



A review of multiscale modeling of metal-catalyzed reactions: Mechanism development for complexity and emergent behavior

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ARTICLE INFO

Article history:

Received 4 February 2011

Received in revised form

21 May 2011

Accepted 30 May 2011

Available online 13 June 2011

Keywords:

Catalysis

Chemical reactors

Kinetics

Multiscale modeling

Catalyst design

Microkinetic modeling

ABSTRACT

We review and provide a perspective on multiscale modeling of catalytic reactions with emphasis on mechanism development and application to complex and emergent systems. We start with an overview of length and time scales, objectives, and challenges in first-principles modeling of reactive systems. Subsequently, we review various methods that ensure thermodynamic consistency of mean-field microkinetic models. Next, we describe estimation of reaction rate constants via quantum mechanical and statistical-mechanical methods as well as semi-empirical methods. Among the latter, we discuss the bond-order conservation method for thermochemistry and activation energy estimation. In addition, we review the newly developed group-additivity method on adsorbate/metal systems and linear free energy or Brønsted–Evans–Polanyi (BEP) relations, and their parameterization using DFT calculations to generate databases of activation energies and reaction free energies. Linear scaling relations, which can enable transfer of reaction energetics among metals, are discussed. Computation-driven catalyst design is reviewed and a new platform for discovery of materials with emergent behavior is introduced. The effect of parameter uncertainty on catalyst design is discussed; it is shown that adsorbate–adsorbate interactions can profoundly impact materials design. Spatiotemporal averaging of microscopic events via the kinetic Monte Carlo method for realistic reaction mechanisms is discussed as an alternative to mean-field modeling. A hierarchical multiscale modeling strategy is proposed as a means of addressing (some of) the complexity of catalytic reactions. Structure-based microkinetic modeling is next reviewed to account for nanoparticle size and shape effects and structure sensitivity of catalytic reactions. It is hypothesized that catalysts with multiple sites of comparable activity can exhibit structure sensitivity that depends strongly on operating conditions. It is shown that two descriptor models are necessary to describe the thermochemistry of adsorbates on nanoparticles. Multiscale and accelerated methods for computing free energies in solution, while accounting explicitly for solvent effects in catalytic reactions, are briefly touched upon with the acid catalyzed dehydration of fructose in water as an example. The above methods are illustrated with several reactions, such as the CO oxidation on Au; the hydrogenation of ethylene and hydrogenolysis of ethane on Pt; the glycerol decomposition to syngas on Pt-based materials; the NH₃ decomposition on single metals and bimetallics; and the dehydration of fructose in water. Finally, we provide a summary and outlook.

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1. Introduction

With the interest for more energy efficient, selective and renewable chemical processes intensifying, the need to control chemical reactions at the molecular level is also rapidly increasing. Controlling reactions at the molecular level depends critically on our ability to describe the elementary reaction steps involved in a chemical transformation from reactants to products and assign a rate constant to each individual step. With this knowledge, one can predict the

'work-flow' of a chemical transformation and develop methods and catalysts to direct a chemical reaction toward a lower energy direction (easier or faster) and/or more selective pathways.

While the above goal has been the dream of the catalysis community for the past century, computational techniques have been lagging spectroscopic characterization. Also, experiments conducted on ideal catalysts (single crystals), under well-defined conditions (ultrahigh vacuum (UHV)), have not been bridged with those on supported catalysts working under realistic operating conditions. These well-known materials and pressure gaps have seriously impeded progress in heterogeneous catalysis driven by fundamentals. With the advent of abundant computational power and more accurate methods over the past decade, first-principles

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techniques, and specifically Density-Functional Theory (DFT), are revolutionizing our thinking of catalytic reactions. Still, our ability to describe, and eventually control, chemical transformations by first-principles modeling, at the molecular level, is hindered by multiple challenges.

In this paper, we provide a perspective on multiscale modeling for the development and simulation of catalytic reaction mechanisms. First, we provide an overview of the length and time scales in reacting systems, of the objectives of multiscale modeling, and of the challenges in first-principles modeling of chemical reactions and reactors. We also underscore the need for detailed reaction models by way of a few examples. The greater part of the review then focuses on mean-field microkinetic models and their hierarchical multiscale refinement. Emerging topics in computation-driven catalyst design and uncertainty quantification are also reviewed. Recent developments in *ab initio* kinetic Monte Carlo simulations are then presented, and structure-dependent microkinetic models are discussed. New methods to describe catalytic chemistry in solution are outlined and an example from the homogeneous catalytic dehydrogenation of fructose to 5-hydroxymethylfurfural is summarized. Finally, concluding remarks and an outlook are given.

2. Overview of multiscale modeling of chemical reactions and reactors

2.1. Scales in reacting systems

There are at least three scales encountered in a chemical reactor (Fig. 1). At the microscopic, or electronic, length and time scales (bottom of Fig. 1), adsorbate–catalyst and adsorbate–adsorbate interactions determine the potential energy surface and thus the free energy barrier and entropy of the chemical transformation. A coarse description at this scale is the free energy of transformation from reactants to the transition state (TS) and then to products. The thermal rate constant is a convenient way of coarse-graining the information from this scale, and quantum mechanical methods are ideally suited, at least in principle (see below), for this task.

