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Machine learning of lateral adsorbate interactions in surface reaction kinetics

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The importance of lateral adsorbate interactions cannot be overstated in describing surface reaction kinetics. To realize the goal of operando computational modeling of catalytic processes, it is crucial to integrate effects of relevant adsorbate coverages and configurations into mean-field kinetic analysis and beyond. Herein, we highlight the recent applications of machine learning (ML) algorithms in the development of adsorbate-adsorbate interaction models, ranging from analytic relationships, to ML-parameterized cluster expansions, and to highly nonlinear deep learning models. We also discuss prospects and challenges in moving the field forward, particularly in the integration of theoretical understanding into ML of lateral adsorbate interactions across the chemistry and materials space.

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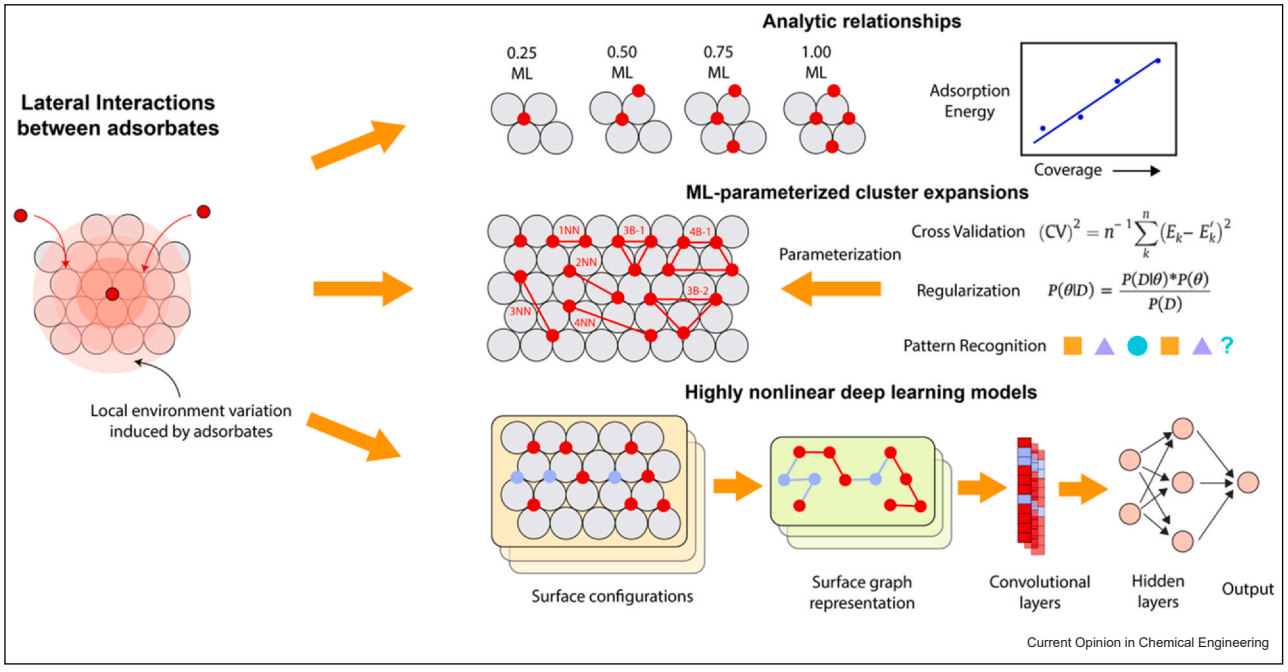
Introduction

Lateral adsorbate interactions on solid surfaces play a crucial role in heterogeneous catalysis, self-assembly, nucleation and growth, and many interfacial phenomena governed by molecular processes [1]. For instance, the outcome of a surface-catalyzed reaction can be greatly influenced by introducing chemical additives as coadsorbed modifiers which promote or inhibit the transformation of kinetically significant intermediates. As being increasingly recognized, intrinsic reaction intermediates at noticeable coverages often synergistically regulate the catalytic cycle with active sites in a self-adjusting manner [2,3]. At the most fundamental level, an ensemble of adsorbate–adsorbate configurations collectively renders the local environment of reacting species by substrate-mediated electronic couplings and through-space electrostatic interactions [4,5], or direct orbital overlaps in some cases [6]. Experimentally, it is possible but remains challenging to measure interaction energies of adsorbates on single-crystal surfaces under ultrahigh vacuum conditions. However, the so-called pressure and materials gaps prevent the generalization of attained knowledge to industrial operating conditions [7]. In this regard, computational chemistry with a vast array of sophisticated tools is invaluable in describing the structures and energetics of complex systems [8]. Particularly, density functional theory (DFT) has proved to be reasonably accurate for capturing kinetic parameters of elementary steps occurring at active sites while considering lateral adsorbate interactions in an ad hoc fashion. The practicability and maturity of this approach have reached such a level that rudimentary energy analyses of reaction pathways can often tell us whether a material candidate can selectively catalyze desired chemical transformations.

