sensitivity analysis and mean-field approximation HAKIM MESKINE, KARSTEN REUTER, MATTHIAS SCHEFFLER, Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin, HORIA METIU, University of California at Santa Barbara, Santa Barbara CA 93106 — We present kinetic Monte Carlo (kMC) simulations for the CO oxidation reaction at $RuO_2(110)$, based on rate constants determined by density-functional theory and transition-state theory. The composition and structure of the catalyst surface are computed in reactive environments ranging from ultra-high vacuum (UHV) to technologically relevant conditions (pressures of several atmospheres and elevated temperatures). This setup enables us to scrutinize frequently employed concepts in the modeling of chemical kinetics: Sensitivity analyses are performed to identify the rate determining steps under the different environmental conditions. While helpful under UHV conditions, this analysis proves to be of little use for catalytically relevant environments, since then a larger number of elementary processes contributes equally to the total rate of product formation. We also check on the mean-field approximation employed in phenomenological microkinetics by comparing rate equations based on the same first-principles rate constants to the kMC simulations, where the spatial distribution of the chemicals at the catalyst surface is explicitly considered. The rate equation activities are found to be in serious error, even failing to identify the correct dominant reaction mechanism.

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