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Identifiability of Microkinetic Parameters from Multimodal Operando Data

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ABSTRACT

Chemical kinetics provides the phenomenological framework for the elucidation of reaction mechanisms, in which ab-initio microkinetic models translate density-functional energetics into catalytic rates. Yet the underlying barriers carry uncertainties of 0.1 to 0.3 eV, and the extent to which a given set of measurements can retrieve them remains largely unquantified. Here, we frame the operando inverse problem as a maximum-likelihood estimation over a differentiable microkinetic model. The pseudo-steady-state surface enters as an algebraic constraint, and parameter sensitivities follow by automatic differentiation through its adjoint, the implicit function theorem applied at the converged root rather than through the solver iterations. These sensitivities propagate the measurement covariance into the parameter covariance, and the resulting Fisher information, the information each experiment carries about each barrier, ranks candidate experiments to establish which measurement determines which barrier.

We analyze two mechanisms as synthetic case studies, a CO oxidation model and a reverse water-gas shift submechanism drawn from a larger CO2-hydrogenation reaction network, and assess the extent to which their barriers can be retrieved across gas chromatography, mass spectrometry, infrared surface spectroscopy, and isotopic transients. Multi-temperature data makes the activation energies and prefactors separately identifiable through the Arrhenius dependence, and gas chromatography alone retrieves the rate-determining barrier to a few meV and its prefactor to a few percent. The remaining steps reside near equilibrium, in which the gas-phase observables carry vanishing sensitivity to their barriers, placing those directions in the nullspace of the Fisher information, so they are unidentifiable from gas data. For the reverse water-gas shift, isotope-resolved infrared spectroscopy of the adsorbed intermediates measures the unidirectional rates of the surface steps rather than their net rates, whereby this sensitivity is restored. Were the O* and OH* surface bands observable, resolving each adsorbed species' infrared signal by isotope label would retrieve all three of its barriers, including the quasi-equilibrated one, without assumed priors and to within tens of meV (joint multi-temperature Fisher, prefactors co-fit). On Rh(211), however, only the CO* band clears the infrared detection floor, whereas the O* and OH* intermediates that carry the quasi-equilibrated barrier lie orders of magnitude below it, leaving that barrier unidentified.

Identifiability is therefore set by the catalyst's intermediate binding energies rather than by the choice of experiment. More broadly, it emerges as a joint property of timescale, experiment, and catalyst rather than of a parameter alone: a barrier is identifiable only where an experiment resolves the step's intrinsic relaxation time, accesses unidirectional rather than net rates, and populates the carrying intermediate above the detection floor. Stated as a model-based design of experiments, this condition turns the modality, temperature, sampling location, and catalyst into the levers it ranks. The same framework could be extended to larger microkinetic models, including CO2-hydrogenation routes to methane and alcohols, where

identifiability-guided operando design would point to the measurements and catalysts that pin the barriers governing activity and selectivity.