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Effect of multiscale model uncertainty on identification of optimal catalyst properties

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ABSTRACT

Computer-based catalyst design has been a long standing dream of the chemistry community for replacing tedious and expensive experimental trial-and-error. While first-principle kinetic modeling emerges as a powerful tool for catalyst selection, it has mainly been limited to using a single catalyst descriptor, simplified chemical kinetic models, and assumptions that question the predictive capability of computational results in the absence of addressing the effect of error in kinetic parameters. Here, we introduce a new framework to address the effect of model uncertainty on optimal catalyst property identification. The framework is applied to the ammonia decomposition reaction for CO-free H_2 production for fuel cells. It is shown that a range of materials, rather than a single material, should be experimentally screened. Among kinetic model parameters, the often neglected adsorbate–adsorbate interactions can have a profound effect on catalyst selection. The importance of lateral interactions is confirmed with recent experimental data.

1. Introduction

The discovery of catalysts has traditionally been an Edisonian process. High throughput experimentation [1,2] has significantly accelerated this process but lacks understanding of the underlying chemistry and is still limited to a fairly narrow parameter range. Model-based design offers the promise of alleviating the bottleneck of high throughput synthesis and evaluation, since the main screening is carried out computationally [3–8].

The first step in catalyst design is to identify optimal catalyst properties (typically termed as descriptors) that provide the best performance, e.g., highest activity, selectivity, stability, etc. Most studies so far have focused on a small number of descriptors, e.g., the heats of chemisorption of key species, and most often on a single descriptor and performance metric (e.g., catalyst activity). An activity volcano curve is then constructed, by varying this descriptor, and the optimum descriptor value, corresponding to the curve maximum, is found. The next step is to identify materials with those optimal properties. The above approach has delivered exciting results in predicting alloys from single metal catalyst modeling with optimal performance using the linear interpolation approach in the periodic table [3] and more recently a density functional theory (DFT)-built library of parameters for single monolayer bimetallics [8] whose properties do not follow the interpolation principle. Some recent work has also been oriented towards multiple descriptors in the context of catalyst selection, for example, see [9–12].

Previous studies have also tacitly assumed that the models are exact. Given a certain kinetic model, a single optimal property set (e.g., corresponding to the maximum of the volcano curve) is predicted. Uncertainty is particularly pronounced in catalytic systems due to inaccuracy in computed energetics and pre-exponentials, even when using DFT calculations. Furthermore, the rate limiting step, pre-exponentials, and the most abundant reactive intermediate are often assumed to be the same on all catalysts in computational work related to volcano curve generation. For example, using the bond-order conservation (BOC) method to compute activation energies on Pt, Ru, Fe, Re for ammonia decomposition and some experimental data, it was concluded that N desorption is the rate-determining step (RDS) for all the metals (no microkinetic models were constructed) [9]. Similarly, nitrogen desorption, assumed to be the RDS, along with $\theta_N + \theta_{NHx} \approx 1$ for site conservation, was used to create a volcano curve [10]. These model uncertainties and assumptions can render optimal property prediction inaccurate and misguide experimental efforts. In addition, these modeling efforts are in contrast to rationalization of experimental

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data whereby the rate determining step was postulated to change on each leg of the volcano curve from N—H bond scission to N desorption [11].

This contribution aims at advancing catalyst discovery strategies by prediction of optimal catalyst properties through *multiple descriptors*, enabled using microkinetic models with no *a priori* assumptions in solving the governing equations, and by elucidating the effect of *uncertainty* on optimal catalyst properties. Finally, the effect of reactor operating conditions (macroscopic scale) on optimal properties (electronic scales) is assessed. To the best of our knowledge, the inclusion of the effect of uncertainty in kinetic parameters and the quantification of the effect of adsorbate–adsorbate interactions on the optimal catalyst properties are presented for the first time. Recent experimental data are consistent with the prediction of the importance of lateral interactions on predicting the optimal catalyst properties.

2. Methods

The framework developed herein is generic. We choose the ammonia decomposition for CO-free hydrogen production

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad (1)$$

as a prototype example for illustration purposes. The reaction network of elementary reactions is given in Fig. 1c and Table 1. Essentially, ammonia gas adsorbs onto the catalyst surface, where hydrogen atoms are abstracted one at a time. Atomic nitrogens and hydrogens recombine to produce N_2 and H_2, respectively.