To provide truly actionable insights for guiding the design of high-performance catalytic systems, rigorous kinetic analysis is required. With recent advances in computing infrastructures and numerical algorithms, kinetic modeling of surface reactions has gained popularity because it directly links atomistic processes with macroscopic observables under relevant conditions [9]. Among various practiced techniques, microkinetic modeling (MKM) with the Brønsted-Evans-Polanyi and linear adsorption–energy scaling relationships is widely used in heterogeneous catalysis by mapping the catalytic outcome of surface reactions onto reactivity descriptors, for example, adsorption energies of key intermediates or their derivatives [10]. It has been shown that when applying the adsorbate interactions to kinetic studies, catalytic reaction pathways and microkinetic predictions like turnover frequency, selectivity and apparent activation energies are different, highlighting the generic consequences of lateral interactions [11]. Although lateral adsorbate interactions can be included in energetics, the spatial distribution of adsorbates on a catalytic surface is not explicitly considered because of the inherent mean-field approximation [12,13]. To go beyond the mean-field treatment [14,15], one of the common approaches is solving a stochastic Markov process within a

Figure 1



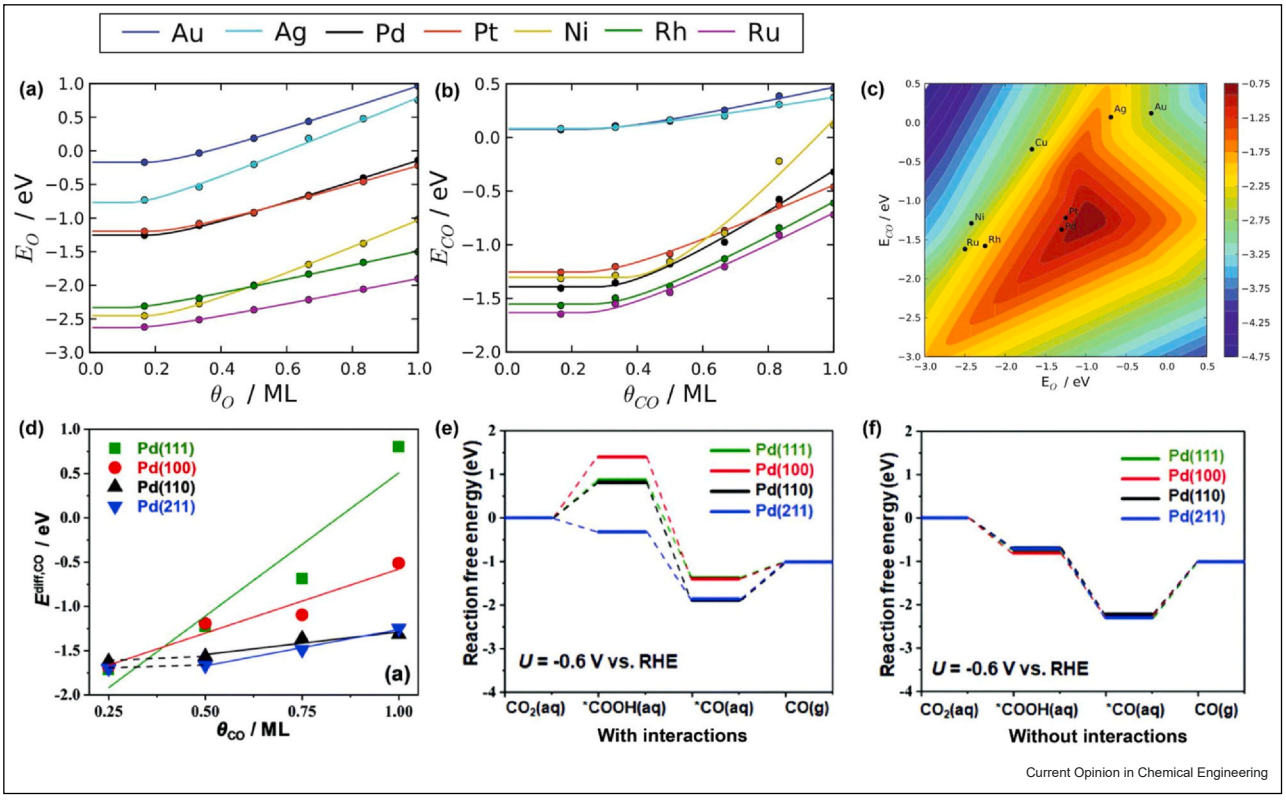
Lateral adsorbate interactions can be considered as the change of the binding energy for a given adsorbate in response to a perturbation of its local environment by co-adsorbates. Analytic relationships between the average (or differential) adsorption energies and the coverage have been employed to determine lateral adsorbate interactions in simple scenarios. Another way that has been widely used is ML-parameterized (cross validation, regularization, pattern recognition, etc.) CEs. An emerging approach is using highly nonlinear deep learning models, for example, graph convolutional neural networks, to predict adsorption energies after seeing a large amount of surface configurations by the algorithms.

