

Mesokinetics as a tool bridging the microscopic-to-macroscopic transition to rationalize catalyst design

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Highlights

- Kinetics-assisted identification and quantification of dominant active site.
- Kinetics-assisted identification of catalytic descriptor for active site.
- Mesokinetics bridging the microscopic properties and macroscopic performance.

1. Introduction

Heterogeneous catalysis forms the foundation of the contemporary chemical industry, and achieving a molecular-level comprehension of these catalysts constitutes the initial and principal objective of modern catalysis research. In contrast to homogeneous catalysts, which exist within small molecules or as transition metal ions or complexes with unequivocal molecular structures, heterogeneous catalysts typically encompass numerous, diverse, and intricate surface sites, including terraces, steps, kinks, and metal adatoms. Originating from Taylor's 1920s proposition of the "active site" concept, it is widely acknowledged that not all surface atoms actively participate in catalytic reactions; rather, specific types of surface sites play a pivotal role. Consequently, the efficient design and engineering of these active sites have proven effective in optimizing catalytic performance. However, the potential for real-world applications is significantly constrained by the absence of effective techniques for active site identification.

Beyond the identification of active sites, the strategy of tailoring these sites requires further exploration. Typically, a heterogeneous catalytic cycle commences with the adsorption of reactants onto active sites, and the adsorption strength should align with the Sabatier principle—neither too weak nor too strong. This principle, in turn, is determined by the geometric and electronic structures of the active sites. Drawing inspiration from early work on model systems by theoretical and surface chemists, considerable progress has been made. A unique property known as the "descriptor" has been identified in model catalysts, governing adsorption strength and providing a quantitative means to screen catalysts and predict functions. Despite this progress, challenges persist in expanding model systems to working catalysts. The dynamic surface chemistry of catalytic materials under realistic reaction conditions can induce significant changes in the properties of active sites. Consequently, while *ex situ* studies offer qualitative insights into the microscopic properties of active sites and macroscopic catalytic performance, achieving a quantitative correlation necessitates a combination of advanced characterization techniques, well-designed *in situ* reaction cells, and related kinetics measurement protocols.

Addressing the gap between the molecular-level description of microscopic geometric and electronic properties of active sites and the comprehensive understanding of macroscopic catalytic performance—the microscopic-to-macroscopic transition—remains both intriguing and challenging. Progress in this direction holds the promise of revolutionizing catalyst design and preparation.

2. Methods

We utilized a combination of multiple characterizations, isotopic kinetics investigations, and multiscale simulations for mesokinetics modeling.

3. Results and discussion

This study introduces mesokinetics modeling as a groundbreaking approach for the quantitative depiction of active site characteristics and related mechanistic insights, serving as a versatile tool to guide rational catalyst design. Illustrated through a pseudo zero-order reaction, the kinetics derived from Pt particle size-sensitive catalytic activity and size-insensitive activation energy point to a single dominant active site. Specifically, Pt(111), with a nearly constant TOF_{111} , emerges as the prevailing active site. Extending this methodology to diverse thermo-, electro-, and photocatalysts in applications such as chemical synthesis, hydrogen generation, and environmental processes enables the identification and quantification of active sites (N_i). Further, by deriving kinetics from the kinetic compensation effects, a thermodynamic equilibrium between activation entropy and enthalpy is revealed, displaying linear dependencies on Pt charge. Consequently, Pt charge is established as a catalytic descriptor facilitating the quantitative determination of TOF_i . This approach is successfully applied to Pt-catalyzed CO oxidation with non-zero-order reaction characteristics, accounting for surface species site coverages.

Integrating the statistical correlations of N_i and TOF_i into the rate equation, $R = \sum N_i \times TOF_i$, yields the mesokinetics model. This model accurately predicts catalytic function and facilitates catalyst screening. Finally, a comprehensive strategy is developed, starting from the interfacial charge distribution and progressing through reaction mechanism, kinetics, and thermodynamics parameters of the rate-determining step, culminating in catalytic performance. This *de novo* approach provides a unified mechanistic and kinetics framework for reactions involving Pt electronic structures.

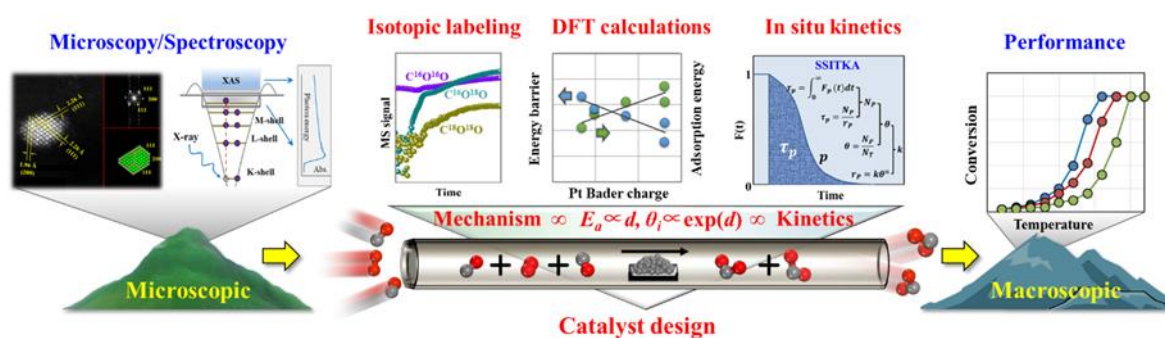


Figure 1. The schematic diagram for bridging the microscopic-to-macroscopic transition.

4. Conclusions

In conclusion, we begin with the kinetics-based methodology to identify and quantify the number (N_i) of dominating active site over catalyst surfaces, and then catalytic descriptor (d) for its quantitative determination of TOF_i . Next, substituting the above statistical correlations of N_i and TOF_i into the rate equation offers the mesokinetics model. The as-obtained Mesokinetics not only showcases considerable potential in elucidating the quantitative interplay between active sites and catalytic activity but also paves the way for a novel research direction in kinetics analysis to rationalize catalyst design.

References

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Keywords

Mesokinetics; Active site; Descriptor; Microscopic-to-macroscopic transition.