The rate constant of each elementary step is modeled via a modified Arrhenius equation as shown below:

$$k_i = A_{0_i}\left(\frac{T}{T_{\mathrm{ref}}}\right)^{\beta_i}\exp\left(-\frac{E_i}{RT}\right), \quad i = 1,\ldots,m \qquad (2)$$

The activation energy depends on both the temperature and the surface coverage of species and is estimated through the Unity Bond Index-Quadratic Exponential Potential (UBI-QEP) theory via two mappings (Fig. 1): the first computes species binding energies from atomic binding energies (panels b and a) and the second activation energies from species binding energies (panels c and b) [13–15].

The UBI-QEP method uses semi-empirical relations to relate the species binding energies to the atom binding energies. NH_2 and NH are typically "strong binding," and NH_3 is a "weak binding" species. The activation energies are computed from the heats of chemisorption of species by assuming a value of bond index (BI), which is typically 0.5, to approximate the transition state with respect to the reactants. However, recent DFT calculations and comparisons to experimental data indicate different values [13,16]. For example, in our recent work, the bond indices were fitted to data and compared with DFT values [13] and are summarized in Table 1. These refined values are used in this work. The nominal pre-exponential values were obtained by refining the model to experimental data as reported in [12]. The temperature dependence in the activation energy arises from the adsorption properties being temperature dependent through statistical mechanics, as explained in [17]. These temperature and coverage dependent atomic binding energies are propagated through the UBI-QEP equations to activation energies of the entire mechanism.

Table 1
Nominal parameter values from [12] for Ru/γ-Al_2O_3 catalyst. *A* stands for pre-exponential and *s* for sticking coefficient (if less than 1), *β* is the temperature exponent in the modified Arrhenius form, and BI is the bond index in the UBI-QEP framework.

Reaction	$A[s^{-1}]$, $s[\,]$	β	BI
$H_2 + 2* \rightarrow 2H*$	0.08	0	0.5
$2H* \rightarrow H_2 + 2*$	2.4×10^{13}	0	0.5
$N_2 + 2* \rightarrow 2\,N*$	2.2×10^{-7}	0	0.8
$2\,N* \rightarrow N_2 + 2*$	1.6×10^{10}	0	0.8
$NH* + * \rightarrow N* + H*$	1.4×10^{13}	0	0.5
$N* + H* \rightarrow NH* + *$	8.8×10^{12}	−0.39	0.5
$NH_2* + * \rightarrow NH* + H*$	7.2×10^{12}	0	0.5
$NH* + H* \rightarrow NH_2* + *$	4.6×10^{12}	−0.39	0.5
$NH_3* + * \rightarrow NH_2* + H*$	1.4×10^{13}	0	0.5
$NH_2* + H* \rightarrow NH_3* + *$	8.8×10^{12}	−0.39	0.5
$NH_3 + * \rightarrow NH_3*$	0.63	0	0.5
$NH_3* \rightarrow NH_3 + *$	4.4×10^{13}	0	0.5

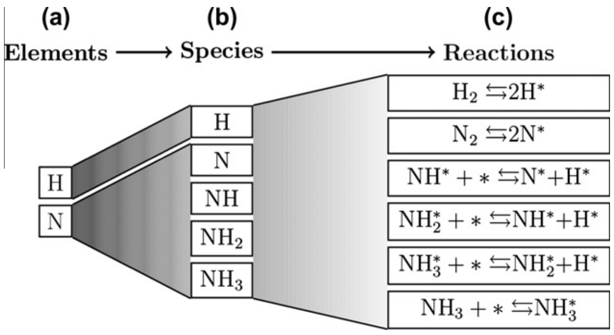

Fig. 1. Illustration of mapping atomic binding energies (a) to species binding energies (b) and then to reaction activation energies (c).

