Which transition states and intermediates control catalyst activity, and how well do we know their energies?

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Introduction

Quantitative knowledge of the relative energies of the adsorbed intermediates and transition states involved in catalytic reactions provides the key information necessary for understanding how the catalyst surface binds the reactants and guides them through their various elementary steps to products. With enough such information, one can develop a full microkinetic model for the overall reaction which involves a list of all the elementary steps in the reaction, their activation energies and their pre-exponential factors. In general, we can only consider that we truly understand a catalytic mechanism if our microkinetic model can reproduce both macroscopic rate measurements (e.g., overall catalyst activity and selectivity) over a wide range of reaction conditions such as temperature and reactant partial pressures) and microscopic rate measurements (rate constants of individual elementary steps involved in the mechanism, or subsets of a few steps). Once such a microkinetic model is available, it offers tremendous potential for catalyst improvement. Not only can it be used to predict the rates at new conditions to optimize a process, but it also can be analyzed quantitatively to identify exactly how one would want to change the catalyst to improve activity and/or selectivity. A new mathematical method for doing this [1] will be described. It can be applied to analyze microkinetic models of multi-step reaction mechanisms to quantify exactly the extent to which the energy of each intermediate and each transition state controls the overall reaction rate (i.e., their "degree of rate control"). Those few key transition states and intermediates with a large degree of rate control hold the key to catalyst improvement: If you can alter the catalyst to stabilize these key transition state(s) while destabilizing these key intermediate(s), or at least not stabilizing them too much, once can make a more active catalyst for the selected product.

The degree of rate control also identifies exactly which energies one must know accurately to get an accurate microkinetic model. Most intermediates and transition states have a low degree of rate control, and therefore the accuracy of the model is nearly independent of the accuracy with which their energetics are estimated. The model's accuracy is very sensitive, however, to the accuracy of the few intermediates and transition states that have high degrees of rate control. This allows one to make accurate kinetic models using rather crude estimates of all the other energies, and focus attention on getting high accuracy for only a few critical energies.

The experimental and theoretical methods which are currently used successfully to provide the quantitative input to microkinetic models (adsorption energies, activation barriers, prefactors) will be reviewed, and their relative accuracies will be assessed. Emphasis will be placed on single-crystal adsorption calorimetry and microkinetic measurements from our own lab, and comparisons of these to DFT calculations.

Materials and Methods

The microcalorimeter and methods have been described in detail previously [2,3]. The measurements were supplemented by a variety of surface analytical and kinetic measurements.

Results and Discussion

Recent calorimetric measurements of the adsorption energies of catalytic intermediates on well-defined single crystal surfaces show that such energies can now be made over a wide range of temperatures (100 K - 350 K) with a precision of 1-2 kJ/mol, a coverage resolution of 1% of a monolayer and an absolute accuracy of 2-5% [4-6]. Comparing these results to state-of-the-art DFT slab calculations for a wide variety of adsorbates shows that the latter can often be accurate within 10%, but they are just as often in error by ~30% (40 kJ/mol or more). Clearly, the same level of potential error also can be expected for DFT estimates of transition-state energies, or even worse if accurate saddle-point-finding methods are not used. This level of accuracy may be acceptable for intermediates and transition states that have a very small degree of rate control, but the key species in microkinetic models require greater accuracy. Thus, accurate experimental adsorption calorimetry and kinetic measurements of activation energies are required until someone develops a theoretical method with much greater accuracy. Statistical mechanical methods for estimating pre-exponential factors [7,8] are usually sufficiently accurate, so long as they are consistently coupled with the measured activation energies (i.e., such that their combination agrees with the absolute value of the rate constant measured).

Significance

Experimental measurements of the energies of adsorbed species on well-defined surfaces serve as essential benchmarks against which to compare theoretical calculations, to test if the necessary approximations in the quantum mechanical approach give results with acceptable accuracy and, if not, to evaluate the accuracy of newly developing methods. Accurate microkinetic models can be developed using a combination of theoretical energies and experimental measurements. These can be quantitatively analyzed to assess the degree of rate control of each transition state and intermediate, which provides the key to catalyst improvement.

References

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