lattice-based kinetic Monte Carlo (kMC) framework. However, it is not feasible to directly compute energetics of every Monte Carlo (MC) step from quantum mechanics across experimentally relevant time and length scales [16]. To address this dilemma, developing surrogate models by learning from ab initio data has become an emerging research frontier of fundamental catalysis [17,18]. Herein, we survey the machine learning (ML) algorithms for predicting lateral adsorbate interactions on solid surfaces, for example, transition metals, ranging from analytic relationships, to ML-parameterized cluster expansions (CEs), and to highly nonlinear deep learning models (Figure 1). We will also discuss prospects and foreseeable challenges in implementing generalizable ML techniques in operando computational modeling of surface reaction kinetics.

Analytic relationships

To include adsorbate coverage effects in MKM, analytic relationships have been developed to describe adsorption energies and reaction barriers as a function of coverages [19–23•]. The analytic relationships do not contain any ML aspects but serve as the initial idea of ways to consider the adsorbate interactions. Grabow et al. [20] found that the differential binding energy changes linearly with the coverage after a certain threshold and applied the piecewise linear model to the kinetic studies of CO oxidation (Figure 2a and b). The activity volcano plot as a function of O and CO binding energies at the low coverage limit is shown in Figure 2c. It was concluded that adsorbate–adsorbate interactions significantly increase the activity of strong binding metals (the bottom left corner of the volcano), but the interactions do not change the relative activity of different metals and have a very small influence on top right corner of the volcano, that is, on which one is the best elemental metal catalyst. Liu et al. [23•] studied the coverage effect of *CO for CO_2 electroreduction on Pd surfaces. The differential CO adsorption energy has a linear relationship with the CO coverage (Figure 2d). With the consideration of the adsorbate–adsorbate interactions, the experimentally measured activity trend of four surface terminations, that is, Pd(111), Pd(100), Pd (110), and Pd(211), can be well captured by theoretical onset potentials (Figure 2e and f). Formulations of coverage and binding energy beyond linear relationships have also been previously employed in microkinetic models [24,25], emphasizing the importance of considering the linear or beyond linear coverage effects in surface reaction kinetics.

Figure 2



Coverage-dependent binding energies for O and CO on fcc(111) of seven transition metals are shown in **(a)** and **(b)**, respectively [20]. **(c)** It shows the contour plot of the CO oxidation activity (defined as $k_BT \cdot ln(r/\nu)$, $\nu = k_BT/h$) under high-temperature conditions (T = 600 K, P_{O_2}= 0.33 bar, P_{CO}= 0.67 bar, P_{CO_2}= 1 bar) as a function of the O and CO adsorption energies at the low coverage limit [23•]. The differential adsorption energies of CO on Pd(111), Pt(100), Pt(110) and Pt(211) surfaces as a function of the coverage of CO [23•]. The reaction pathways of CO_2 electroreduction to CO at the applied potential (–0.6 V vs. RHE) with and without the consideration of adsorbate-adsorbate interactions are shown in **(e)** and **(f)**, respectively [23•].