The importance of lateral interactions on reaction rates and macroscopic reactor performance cannot be understated. For example, it was shown that the strong N—N interactions impact drastically model predictions [13]. For this reason, some computational groups have been incorporating interactions in mean field and Monte Carlo microkinetic models [14–17]. Furthermore, significant effort has been devoted by Kitchin and co-workers to deriving a theoretical framework describing lateral interactions of different adsorbates on various metals [18]. While earlier efforts employed semi-empirical methods to account for interactions, DFT has more recently been used to understand the effect of lateral interactions on the reaction barriers [15–17].

The atomic binding energies are assumed to be independent of each other (although correlation due to the electronic structure of catalysts is likely) and of the form:

$$\begin{aligned} Q_H(\theta_H) &= Q_H(\theta_H = 0) + C_1\theta_H \\ Q_N(\theta_N) &= Q_N(\theta_N = 0) + C_2\theta_N \end{aligned} \qquad (3)$$

where $Q_H(\theta_H)$, $Q_N(\theta_N)$ are the coverage dependent binding energies, $Q_H(\theta_H = 0)$, $Q_N(\theta_N = 0)$ are the binding energies on a clean surface, and C_1, C_2 describe the surface coverage effect (assumed to be linear). Each pair ($Q(\theta = 0)$, C) is an attribute of a particular catalyst. In essence, the energetics of a microkinetic model is written as a function of the atomic binding energies, $Q_H(\theta_H)$ and $Q_N(\theta_N)$. This double mapping (Fig. 1) is important to enable rigorous optimization discussed elsewhere.

In constructing a microkinetic model, to avoid the combinatorial problem of computing interactions among all surface species, these adsorbate–adsorbate interactions are identified and quantified via a hierarchical multiscale approach: Once the dominant coverages are determined by running the microkinetic model, DFT is performed to include interactions of the dominant species only [19] and calculate their values, and the procedure is iterated until no changes are found between what is assumed as dominant species and what the simulation predicts. Guided from DFT calculations, the atomic binding energies are assumed to vary linearly with coverage and values are taken from Ref. [8] and do not vary considerably with metal; they are rather a strong function of the atom (in our case N and H). The values taken for C_1 and C_2 are those determined previously on Ru. Recent work (see Table 1 in Ref. [8]) shows the interaction energies for nitrogen range from −27 to −43 kcal (mol ML nitrogen)$^{-1}$ for a number of metal catalysts. The average interaction energy of these 9 metals is −35 kcal (mol ML nitrogen)$^{-1}$. The Ru interaction energy in that work was reported to be approximately −36.9 kcal (mol ML nitrogen)$^{-1}$ and therefore a fair representation of the average interaction energy for doing a global catalyst search.

Specific to the ammonia chemistry, the coverage dependence of the binding energies of H and N is propagated through the UBI-QEP framework to the binding energies of molecular species and activation energies of elementary reactions. In all calculations, lateral interactions are included, unless otherwise stated, through the parameters C_1 and C_2. For simplicity, below the atomic binding energies refer to the zero-coverage limit $Q_H(\theta_H = 0)$ and $Q_N(\theta_N = 0)$ since the coverages, computed from the microkinetic model, vary with reactor location, operating conditions, and catalyst (it is impossible to report millions of coverage values and are not of any interest for the results presented here).

The microkinetic model is combined with a steady state plug flow reactor-scale model (refer to [13,14] for typical operating conditions). The microkinetic and reactor model is then solved numerically (integrated along the length of the reactor) and used to predict conversion, gas-phase mole fractions, and fractional coverage of surface species. No assumptions about fast elementary steps, a rate determining step, or the most abundant reactive intermediate are made. While the full microkinetic model is solved, the model is still approximate; for example, it is a mean field model, it lacks detail information on the active site, it assumes an average interaction energy, it uses the UBI-QEP framework, etc. For these reasons, the model predictions should be considered as a guide only. Experiments are necessary to confirm model predictions.

We now describe the search method for the calculation of the optimal catalyst properties (atomic binding energies at zero coverage). A Monte Carlo search, which was found to be more efficient optimization method than a regular grid search [19], was conducted over a range of zero coverage hydrogen and nitrogen binding energies. Pairs of (H and N) zero coverage binding energies were randomly generated within this range. For each pair of binding energies, a few thousand runs were sufficient to identify the optimal catalyst properties, i.e., the (zero coverage) atomic binding energies that give the maximum conversion of ammonia. We prefer to plot the results vs. the atomic binding energies and quantify the effect of uncertainty on those since these have recently been used to identify new catalysts [8]. The results were compiled in a response surface vs. the two binding energies. Fig. 2 shows a typical example.

