Journal of Catalysis 330 (2015) 197–207

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Degree of rate control approach to computational catalyst screening

Christopher A. Wolcott [a,1], Andrew J. Medford [b,c,1], Felix Studt [b,c], Charles T. Campbell [a,d,*]

[a] University of Washington, Department of Chemical Engineering, Seattle, WA 98195-1700, USA
[b] Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA
[c] SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA
[d] University of Washington, Department of Chemistry, Seattle, WA 98195-1700, USA

ARTICLE INFO

Article history:
Received 15 February 2015
Revised 6 July 2015
Accepted 8 July 2015

Keywords:
Catalyst screening
Computational catalysis
Density functional theory
Degree of rate control

ABSTRACT

A new method for computational catalyst screening that is based on the concept of the degree of rate control (DRC) is introduced. It starts by developing a full mechanism and microkinetic model at the conditions of interest for a reference catalyst (ideally, the best known material) and then determines the degrees of rate control of the species in the mechanism (i.e., all adsorbed intermediates and transition states). It then uses the energies of the few species with the highest DRCs for this reference catalyst as descriptors to estimate the rates on related materials and predict which are most active. The predictions of this method regarding the relative rates of twelve late transition metals for methane steam reforming, using the Rh(2 1 1) surface as the reference catalyst, are compared to the most commonly-used approach for computation catalyst screening, the Nørskov–Bligaard (NB) method which uses linear scaling relationships to estimate the energies of all adsorbed intermediates and transition states. It is slightly more accurate than the NB approach when the metals are similar to the reference metal (<0.5 eV different on a plot where the axes are the bond energies to C and O adatoms), but worse when too different from the reference. It is computationally faster than the NB method when screening a moderate number of materials (<100), thus adding a valuable complement to the NB approach. It can be implemented without a microkinetic model if the degrees of rate control are already known approximately, e.g., from experiments.

1. Introduction

The dominant role of heterogeneous catalysis in the production and utilization of fuels, bulk chemical processing and pollution clean-up means that even minor improvements in catalyst performance could result in massive improvements in the utilization of natural resources, environmental benefits and process performance [1–3]. Thus, the motivation to find better catalyst materials is great.

One method for finding better catalysts has been high-throughput experimental screening of many materials for their catalytic performance (activity, selectivity, lifetime) [4]. However, this is costly, and with the evolution of fast computational methods that can predict catalytic reaction rates for different materials with increasing speed and accuracy [5], one expects that computational pre-screening of materials for catalytic activity or selectivity to find the best candidates for experimental testing will soon become a faster route to the discovery of new catalysts. Indeed, there have already been some successes in using high-throughput computational screening to accelerate the discovery of new catalysts [6–12]. We describe here a new approach for computational screening of new catalysts that relies on the degree of rate control (DRC) [13] to identify descriptors and estimate reaction rates on new materials. The new approach does not rely on a full mechanistic model (provided the degrees of rate control are known) and, in some circumstances, is faster and more accurate than the most widely used method.

Perhaps the most successful method for computational screening of solid catalysts has been the descriptor-based, linear-scaling approach developed by Nørskov, Bligaard and coworkers [5,6,14–17], which we will refer to here as the "NB method". It relies on the following approach to calculate the rate or selectivity on a new material:

1. Determine the reaction's mechanism and active site on a good known catalyst in a certain class of materials through a combination of experiment and theory. We will refer to this as the reference material (RM).

* Corresponding author at: University of Washington, Department of Chemical Engineering, Seattle, WA 98195-1700, USA.
E-mail address: campbell@chem.washington.edu (C.T. Campbell).
[1] These authors contributed equally.

http://dx.doi.org/10.1016/j.jcat.2015.07.015
0021-9517/

2. Develop a microkinetic model for that mechanism that can reproduce experimental trends of the reaction rate for the RM at a variety of conditions, but relies on knowing the energies of all the adsorbed intermediates and transition states involved in every elementary step as it occurs on that RM.
3. Assume that the same mechanism and active site of the RM apply to all materials in its class, and then use electronic structure theory to compute the energetics of all necessary adsorbed intermediates and transition-states for a representative set of materials from the same class as the RM.
4. Develop "linear scaling relations" which relate all the needed intermediate/transition-state energies to one or two key "descriptors" (typically the adsorption energies of atomic species such as C∗, O∗ and N∗). The necessary intermediate/transition-state energies of any given new material can then be estimated by knowing only these few descriptor energies, which can be computed using an electronic structure method such as density functional theory (DFT). This step relies on the demonstrations by Nørskov's group that the energies of most adsorbed intermediates vary approximately as linear combinations of the adsorption energies of two elemental adatoms (e.g., C∗, O∗ or N∗) [14,18,19], and that the activation energy for an elementary surface reaction varies linearly from material to material with the changes in the reaction's internal energy (i.e., a form of Brønsted or Evans–Polyani relationship) [15,20].
5. Choose a new material and calculate the "descriptor" energies (e.g., the energies of two adsorbed adatoms, C∗ and O∗). Use the "scaling" relations from step 4 to estimate the energies of all the intermediates and transition states in the mechanism, and from these energies, calculate the rate for the new material to the product(s) of interest at the desired reaction conditions. Since a typical microkinetic model requires the energies of more than 10 adsorbed intermediates and 10 transition states, and these are estimated using only one or two descriptors that are much faster to calculate than even one transition state, this can reduce the computational time needed to calculate rates on a new material by orders of magnitude, provided the linear scaling relations have already been developed.
6. Repeat step 5 for all the new materials to be screened, and generate a volcano plot of rates versus descriptors' energies.

