Prediction of Transition-State Energies of Hydrodeoxygenation **Reactions on Transition-Metal Surfaces Based on Machine Learning**

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Supporting Information

ABSTRACT: Computational catalyst discovery involves identification of a meaningful model and suitable descriptors that determine the catalyst properties. We study the impact of combining various descriptors (e.g., reaction energies, metal descriptors, and bond counts) for modeling transition-state energies (TS) based on a database of adsorption and TS energies across transition-metal surfaces for the decarboxylation and decarbonylation of propionic acid, a chemistry characteristic for biomass conversion. Results of different machine learning models for more than 1572 descriptor combinations suggest that there is no statistically significant difference between linear and nonlinear models when using the



right combination of reactant energies, metal descriptors, and bond counts. However, linear models are inferior when not including bond count and metal descriptors. Furthermore, when there are missing data for reaction steps on all metals, conventional linear scaling is inferior to linear and nonlinear models with proper choice of descriptors that are surprisingly robust.

INTRODUCTION

Computational catalyst screening typically involves developing a microkinetic reaction model whose parameters are determined from transition-state theory with the (free) energies of all adsorbates and transition states can, in principle, be determined from density functional theory (DFT) calculations.^{1,2} The computational effort can become very large when the goal is screening of tens or hundreds of possible active-site structures. A particular burden is the computation of transition-state energies given that the identification of transition states is computationally about 1 order of magnitude more time intensive than the computation of ground states and that a reaction network generally consists of many more reactions (i.e., transition states) than surface intermediates (i.e., ground states). Particularly for biomass conversion reactions, the reaction network is often very complex and it is challenging to priori identify dominant reaction pathways and key reaction states.

To reduce the computational cost in transition-state calculations, linear scaling relations such as Bronsted-Evans-Polanyi (BEP)³ and transition-state scaling (TSS) relations have been developed to correlate the activation energy and transition-state energy to the reaction energy and product energy, respectively.⁴⁻⁷ Despite the great success of these linear relations in predicting transition-state energies of methane and methanol dissociation on different single metal and bimetallic surfaces,^{8,9} ammonia decomposition on various mono- and bimetallic transition-metal surfaces,^{10,11} synthesis

gas conversion on fcc(111) transition-metal surfaces¹² and other hydrocarbon dehydrogenation, C-C and C-O bond scission reactions on close-packed transition-metal surfaces,^{13–15} the applicability of these relations in more complex systems, such as biomass hydrodeoxygenation, is still unknown.^{5,16–20}

In this paper, we study various descriptors for modeling transition-state energies (TS) including conventional descriptors such as reaction energies and dissociated product energies as well as adsorption energies of other surface intermediates and information related to the chemical bonding in the surface species that are the reactants and products of elementary surface reactions. We consider a database consisting of the most-stable ground-state adsorption energies (Gibbs free energies computed within the harmonic approximation at a temperature of 473 K) of a group of intermediate species and transition states from the hydrodeoxygenation of propionic acid on six different close-packed metal surfaces (Ni, Pt, Pd, Ru, Rh, and Cu).^{21–25} We analyzed more than 1572 descriptor combinations with a linear model to see if there is a specific combination that can achieve a significant difference to the commonly used descriptors in BEP and transition-state scaling.^{26–28} Also, we compare these linear models with and without regularizations (L2 norm)²⁹ with the best descriptors to nonlinear models. Following previous studies³⁰⁻³² on

Received: November 8, 2019 Published: November 14, 2019 predicting thermodynamic properties of a chemical compound, we considered nonlinear kernel regression models such as support vector regression (SVR),³³ Gaussian process (GP),³⁴ and kernel ridge regression (KRR).³⁵ In this way, we study if there is a significant difference between different regression models. Furthermore, there are different ways to train these models based on grouping the reaction steps: either train a model per reaction step, i.e., no data grouping, train a model per cleavage, which groups the reaction steps based on their cleavage type, or train one model for all reaction steps, i.e., one group. Therefore, we analyzed if there is a significant difference between various data grouping approaches. Finally, we studied the robustness of all of these models when removing information about some elementary steps from the training dataset, which will be very useful for reactions involving a very large reaction network where we cannot have information for all elementary reactions.