For a fixed set of operating conditions and kinetic model parameters, the above optimization provides the values of optimal binding energies. The question that we address next is how much these optimal binding energies vary due to uncertainty in kinetic model parameters. This is achieved through an uncertainty analysis. Uncertainty analysis entails varying the kinetic parameters a few hundred to thousand times using again the Monte Carlo search technique. For each set of parameters (e.g., pre-exponentials), deterministic microkinetic simulations are performed, such as the one whose results are depicted in Fig. 2, to identify the new optimal values of binding energies. The uncertain kinetic parameters were sampled from a uniform distribution for these simulations. The Monte Carlo method discussed herein differs from Monte Carlo simulations of surface kinetics. It is simply used to perturb parameters from a distribution. In our case, we carry out a double Monte Carlo search. We perturb kinetic parameters, and for each set of kinetic parameters, an optimization is conducted, such as the one shown in Fig. 2. The locus of optimal binding energies provides the distribution of optimal points and indicates how uncertain the optimal set is. This combined uncertainty and optimization (i.e., uncertainty in the optimal values) resulted in up to 1,000,000 simulations for each graph and takes a few days on a standard PC. The approach is fully parallelizable to reduce computational cost and be applied to complex reaction mechanisms.

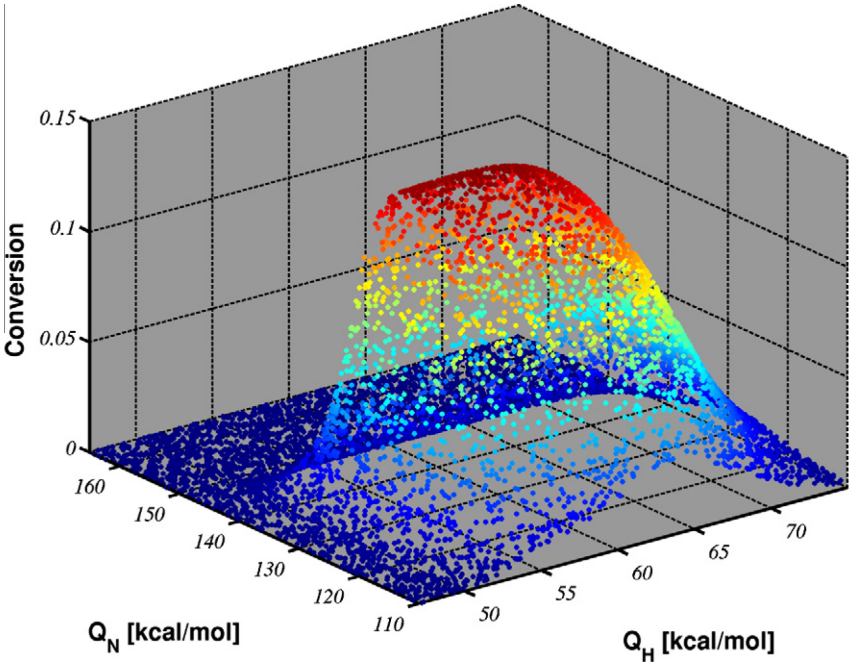

Fig. 2. Ammonia conversion vs. binding energies of hydrogen and nitrogen. Optimization results at 700 K obtained from a Monte Carlo search. Simulations conducted in a microreactor of 1.7 cm in length, an internal diameter of 0.4 cm, operating at 1 atm, a flow rate of 200 sccm, with a site density of 1.66 × 10^{-9} mol/cm^2, and surface area per volume of 6000 cm^2/cm^3. The response surface has a single maximum in conversion at approximately Q_H = 58 kcal/mol and Q_N = 128 kcal/mol.

