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Mesoscale model for heterogeneous catalysis based on the principle of compromise in competition

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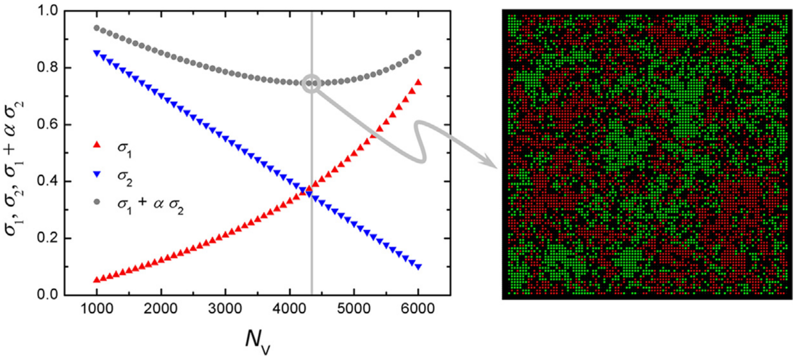
HIGHLIGHTS

- This is the first compromise-based mesoscale model for heterogeneous catalysis.
- This model avoids the shortcomings of both the macroscopic and microscopic models.
- This model accounts for structural heterogeneity with low computational cost.
- Two competing tendencies are identified, corresponding to two competing mechanisms.
- Compromise between the tendencies is established to act as a stability condition.

GRAPHICAL ABSTRACT



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ABSTRACT

Heterogeneous catalysis is vital in modern industries, and its basic problems always attract intense academic interest. The heterogeneous distributions of adsorbates on catalyst surfaces violate the mean field assumption and relevant macroscopic models. On the other end, microscopic models are commonly unacceptable for practical spatiotemporal scales. Therefore, mesoscale models are especially desirable, which capture the essential structural features at the mesoscale with acceptable computational cost. The present work proposed a new mesoscale model for heterogeneous catalysis, based on conservation relationships and a stability condition that was built from the principle of compromise in competition. In the conservation equations variables accounting for structural heterogeneity are incorporated, and thus the equations are not closed, so a stability condition is necessary to act as an additional constraint. Following the principle of compromise in competition, two structural quantities are identified, which exhibit mutually competing tendencies, roughly corresponding to two competing mechanisms, and depending on various kinetic processes. A combination (reflecting the compromise) of these two tendencies forms the additional constraint to close the conservation equations. The relative dominance of the two tendencies can be described more accurately via including kinetic constants. Since there is no time in this model, the steady states (including structural and apparent quantities) can be achieved readily with no need of time evolution, and thus the computational cost may be even lower than that of macroscopic models. Results in various cases have been compared with those of kinetic Monte Carlo simulations.

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1. Introduction

Heterogeneous catalysis can produce complex distributions of adsorbates on catalyst surfaces (Ertl, 1991; Wintterlin et al., 1997; Sachs et al., 2001), which might violate macroscopic description of reactions based on mean field (MF) approximation. Taking the Langmuir–Hinshelwood scheme as an example, reactions actually occur on the domain boundaries (Wintterlin et al., 1997), and thus correlating reaction rates with the boundary length is more reasonable than with the coverage. MF assumption requires ideally homogeneous mixing and thus infinite diffusion rates compared with the rates of other parallel kinetic processes. When this requirement for rates is violated and heterogeneous structures exist, MF approximation fails consequently. When diffusion is neglected (i.e., no diffusion), MF approximation might mistake not only the positions but also the number of steady states (Prakash and Nicolis, 1997).

When MF-based macroscopic models (usually partial differential equations) do not work, one attempt is to turn to microscopic models. For heterogeneous catalysis, such microscopic ones are commonly the master equation. However, it is not easy to analyze or solve it directly, and a common way to find the solutions is to conduct simulations, e.g., via kinetic Monte Carlo (KMC) (Bortz et al., 1975) techniques. Since searching with too many degrees of freedom, this route is still faced with very limited spatiotemporal scales at acceptable computational cost.