METHODOLOGY

All of the DFT calculations for adsorption and transition states of the six metal surfaces (Ni111, Pt111, Pd111, Ru0001, Rh111, and Cu111) were performed using the Vienna Ab Initio Simulation Package (VASP) with the projector augmented wave (PAW) method.³⁶ The generalized gradient approximation (GGA) with the Perdew-Wang 1991 functional (PW91) was used to describe the exchange-correlation effects.^{37,38} A combination of climbing image nudged elastic band (CI-NEB) and dimer method was used to locate the transition states.^{39–41} For all of the calculations, we used a $3 \times$ $2\sqrt{3}$ surface slab with four metal atom layers separated perpendicularly by a 15 Å vacuum space. An energy cutoff of 400 eV and the energy convergence criterion of 10^{-7} eV were set to all calculations. All structures were relaxed until the Hellmann-Feynman force on each atom was smaller than 0.01 and 0.02 eV \mathring{A}^{-1} for the optimization of the surface intermediates and transition states, respectively. Except for the calculations on the Ni (111) surface, all calculations were not spin-polarized. The Brillouin zone integration was sampled by $4 \times 4 \times 1$ k-points for the surface using the Monkhorst-Pack scheme.⁴² With the DFT calculations from the above six metals, we first calculate the corresponding adsorption energies for various species on different metal surfaces according to the following equations

$$\begin{split} E_{\rm H} &= 0.5 E_{\rm H_2} \\ E_{\rm C} &= E_{\rm CH_4} - 2 \times E_{\rm H_2} \\ E_{\rm O} &= E_{\rm H_2O} - E_{\rm H_2} \\ E_i &= E_{\rm total,i} - {\rm x} E_{\rm C} - y E_{\rm O} - z E_{\rm H} - E_{\rm slab} \end{split}$$

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where x, y, and z are the numbers of C, H, and O atoms that the surface species is made up of. Then, we calculate all reaction step-related descriptor values for our analysis based on a dissociation reaction form reactant \rightarrow product₁ + product₂. Next, we split the data into training and test sets to model the transition-state energies and evaluate our trained modeldescriptor pairs. We use five of the metals for training and test on the sixth one. To get stable results, we applied the 6-fold cross-validation technique where we evaluate one metal given the other five metals as training. Then, we calculate the mean absolute error (MAE) and standard deviation (STD) over all metals. As we predicted all of the TS energies for all tested metals (6 metals \times 39 testing reactions), we calculate the STD over all absolute errors (234 testing reactions) between the predicted energies and true-referenced DFT energies.

In our experiments, we evaluated different nonlinear models such as the Gaussian process (GP),³⁴ which is a nonparametric statistical model that compactly describes distributions over functions with continuous domains. A GP models a collection of random variables as a multivariate normal distribution with mean μ and covariance function $K(X^*, X)$. The covariance function or the kernel defines the relation between any pair of data points. Given that the Gaussian process prior is zero mean with a valid covariance function k, the posterior mean $\mu_{\rm p}$ and the posterior variance \sum_{p} can be calculated as

$$\mu_{p} = K(X^{*}, X)(K(X, X) + \sigma_{n}^{2}I)^{-1}Y$$

$$\sum_{p} = K(X^{*}, X^{*}) - K(X^{*}, X)(K(X, X) + \sigma_{n}^{2}I)^{-1}$$

$$K(X^{*}, X)$$

where σ_n^2 is the noise variance. The covariance matrix K is an N \times N matrix where N is the number of training data points. Each element in the covariance matrix can be evaluated using the kernel function. In this work, we examined different kernel functions such as radial basis function (RBF) and Matern, Linear, and Polynomial functions. Also, we used support vector regression (SVR),³³ which is also a kernel method. As with GP, there is a choice of kernels that depends on the prediction task at hand. In our experiments, we evaluated the linear and RBF kernels for SVR, as shown in the Supporting Information Tables. In addition, kernel ridge regression (KRR)³⁵ uses a different loss function than SVR and its estimation can be done in a closed form. We tested the linear and Gaussian kernels for KRR.

In the missing data experiments, we use 6-fold crossvalidation between metals, i.e., we use five metals for training and the sixth one for testing. Then, we iterate over all combinations. For the training metal data, we randomly remove n% of the TS energies from each metal; then, we train the models on the remaining data. After that, we test these models to predict all of the TS energies for the test metal. Because we remove the data randomly, we repeat these experiments 10 times such that we get the MAE and STD over all of the absolute errors of the TS energies.