Given a list of reaction events and their rate constants, adsorbates arrange themselves in spatial configurations or patterns, as a result of the collective behavior of the ensemble of all species. At this mesoscopic scale (middle of Fig. 1), the collective behavior has to be averaged over length and time scales that are much larger than the characteristic length and time scale of the

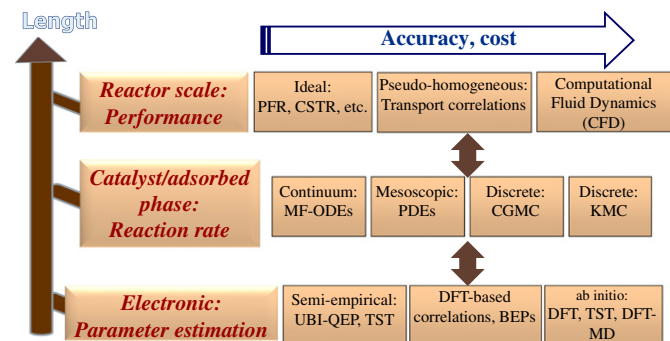


Fig. 1. Schematic of three scales and a possible hierarchy of models at each scale. At each scale, additional models may exist. The accuracy and cost increase from left to right. Acronyms from top to bottom: PRF, plug flow reactor; CSTR, continuously stirred tank reactor; ODE, ordinary differential equation; PDE, partial differential equation; CG-KMC, coarse-grained kinetic Monte Carlo; KMC, kinetic Monte Carlo; UBI-QEP, unity bond index-quadratic exponential potential; TST, transition state theory; DFT, density functional theory; GA, group additivity; BEP, Brønsted–Evans–Polanyi; QM/MM, quantum mechanics/molecular mechanics.

underlying pattern – or what is known as the correlation length – in order to compute the reaction rate. This can be achieved via non-equilibrium statistical mechanics techniques. Due to the fast vibrations of adsorbates with respect to the reaction time scales, adsorbates are typically thermally equilibrated, and reaction events can be thought of as rare events, i.e., over the time scale of a chemical reaction, the system loses its memory and can be approximated as a Markov process. The kinetic Monte Carlo (KMC) method is the most commonly used statistical technique for averaging spatiotemporal events and providing the reaction rate (Bortz et al., 1975; Chatterjee and Vlachos, 2007).

At the macroscopic (reactor) scale (top of Fig. 1), there are gradients in fluid flow, concentration and temperature fields over scales that are typically much larger than the spatial inhomogeneity of the patterns of adsorbates. As a result, the reaction rate computed at the mesoscopic scale can be applied over a certain length scale (discretization size) of a chemical reactor. Due to spatial macroscopic gradients, the rate has to be evaluated at all discretization points of the macroscopic (reactor) domain.

At each scale, computation can be done with various methods whose accuracy and cost vary. As one moves from left to right of the graph at each scale, the accuracy increases at the expense of computational intensity. Thus, at each scale, one can think of a hierarchy of methods. The accuracy of these methods does not vary in a continuous fashion, i.e., each method is different. Typical methods are depicted in Fig. 1. Hierarchy adds a new dimension to multiscale modeling: at each length and time scale, more than one model can be employed in the same simulation scheme, in order to refine the results or calculate error estimates.

2.2. Objectives of multiscale modeling

The early vision of multiscale modeling was rooted in the bottom-up modeling strategy for predicting the macroscopic (reactor) behavior from microscopic scale calculations (Raimondeau and Vlachos, 2002), as shown in Fig. 2. This approach naturally leads to process design, control, and optimization with unprecedented accuracy. It departs significantly from the empirical process design and control strategies of the past, whereby fitting to experimental data was essential to model building.

Due to the disparity in length and time scales over which various tools apply (Fig. 2), the straightforward, if not the only, way to reach macroscopic scales is by coupling models describing phenomena at different scales. Over the past 15 years or so, several algorithms have been developed to achieve this bi-directional or two-way coupling (the branches of multiscale modeling are discussed elsewhere (Vlachos, 2005)). The structural difference of models across scales (continuum vs. discrete and deterministic vs. stochastic) leads

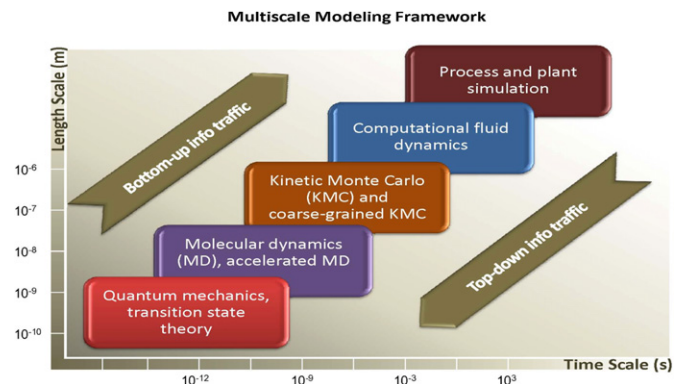


Fig. 2. Schematic of various models operating at various scales. Redrawn from Vlachos (2005).

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