This approach results in a plot of catalytic activity as a function of the one or two descriptor variables which exhibits a characteristic "volcano" shape that determines the optimal descriptor values for maximizing the rate within a given reaction mechanism and active site structure. We denote this type of plot as a "NB rate volcano".

Here, we introduce an alternate approach to the method outlined above which focuses instead only on the most relevant energies that most directly control the catalyst's activity. This can significantly simplify the analysis of reactions in any multi-stepped catalytic reaction mechanism, like methane reforming, since a small change in the internal energy of any particular intermediate or transition-state energy usually does not have any significant effect on the reaction rate, which is instead sensitive to only a few of these species' energies [13]. It is therefore reasonable to assume that one can simplify computational screening by identifying a small number of rate-controlling species (intermediates and transition states) whose energies most strongly affect the reaction rate, and develop a screening model based on these energies alone.

The "degree of rate control" (DRC) developed by Campbell et al. [13] is a rigorous method for quantifying the extent to which each species' standard-state free energy affects the net reaction rate to any product (or the rate of consumption of any reactant). The DRC of any such species i (which could be any intermediate or any transition state) is defined as follows:

$$X_i = \left(\frac{\partial(\ln r)}{\partial\left(\frac{-G_i}{RT}\right)} \right)_{G_{j\neq i}}, \quad (1)$$

where r is the rate to the product of interest at the chosen reaction conditions, and G_j is the standard-state Gibbs free energy of species j. The DRCs, X_i, will depend on reaction conditions and the reaction mechanism investigated. There is an useful analogy between the DRC and the concept of a rate-limiting step: In the case that there is a single mechanism and a single rate-limiting step, the DRC of that transition-state will be unity, while the DRC for all other transition-states will be zero [21]. For more complex reactions without a clearly defined rate-limiting step, multiple transition-states will have a nonzero DRC. Furthermore, the X_i of all transition-states will sum to one for each serial pathway through a reaction network, while the sum over X_i of all adsorbed intermediates will fall between zero and a small negative integer [22–24]. For most reactions only a few transition-states and adsorbed intermediates exhibit non-negligible DRC, [25,26] with all other transition-states and intermediates being essentially zero.

By quantifying the impact that changing the standard-state free energy of a particular species in a reaction landscape will have on the net reaction rate, it is straightforward to see that any species whose degree of rate control has a large magnitude can be categorized as a "rate-controlling" species. By shifting the focus from the kinetics of a large number of reaction steps to the standard-state free energy of a small number of chemical species, it is substantially more straightforward to determine descriptors that are useful in finding improved catalysts. This is especially true since the entropy contribution to the standard-state free energy of each adsorbed species differs very little across different materials [27,28], whereas the internal energy dominates the differences in standard-state free energies between different materials. Thus, instead of looking for a catalyst with a faster rate directly, all that is necessary is to identify a catalyst with improved zero-Kelvin adsorption/transition-state internal energies for a small number of species. For example, when there is a single rate-determining transition state, one wants a material with a lower internal energy for that transition-state. On the other hand, when there is a single rate-determining intermediate adsorbing so strongly that it blocks the active sites, one wants to raise its internal energy. Often these quantities are correlated, so that a lower-energy transition state will also often lead to a more strongly adsorbed intermediate. It is therefore necessary to include all species with significant DRCs. The best catalyst might be, for example, a material where this undesirable correlation is weakest.

The NB method is a very powerful approach for computational catalyst discovery since it offers a fast way to estimate catalytic activity. However, it has some shortcomings. Most obviously, there exists scatter around each of the linear scaling relationships due to real errors in assuming that each energy scales linearly with the descriptor(s), leading to inaccuracies in their energy estimates and thus in the rate predictions. Additionally because of the large number of species-surface combinations one needs to calculate by quantum mechanics to generate the needed M-A vs M-AH_x, M-C vs. M-CO and other linear scaling relationships, there is a very serious initial cost associated with the large computational time needed for this [29]. We show below that the DRC method can circumvent some of these shortcomings in many situations when working with similar materials, but that the NB method is more robust to large changes in material type.

The main question we address here is: *How does the DRC method perform compared to the more commonly used NB method in*