RESULTS AND DISCUSSION

One-Step Approach (No Grouping). Similar to the most common approach, we apply various predictive models based on linear and nonlinear techniques to model the transitionstate energy of each step. Given six metals and 39 TS steps for each metal shown in Table S1, we use one predictive model per TS step to be trained on five metals and tested to predict the TS energy of the sixth metal. Similar to the work by Chowdhury et al.,⁴³ we use metal descriptors (such as $E_{\rm H}$, $E_{\rm C}$, $E_{\rm O}$, $E_{\rm OH}$, $E_{\rm CH_3CH}$, and $E_{\rm CHCHCO}$) and bond counts of species (such as the bond count of reactant Br) to describe the variabilities of the transition-state (TS) energies. In addition, we consider other descriptors such as the adsorption energy of the reactant (Er), the sum of adsorption energies of the products (sP = Ep1 + Ep2), and reaction energies (Er - sP) (see the Supporting Information for more details). We note that electronic structure descriptors have recently been

introduced as metal descriptors.44,45 While such metal descriptors might be beneficial for large-scale screening studies, we refrained from using such metal descriptors but rather focus this paper on comparing conventional scaling relations that are based on adsorption energies with various machine learning models that utilize similar adsorption energy information (both as metal descriptors and reaction descriptors) and other bond count information that is freely available when having determined the thermodynamics of surface reactions. Except when otherwise specified, the TS energies we aim to predict in this work are free energies calculated at a temperature of 473 K such that the results can directly be used in a microkinetic model. Then, we calculate the mean absolute error (MAE) and its standard deviation (STD) over all steps and metals. We found that the best model is linear with L2 regularization using Er, Ep1, Ep2, Br – Bp1, E_{OH} , $E_{CH,CH}$ as descriptors with MAE = 0.179 eV and STD = 0.157 eV where Br is the reactant bond count and *Bp*1 is the bond count of the bigger product species, as shown in Table 1 (more details are shown in Tables S2, S6, S7, S23–S28 and Figure S3 in the Supporting Information).

Table 1. Average MAE (in eV), Standard Deviation for All Absolute Errors (SD-AE) of Tested Reactions, and Standard Deviation of MAEs (SD-MAE) over Six Testing Metals for Different Models and Groupings of Data (Predicting Data on the Sixth Metal from Data of the Other Five)

app.	model	desc.	MAE	SD-AE	SD- MAE
one- step	ridge	<i>Er, Ep1, Ep2, Br</i> — Bp1, <i>E</i> _{OH} , <i>E</i> _{CH3CH}	0.179	0.157	0.039
one- step	ridge	Er, E _{CH3CH}	0.201	0.169	0.028
one- step	linear	Er	0.298	0.344	0.095
one- step	linear	sP	0.276	0.239	0.080
one- step	BEP	Er - sP	0.244	0.241	0.093
per-clvg	GP- Matern	Ep1, Br, Bp2, $E_{\rm C}$, $E_{\rm O}$, $E_{\rm H}$	0.176	0.162	0.077
per-clvg	GP-RBF	sP, Br, E _{CHCHCO}	0.201	0.178	0.045
one- model	BEP	Er - sP	0.267	0.184	0.037
one- model	GP- Matern- ard	sP, Bp1, Bp2, E _C , E _O	0.169	0.145	0.030
one- model	ridge	Er	0.322	0.278	0.077
one- model	linear	Er, Ep1, Ep2, Br, Bp1, Е _{СН3} СН	0.189	0.165	0.040

We have looked at all of the models that lead to no statistically significant difference in results than the best ones (using *p*-value < 0.05). There are 835 different linear/ nonlinear models that are not significantly different from the best ones. Among these best models, linear models can achieve this with the smallest number of descriptors. Only two descriptors, the adsorption energy of the reactant *Er* and the adsorption energy of CH₃CH as metal descriptors, are needed for a regularized linear model to achieve MAE = 0.201 eV and STD = 0.169 eV. On the other hand, all of these best models are significantly different from the linear scaling method with *Er* as the descriptor, which achieves MAE = 0.298 eV and STD = 0.344 eV (shown in Table S8 in the Supporting

Information), and the linear scaling method with sP as the descriptor, which achieves MAE = 0.276 eV and STD = 0.240 eV (shown in Table S9 in the Supporting Information). We also trained the data using the BEP model (Er - sP), and the results show MAE and STD of 0.244 and 0.241 eV, respectively, which demonstrates that BEP has inferior performance in this context although it appears superior to TSS with sP as the descriptor.

The conclusion from the per-step approach is that the linear model needs at least a metal descriptor (such as E_{CH_3CH}) in addition to the reactant energy Er to achieve results that are not statistically different from the best results, as shown in Figure 1. Also, regularized linear models can easily compete with advanced machine learning models such as SVR with polynomial kernel given suitable descriptors, as shown in Table S7 in the Supporting Information.

