Automatic generation of microkinetic mechanisms in heterogeneous catalysis

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Introduction

Accurate prediction of the reactivity and selectivity of catalytic materials under industrially relevant conditions requires a detailed list of elementary surface reactions, or a *microkinetic mechanism*. The development of reliable microkinetic mechanisms is time consuming and error prone. For a given catalytic system the relevant elementary reactions must be determined, the rate coefficients must be estimated accurately yet efficiently, and the resulting mechanism must be made thermodynamically consistent. These problems are compounded because the mechanism grows exponentially with the size of the reactants, and because real-world catalysts have multiple crystalline facets with distinct kinetics.

In this talk, we present recently developed software that can generate microkinetic mechanisms for heterogeneous catalysis automatically. For a given catalyst, the user provides the initial conditions (e.g. temperature, pressure, and gas-phase composition), and the computer automatically determines which reactions are important, obtains parameterizations of the thermodynamic properties and rate coefficients, and solves the governing equations – without subsequent human intervention.

Materials and Methods

The software is based upon the open-source software Reaction Mechanism Generator (RMG) [1,2], which was originally developed for gas-phase combustion and pyrolysis. The new code is referred to as RMG-Cat. By building our software on preexisting code for automatic mechanism generation, we can take advantage of RMG's ability to solve several key problems in computer-generated chemical kinetics. RMG-Cat can automatically:

- Recognize when two or more species in the mechanism are equivalent
- Predict all the possible elementary reactions for each species and pair of species
- Determine which of the possible reactions are actually important
- Estimate all the necessary thermodynamic and kinetic parameters
- Ensure that the mechanism is thermodynamically consistent
- Include flexibility for new reactants on novel materials
- Accomplish all of the above more quickly than a human

Results and Discussion

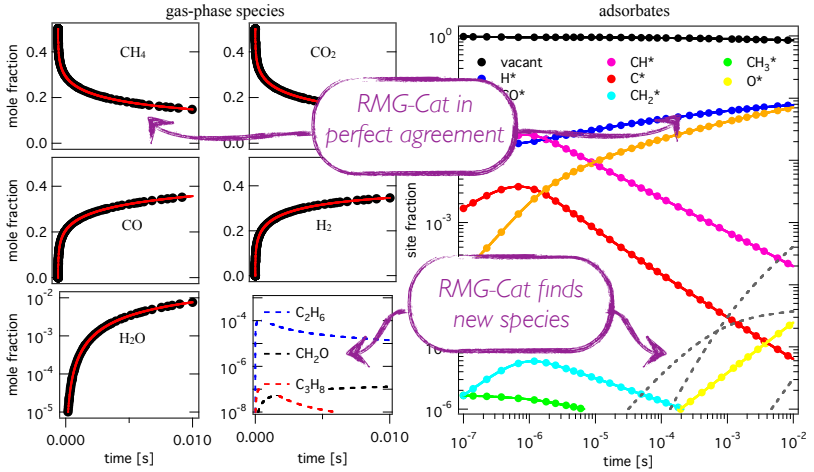
We have added three new reaction families to RMG-Cat: adsorption, surface dissociation, and surface abstraction. These families were populated with rate rules taken from the literature. Additionally, we populated the thermodynamic database with data for small-molecule chemistry on Ni (111). We developed a novel method for predicting the thermodynamic properties of adsorbates, principally the temperature-dependent free energy, using simple rules of thumb [3].

As a proof-of-concept, RMG-Cat was tested on methane steam reforming, dry reforming, and partial oxidation on Ni (111). The results were compared to a literature mechanism developed by Olaf Deutschmann and co-workers [4]. Additionally, RMG-Cat successfully developed a mechanism for the catalytic combustion of methanol, even though methanol is not part of the Deutschmann mechanism.

Significance

RMG-Cat automatically generated a detailed, thermodynamically consistent mechanism in a matter of minutes using only a list of reagents.

Figure 1. Proof-of-concept for dry reforming of methane at 1000 K and 1 bar. Symbols are predictions from literature mechanism, and lines are the mechanism predicted my RMG-Cat.



References

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