3. Effect of reactor conditions and uncertainty on optimal catalyst properties

Fig. 2 shows an optimization example for nominal parameter values where the conversion is plotted vs. the atom binding energies obtained from 5000 simulations. This "mountain" is a generalization of the well-known volcano curve obtained when a single descriptor varies. The conversion of ammonia is strongly dependent on both binding energies, with a maximum at about $Q_H = 58$ kcal/mol and $Q_N = 128$ kcal/mol, which denote the optimal catalyst properties for the nominal set of kinetic parameters. As mentioned earlier, coverages vary with operating conditions and along the reactor as well as with the location on the volcano curve. Under nominal conditions corresponding to Ru catalyst, significant fractions of N and H are found on the catalyst [13–15]. Changes in model parameters (such as in pre-exponentials) or operating conditions may also lead to change in the most abundant reactive intermediate (MARI) and/or RDS, as indicated in Ref. [12]. These changes are automatically predicted during optimization. For example, at lower binding energies of N, adsorbed H dominates with N being up to 0.2 ML, whereas at higher binding energies of N, the coverage of N is higher, consistent with recent predictions (see Supplementary Fig. S4 in Ref. [8] where one parameter optimization was performed). Due to the strong repulsive interactions, the maximum coverage of N is typically below ∼0.5 ML. In addition, some of metals with high affinity to N, such as Co and Fe, are known to form bulk nitrides [20]. Similarly, metal hydrides may form for some of the chosen H binding energies. Formation of such compounds may happen away from the optimal value of the volcano mountain and is not considered in our simplified model. Considering nitrides and hydrides as additional stable structures over a certain range of binding energies of N and H atoms is feasible by explicitly accounting for binding of species on such materials and worth considering in future work.

In order to link macroscopic and electronic scales, the effect of operating conditions on optimal catalyst properties was studied. The reactor temperature and inlet composition were varied (temperature from 600 to 800 K; inlet fraction of ammonia from 30% to 100% (balance Ar) with and without H_2 co-feed). For each new operating condition, an optimization, as shown in Fig. 2, was performed to find the optimal properties. The inlet composition has a negligible effect, whereas temperature changes the H binding energy between 58 and 60 kcal/mol and the N binding energy between 123 and 132 kcal/mol over this temperature range, i.e., by less than 10%. Overall, the optimal catalyst properties vary slightly with reactor conditions, and thus, a single optimal catalyst can be used throughout the reactor for the ammonia decomposition reaction at 1 atm.

Next, we investigate the effect of model uncertainty on the prediction of optimal properties. Each pre-exponential pair was perturbed within an order of magnitude (chosen logarithmically while maintaining thermodynamic consistency), and each bond index of a reaction pair was adjusted within 25% (chosen linearly, capped at 1; this is a fairly large perturbation in activation energies, well beyond the error of UBI-QEP or DFT method). The parameters (e.g., all pre-exponentials) of all elementary reactions were simultaneously perturbed. Entropic contributions to rate constants (pre-exponential factors and sticking coefficients) can be obtained by expensive calculations either through vibrational analysis and transition state theory for activated processes or molecular dynamics if the activation barriers are low. For catalyst screening, this estimation approach is impractical. Instead, pre-exponentials can be approximated based on the type of surface reaction or activation of adsorption as described by Dumesic and co-workers [21]. For example, for immobile surface species without rotation, a value of 10^{13} is reasonable. These approximate values provide order of magnitude estimates of pre-exponential factors and are subject to one to two orders of magnitude uncertainty. Similarly, differences between catalysts of the same order of magnitude may be expected. In the present work, the variability of molecular binding energies based on atomic binding energy descriptors would no doubt reflect variability in surface mobility and suppressed translational and rotational barriers of surface intermediates [22]. An order of magnitude uncertainty in rate constant is more of a lower bar to this type of variability across diverse metal catalysts proposed in this study.

Another perspective to our pre-exponential variation is that an uncertainty of an order of magnitude in pre-exponential factor (equal to an order of magnitude uncertainty in rate constant) reflects an uncertainty of about 2–3 kcal/mol in the reaction barrier. A 2–3 kcal/mol uncertainty in the calculation method of reaction barriers is reasonable [23,24]. Finally, the perturbation size of bond indices was motivated by their recent estimation against experimental data [25] from the nominal value of 0.5 [24].