Even though it is very common to use one-model per step, we also extended our analysis to one-model per cleavage and one model for all of the steps. In this way, we find the best model/descriptor per elementary reaction grouping method.

Per-Cleavage Grouping Approach. Instead of having 39 predictive models to learn about 39 TS steps separately as we did in the previous approach, here we split the TS data based on the cleavages (C-OH, C-H, C-C, and O-H bond cleavages). We used different cleavages: C-OH with six reaction steps, C-C with 11 reaction steps, C-H with 17 reaction steps, and O-H with five reaction steps per metal surface. Then, we train one predictive model for each cleavage group.^{6,7} Given six metals and cleavage groups, we use one predictive model to be trained on all TS steps within a cleavage group from five metals and tested to predict the TS energies within the same cleavage group from the sixth metal. Then, we calculate the MAE with STD over all steps and metals. We also studied all of the linear and nonlinear techniques that we used in the previous approach and we found that the GP-Matern using Ep1, Br, Bp2, E_C, E_O, E_H can achieve the best results among all of the models in this case with MAE = 0.176 eV and STD = 0.162 eV. Also, we found 1801 models that are not statistically significantly different from the best ones. The lowest number of descriptors among these models is three descriptors, which can be achieved only by nonlinear models such as GP-RBF, which only uses sP, Br, E_{CHCHCO} with MAE =0.201 eV and STD = 0.178 eV. However, for linear models, at least four different descriptors are needed to give predictions as good as the best model. Among all of these models, we found that the linear models have no significant difference from the nonlinear models when using the right descriptors. Samples of these models are shown in Tables S10-S12 and Figure S4 in the Supporting Information. The results show that using simple descriptors such as Er or sP will always lead to high MAE regardless of the model used; however, adding bond counts and/or metal descriptors yields better TS predictions.

One-Model Grouping Approach. In contrast to the previous two approaches, here, we use one predictive model to learn all of the TS energies together. Given six metals and a predictive model, we trained the model on all TS steps from five metals and tested to predict all of the TS energies of the sixth metal. By using all of the linear and nonlinear techniques, we found that the GP-Matern-ard with *sP*, *Bp1*, *Bp2*, E_C , E_O as descriptors achieved the best MAE of 0.169 eV and STD = 0.145 eV. These descriptors include all three different types of descriptors studied, i.e., reactant/product energies, bond



Figure 1. Predicted energy (after referencing) vs actual energy (after referencing) for modeling the TS energy using the one-step approach for the prediction of the TS energies on Ni(111). (a–c) Show how linear scaling models behave with simple descriptors such as Er (energy of reactant), sP (energy of sum of products), or Er - sP, respectively. (d) Illustrates how the regularization reduces the MAE from 0.311 eV in (a) to 0.221 eV. The addition of a metal descriptor such as E_{CH_3CH} improves the results, as shown in (e). (f) Shows the best model (lowest MAE) using the one-step approach.

counts, and metal descriptors. Also, there is no significant difference between 713 different models and the best ones. The lowest number of descriptors among these models is four descriptors, which can only be achieved by nonlinear models, as shown in Table S13 in the Supporting Information. However, the linear models are not significantly different than the best nonlinear model when at least 5 different descriptors are used, as shown in Table S13 in the Supporting Information. In these two cases, all of the linear and nonlinear models are using Er, the reactant energy. In addition, each one of these models has one metal descriptor, which reflects the

importance of including the metal descriptors for more variability when including multiple metals for training. The best descriptors for each model are shown in Figure S5 and Table S14 in the Supporting Information. On the other hand, using one model with simple descriptors such as Er or sP leads to high MAE. For instance, the Ridge model with Er as the descriptor gets MAE = 0.322 eV and STD = 0.278 eV, as shown in Tables S15 and S16 in the Supporting Information.

The main conclusion of this descriptor analysis over the three grouping methods is that the number of descriptors required to achieve the best results depends on the grouping



Figure 2. Significant difference between different models from the three different grouping approaches. It is noticed here that the linear scaling models with simple descriptors and per-step approach are significantly different from the best models of all approaches. No significant difference is observed between the one-model grouping approach and the per-step approach given the best regression model and descriptors.