Therefore, to account for such heterogeneity with practically meaningful computational efficiency, new models are necessary, and many efforts have been made. One typical top-down way is to modify the rate constants in macroscopic models as functions of coverage. For example, the rate constants for desorption and reaction have been multiplied by a correcting factor containing coverage to take into account lateral interactions (Raimondeau and Vlachos, 2002), and even more complicated expressions of coverages have been adopted before (Makeev and Nieuwenhuys, 1998). The diffusion coefficients are reckoned to be coverage dependent as well (Tammaro and Evans, 1998). However, coverage is always a MF quantity, and the same coverage can correspond to different distributions (Kaukonen and Nieminen, 1989), so such functions might not be well transferable in principle. Another bottom-up way is to coarse-grain the microscopic master equation and create the so-called mesoscopic model via introducing effective potentials (Hildebrand and Mikhailov, 1996), but the construction of the potentials is not trivial, and the utilization of local coverage might limit its scales of utilization as well.

Based on the experience on fluidized and fluid systems (Li et al., 1988, 1999; Yang et al., 2007), we have recognized that mesoscale models might be built through another route, that is, using a stability condition along with conservation equations, and the key stability condition can be built from the compromise among competing mechanisms (Li et al., 2013; Li and Huang, 2014). In this work, we extracted two structural quantities for heterogeneous catalysis, which show apparent competing tendencies, and their compromise can act as a stability condition to close the conservation equations of the global balance with structural details (and thus capable of accounting for structural heterogeneity). Rate constants can serve as the control parameter to reflect the relative dominance of the competing tendencies. This new mesoscale model can capture the main features of the bistable steady states of a model system, agreeing with the results of KMC simulations.

2. Simulations and the mesoscale model

2.1. Simulation details

A model system was employed to reflect a simple heterogeneous catalysis process. As illustrated in Fig. 1, a Langmuir–Hinshelwood scheme is assumed, where species A and B adsorb from the gas reservoir to the surface, and the adsorbed A and B can desorb from the surface into the gas reservoir, diffuse on the surface, or react with each other to produce AB when they encounter. The system is kept away from equilibrium via maintaining a constant partial pressure of each species in the gas reservoir, and removing the AB products from the system immediately after formation (i.e., the reactions are assumed to be completely irreversible).

The process is also expressed in (Eqs. (1)–5), where "V" means a vacant adsorption site on the surface, and the superscript "a" means adsorbed. (Eqs. (1) and 2) describe the reversible adsorption and desorption processes, (3) and (4) show the reversible diffusion processes, and (5) denotes the irreversible reaction.

$$A + V \leftrightarrow A^a \tag{1}$$

$$B + V \leftrightarrow B^a \tag{2}$$

$$A^a + V \leftrightarrow V + A^a \tag{3}$$

$$B^a + V \leftrightarrow V + B^a \tag{4}$$

$$A^a + B^a \rightarrow AB + 2V \tag{5}$$

The processes were simulated using a KMC method, where a 100×100 square lattice was adopted with periodic boundary conditions, and the number of nearest neighbors (coordination number) is four. An empty surface was taken as the initial state. The simulation time is set to be 500, which ensures the stability of the structural characteristics. A series of kinetic constants were employed by varying the energy barrier for each process, and no site energy was accounted for to reveal the pure influence of kinetic factors.

2.2. Theoretical model

The purpose of establishing a mesoscale model is to overcome the shortcomings of both macroscopic (i.e., macroscale or system scale (Li and Huang, 2014)) partial differential equations (PDE) and the microscopic (i.e., microscale or element scale (Li and Huang, 2014)) master equation. For the former, microscale correlations and fluctuations are commonly neglected and MF approximation

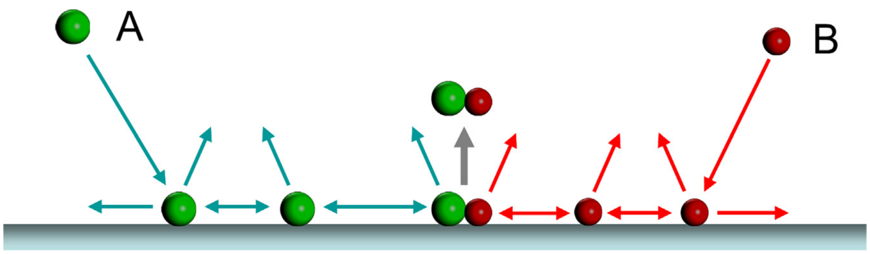

Fig. 1. Illustration of the model system.