The outcome of an uncertainty calculation is a distribution function of optimal properties rather than a single value. Examples are shown in Fig. 3. Despite the strong effect of pre-exponentials on conversion (not shown), their effect on optimal properties is minor, as shown in Fig. 3a: ∼0.9 kcal/mol for hydrogen and 2.9 kcal/mol for nitrogen, N. Uncertainty in bond indices resulted in similar deviations (∼0.7 kcal/mol for hydrogen and 3.1 kcal/mol for nitrogen, N), as shown in Fig. 3b. Our results indicate that error in kinetic parameters within the expected uncertainty range does not likely have a large impact on the identification of optimal binding energies used for catalyst discovery. The lack of sensitivity of the optimal catalyst properties on pre-exponentials is an important

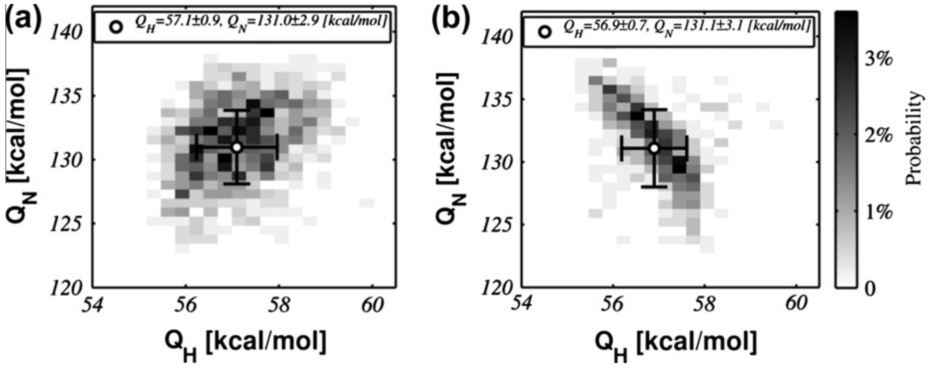

Fig. 3. Optimal catalyst properties predicted due to uncertainty in pre-exponentials (a) and bond indices (b). The circles and crosses indicate the average and standard deviation of the optimal binding energies in each case. The scale indicates the probability of obtaining a certain interval of elemental binding energies.

result, because it indicates that the (common) assumption of using the same set of pre-exponentials in microkinetic models for screening catalysts should not affect catalyst selection. Bypassing vibrational frequency calculations in catalyst design simplifies simulations considerably. In these simulations, it is important to note that while the pre-exponential pairs (or bond indices) are perturbed simultaneously, they are varied independently, i.e., the inputs to the uncertainty analysis are not correlated. The spread of the optimal binding energies for nitrogen and hydrogen is found to be weakly correlated when uncertainty in pre-exponential factors is taken into account, but the correlation is more pronounced when bond indices are perturbed.

The importance of coverage dependent elemental binding energies was then investigated by omitting the interactions (i.e., by setting $C_1 = C_2 = 0$). The results, while considering the effect of uncertainty in pre-exponentials, are shown in Fig. 4. A substantial shift by more than 25 kcal/mol of the optimum set of binding energies is seen. Also, the (weak) correlations between the spread in optimal binding energies of nitrogen and hydrogen are different for the case with and without adsorbate–adsorbate interactions. Interestingly, the average optimal elemental binding energy of nitrogen is decreased, while that of hydrogen is increased. Importantly, using DFT-computed binding energies of N on Ni, Pt and the Ni–Pt–Pt-surface and Pt–Ni–Pt sub-surface configurations (Table 2), different materials are predicted as potentially optimal catalysts. Specifically, when adsorbate–adsorbate interactions are included, the single monolayer of Ni on top of Pt is predicted to be a good NH_3 decomposition catalyst. This finding is an excellent agreement with recent experimental data [8]. In contrast, when interactions are not accounted for, Ni and Pt are predicted to be good catalysts, contradicting experimental data [8]. Obviously, identification of optimal catalyst properties and the effect of parametric model uncertainty on these properties is just the first step toward computational materials design. Catalyst stability and synthesis of these materials are important next steps that need to be considered.