Figure 3. MAE in eV for a small number of models across various missing data scenarios. (a) It is noticed here that linear models with simple descriptors such as reaction energy, *Er*, or *sP* give higher MAE and have a significant difference from the models with multiple descriptors. The MAE for the linear models such as BEP and TSS are above 0.26 eV regardless of the percentage of the missing data. This can be explained as *Er* or *sP* is a linear component and can be easily modeled by linear functions. So with a lower number of data points, we can still fit the linear model with similar performance. (b) When we consider more features from bond counts and metal descriptors, e.g., a linear model with *Er*, *Br*, *Bp2*, *E*_{CH₃CH}, we can get lower MAE with a significant difference from simple descriptors such as *Er* only. Considering more descriptors with a regularized linear model leads to improved model accuracy, e.g., Ridge *Er*, *Ep1*, *Ep2*, *Br*, *Bp2*, *E*_{CH₃CH}. (c) In addition to linear models, the advanced machine learning models with complex kernels such as GP with Matern kernel can give slightly lower MAE but with no significant difference from the linear model that has more descriptors. (d) Also, the linear and nonlinear models with the same descriptors perform similarly such as Ridge and GP with RBF kernel and *Er*, *Ep1*, *Ep2*, *Br*, *Bp2*, *E*_{CH₃CH}.

method. For one-model per step, only two descriptors with the regularized linear model can give good results. However, at least five descriptors are needed for a linear model in the case of the one-model grouping approach. Note that to achieve a lower MAE with linear/nonlinear models, the descriptor set should include at least the adsorption energy of the reactant/ product and a metal descriptor. However, to achieve higher accuracy, bond counts should also be considered. Interestingly, the nonlinear complex models cannot achieve significantly different results from the linear ones when the right descriptors are used for the linear models.

Comparison of Elementary Reactions' Grouping. Finally, we study if there is a significant difference between various types of groupings of elementary reactions such as one-model per step, one-model per cleavage, and one model for all reaction steps. Here, we found that with the right model and descriptors, there will be no statistically significant difference between these types of groupings, as shown in Figure S6 in the Supporting Information. For example, linear scaling, which is a per-step linear model with Er as a descriptor, gives worse results than the linear one-model grouping approach with Er, Ep1, Ep2, Br, Bp1, $E_{CH,CH}$ as descriptors, as shown in Table 1

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and Figure 2. The conclusion that the best models in the onemodel approach are not statistically different from the best models in the other two approaches is very useful because the one-model approach has a high potential to be used in the case of missing various reaction steps as described in the next experiment.

Missing Reaction Steps. In the case of missing transitionstate steps on all metal surfaces, the one-step approach will not be applicable and presumably the per-cleavage also not, given that very few reactions might be in a specific bond cleavage grouping. Therefore, we examine only the one-model grouping approach in various missing data situations to identify the most stable model/descriptors in these different scenarios. We study the data with n% missing steps where n = 0, 10, 20, 30, 40, 50,60. We found that the linear models are very stable when five descriptors are used from combinations of adsorbate energies (Er, Ep1 or Er, Ep1, Ep2), bond counts (combinations of Br, Bp1, Bp2), and $E_{CH,CH}$ as the metal descriptor. However, the nonlinear models can achieve nonsignificantly different results with the same descriptors in addition to others including product energies (sP) and metal descriptors ($E_{C_{i}}$, $E_{O_{i}}$, E_{H}). Figure 3 shows the same descriptors for linear and nonlinear models in different missing data scenarios.

CONCLUSIONS

In conclusion, we compared linear models versus advanced machine learning models using more than 1572 descriptor combinations. The analysis shows that considering bond counts and metal descriptors can help to achieve lower MAE for both linear and nonlinear models. Besides, the nonlinear complex models cannot achieve statistically significantly better results than the best linear ones. In addition, we discuss various elementary reaction grouping approaches, which show that the one-model approach can perform similarly to the one-step approach, which might be a benefit when reaction data on various metals are missing. The same conclusion has been reached in the missing data study, which demonstrated that conventional descriptors (product or reactant energy) will give higher MAE compared to the ones that also use bond count information and metal descriptors. This is shown in the ridge/ GP RBF models for descriptors Er, Ep1, Ep2, Br, Bp2, E_{CH,CH} that perform very well. Finally, we highlight that while our best models possess an MAE that is only 0.1 eV smaller than traditional BEP correlations for predicting transition-state energies, a difference in an activation barrier of 0.1 eV leads to a reaction rate constant that changes by a factor 12 at typical biomass conversion temperatures of 473 K. Thus, these differences can become important when correlating computational predictions with experimental data such as turnover frequencies, selectivity, reaction orders, etc.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.9b10507.

PCA and varimax analysis; descriptor analysis; results for the one-step approach, per-cleavage grouping approach, and one-model grouping approach; missing reaction TS steps using the three grouping approaches (PDF)

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Notes

The authors declare no competing financial interest.

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