A Unified Modeling Framework for Design of Multi-Site Catalysts: Application to NH_3 Decomposition for H_2 Production

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Introduction

Ammonia is an alternative fuel for hydrogen production. It liquefies at moderate pressures at room temperature, it contains a large fraction of hydrogen, and it decomposes on a number of catalysts to produce hydrogen that is free of CO. The elimination of water-gas-shift and other CO cleaning technologies renders coupling of NH_3 cracking reactors with PEM fuel cells considerably simple. Among single metal catalysts, Ru is the best. For the aforementioned reasons, ammonia is considered by many as an ideal transportation fuel [1]. Major challenges to meet DOE targets include increasing catalyst activity (or lowering of 'ignition' temperature) and developing cheaper catalysts. Multi-site catalysts are an obvious target toward this goal.

Current catalyst discovery practices are based either on high throughput screening or quantum mechanical theory. While both approaches have merits, they also have a number of limitations [2]. The aim of this paper is to develop a unified modeling framework for understanding and designing multi-site catalysts, such as bimetallics, in order to meet the aforementioned challenges. In this work, we develop a microkinetic models based approach for rational catalyst design. Our focus is on multi-site catalysts and specifically on the NH_3 decomposition.

Methodology

We have recently proposed that microkinetic models, where a detailed reaction mechanism of all relevant reactions is considered, form a suitable framework for catalyst design [2]. However, most microkinetic models are based on the mean-field approximation, which assumes that the catalyst surface is homogeneous, and are typically 'structureless'. In contrast, a catalyst consists of various crystallographic planes, steps and defects, and two or more chemical components (e.g., islands of different metals), all of which form two or more, often interacting types of sites. In order to derive predictive models for these spatially distributed situations, the kinetics on different sites as well as interactions between them need to be captured. These interactions, which can be inferred from quantum calculations, 'couple' microkinetic models and it is herein shown that these couplings are subject to thermodynamic constraints.

Here, we first develop multi-site microkinetic models that are able to capture interactions between different types of sites via suitable thermodynamic constraints. Next, we compute reaction rates for spatially distributed (multi-site) systems. Spatial models typically rely on the Kinetic Monte Carlo (KMC) method, which is computationally intensive for reactor and/or catalyst design, especially if complex chemistry is modeled. The applicability of interacting mean-field models is assessed, as an alternative, by developing suitable criteria validated via KMC simulations.

Results and Discussion

The first example system we consider is ammonia decomposition on a bimetallic catalyst containing Platinum (Pt) and Ruthenium (Ru). These two catalysts fall on the same side of the "volcano curve" [3], which implies that the rate-determining step of ammonia decomposition is the same on both catalysts. Figure 1 shows, as an illustrative example, the ammonia conversion as a function of the percentage of Ru in the catalyst, with the rest made of Pt. The solid line represents the non-interacting catalyst case, i.e., the rate of NH_3 decomposition is just a weighted sum of reaction rates on each individual catalyst. The experimental scenario here is well-mixed particles in a reactor with different catalyst on each particle. The dashed line represents yet another case in which two catalysts interact weakly, i.e., species adsorbed on the surface of one catalyst can diffuse to and react on the other catalyst surface with consistent coupling parameters. The predictions of the interacting model are clearly different (albeit differences are small for this example) from the non-interacting case. Since both the metals lie on the same arm of the volcano curve, pure Ru is the best catalyst, as expected. This approach is being extended to a library of catalysts and best bimetallic catalysts will be discussed. In addition, the effect of steps on ammonia decomposition on Ru catalyst will be illustrated to underscore the relative importance of sites.
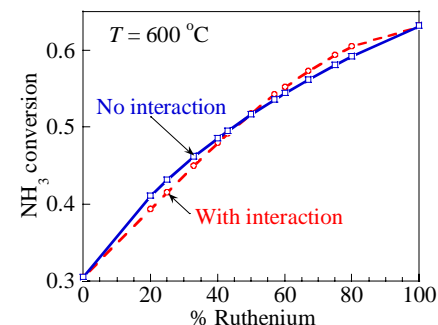

Figure 1. Effect of interactions between multiple catalysts on the NH_3 conversion as a function of the fraction of Ru in a Pt-Ru mixed catalyst.

Significance

The major impact of this work is the generation of a unified modeling tool for rational catalyst design from first principles. This framework is applied to the design of bimetallic catalysts and stepped surfaces for NH_3 decomposition.

References

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