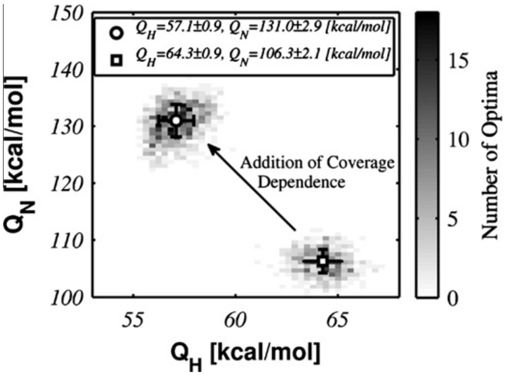

Fig. 4. Impact of coverage dependence of heats of chemisorption on optimal (zero coverage) elemental binding energies. The points and crosses indicate the average and standard deviation of the optimal binding energies due to uncertainty in pre-exponentials. The gray scale indicates the number of runs (among 600) within an interval of elemental binding energies. Adsorbate–adsorbate interactions have a profound effect on optimal catalyst property prediction.

Table 2
Library of DFT binding energies at a 1/9th ML N coverage on Ni, Pt, and two single monolayer bimetallics [8]. These low-coverage values are close to the zero coverage limit reported in the graphs. Lateral interactions are included by carrying out DFT calculations for several coverages from 1/9th to a full monolayer, as reported in [8] (note that high coverages of N are not thermodynamically favorable under typical conditions). Inclusion of adsorbate–adsorbate interactions (Fig. 4) indicates that a monolayer of Ni on Pt is a good NH_3 decomposition catalyst, in agreement with recent experiments [8], whereas the lack of interactions points to Pt and Ni being good catalysts, in contradiction to experimental data [8].

Metal surface (1 1 1)	Nitrogen binding energy (kcal/mol)
Pt–Ni–Pt	87.5
Pt	102.1
Ni	113.8
Ni–Pt–Pt	130.7

Our results indicate that accounting for coverage dependence in binding and activation energies is critical for catalyst discovery. Given the strong N—N, C—C, and O—O interactions on transition metals, we expect also a profound effect of interactions for many catalytic reactions of hydrocarbons and oxygenated molecules. Our results also suggest that a single metric, such as the elemental binding energy at a certain surface coverage (e.g., a quarter monolayer computed with a 2 × 2 unit cell in DFT), may be insufficient to appropriately identify optimal catalyst properties since it lacks the explicit effect of adsorbate–adsorbate interactions that we have considered here.

4. Conclusions

Reaction kinetics based on intuitive assumptions of a rate limiting step have been successful for understanding simple reaction systems, like the decomposition of ammonia, and for assisting with the identification of new catalysts. As the attention turns to more complicated chemistries, methods for predicting kinetics and optimal catalyst formulations will be necessary. Making this leap requires the development of full microkinetic models without simplifying assumptions in solving them and an understanding of how much uncertainty is tolerable in microkinetic models for the purposes of catalyst discovery.

Herein, a framework was introduced for assessing the effect of uncertainty on catalyst selection. Specifically, the impact of elemental binding energies on catalyst activity was studied through activation energy–binding energy mappings using a full microkinetic model without invoking assumptions about the rate limiting step or the most abundant intermediate. The errors associated with the kinetic parameters of multiscale microkinetic models were explored through a parametric uncertainty in pre-exponentials and bond indices; within the UBI-QEP method, the latter are loosely related to the location of the transition states.

Importantly, optimal binding energies were shown to be independent of reactor conditions (for ammonia decomposition), suggesting that a single optimal catalyst could be used throughout a reactor. We expect this to be reaction specific. Uncertainty in the kinetic parameters (pre-exponentials and bond indices) within reasonable ranges had little effect on optimal binding energies. The insensitivity on pre-exponentials is an important finding that indicates that one may bypass the expensive computation of vibrational frequencies in catalyst searches and focus on energetics. In addition, since there is lack of semi-empirical (scaling) methods relating pre-exponentials with electronic properties, current optimizations are limited to assuming the same pre-exponentials for all catalysts. Our results indicate that this assumption does not affect significantly model predictions. Coverage dependence was shown to be the most critical attribute of a microkinetic model at least for ammonia decomposition. Consequently, it appears impossible to narrow down the catalyst selection in terms of optimal binding energies to a single material. Rather, materials within a range (∼20%) around the optimum should be exploited experimentally. Work on additional reactions will be essential to further understand the effect of uncertainty on optimal catalyst properties and catalyst discovery.

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