Machine learning-parameterized cluster expansions

Lateral adsorbate interactions can be considered in kMC simulations by employing CEs, one common type of lattice-gas models with parameterized Hamiltonians. The CE-based models are physical models and not ML methods but determining Hamiltonians in CE-based models employs ML methods for fast and accurate parameterization. Wu et al. [26] first applied CEs in kinetic models to estimate the catalytic rates, and CEs gained popularity with different frameworks (Alloy Theoretic Automated Toolkit (ATAT), UNiversal CLuster Expansion (UNCLE), Integrated cluster expansion toolkit (ICET), Zacros, kmos, etc.) [27–30] developed and applied to surface catalytic reactions, for example, NO oxidation reaction, CO oxidation, and Fischer-Tropsch synthesis [12,26,31–34]. CEs have advantages over simplified linear models since they can predict energetics of elementary steps with the consideration of the spatial environment of surface species on lattice sites [35•]. The origin of CEs can be traced back to the early 1950s, when Kikuchi [36] developed an Ising model-based cluster variation method to study order–disorder phenomena. In 1984, Sanchez et al. [37] developed a general formalism for the description of configurational CEs in terms of a complete basis set expansion. In simple terms, CE decomposes the energy of a configuration into one-body, two-body, and higher order interaction terms ('clusters'), and each term has a corresponding weight called effective cluster interaction (ECI) analogous to the interaction strength [38]. The energy can be exactly reproduced only if all clusters are included in the CE. However, the ECIs for clusters that contain a large number of sites or a large distance between sites are usually negligible. Therefore, the CEs can be truncated to a sum over finite numbers of cluster functions with little loss of accuracy.

The construction of CEs includes data generation by DFT calculations, structure selection, and cluster selection. When referring to surface reactions, the training becomes more challenging due to the loss of translational symmetry at the interface and the increase of the complexity of adsorbate interactions and the number of

surface species. While DFT calculations typically require a large number of computational resources, it has become more or less standardized in catalysis research. In contrast, the algorithms driving structure selection and cluster selection are arguably more critical to the overall accuracy of the CEs. Therefore, significant efforts have been put into developing approaches to generate effective clusters for a given training set. The goal of the selection algorithm is to find the clusters that have physical contributions to lateral interactions. Early CEs relied on heuristic methods to manually select clusters, while recent approaches incorporate automated ML approaches to systematically optimize the selection process. Multiple automated selection algorithms have been developed for CEs including MIT Ab-initio Phase Stability [27], genetic algorithm [39,40], and steepest descent [41], which incorporate various well-established ML approaches such as cross validation [27,42], feature selection, pattern recognition [43], and regularization [44–46]. Pattern recognition has been employed by Vignola et al. [43] to develop a set of ML tools to produce unbiased CEs. They developed an approach that is based on the pattern recognition algorithm to automatically determine model Hamiltonians for a given system.

Bayesian optimization, as one of the regularization approaches, has been widely applied to CE models [44–46]. Mueller et al. [44,46] have a series of work of applying Bayesian approach to CEs. In 2009, Mueller and Ceder [44] applied the Bayesian approach to fit CEs with a prior probability distribution to ECI values, and cross validation is used to determine the hyperparameters of the prior distributions and identify clusters during cluster selection. As one of the benefits of the regularization approach, the Bayes' theorem helps to generate more clusters and ECIs for a given training set which allows for more accurate description of energies of low symmetry surfaces. The method used a physically meaningful prior distribution to serve as a prior guess of the ECI values and to accelerate the convergence of CEs. For example, when considering ECIs for surface adsorption energies, the prior probability distribution is able to initiate the magnitude of ECIs on the order of meV/atom instead of keV/atom, which is usually the case for surface adsorption.

Besides the development of CE-based kMC models, efforts have been made to improve the mean-field MKM with spatial-aware lateral interaction models [47], because MKM can shed light on cases where kMC is limited by the time scale or computational cost. Li and Grabow [35•] evaluate the kMC and MKM with the consideration of lateral interactions using CO oxidation as an example. They found that MKM makes reasonable predictions with a computational cost that is around three orders of magnitude lower than kMC. Pineda and Stamatakis [15] developed a framework using the cluster mean-field approach to treat the spatial correlations at a progressively higher level of approximations. Tian et al. [48•] also presented an ML algorithm to correct the mean-field assumption in microkinetic models to incorporate adsorbate interactions and surface inhomogeneity at the fast diffusion limit. The workflow is shown in Figure 3a, in which a simple reaction, $A^*+B^* \rightarrow C^*+*$, is used as an example. For adsorbates A and B at a specific coverage θ_A and θ_B, a lattice MC model is used to compute the reaction rates of the elementary step with the consideration of lateral interactions. So for a set of different coverages, there are corresponding numbers of reaction rates calculated. As shown in Eq. (1), reaction rates from MC can also be derived as the reaction rates of mean field multiplied by the exponential of a correction term ξ, which can be considered as the correction induced by the lateral interactions from MC models. Thus, they can generate a dataset of different coverages of adsorbates and the corresponding correction terms.

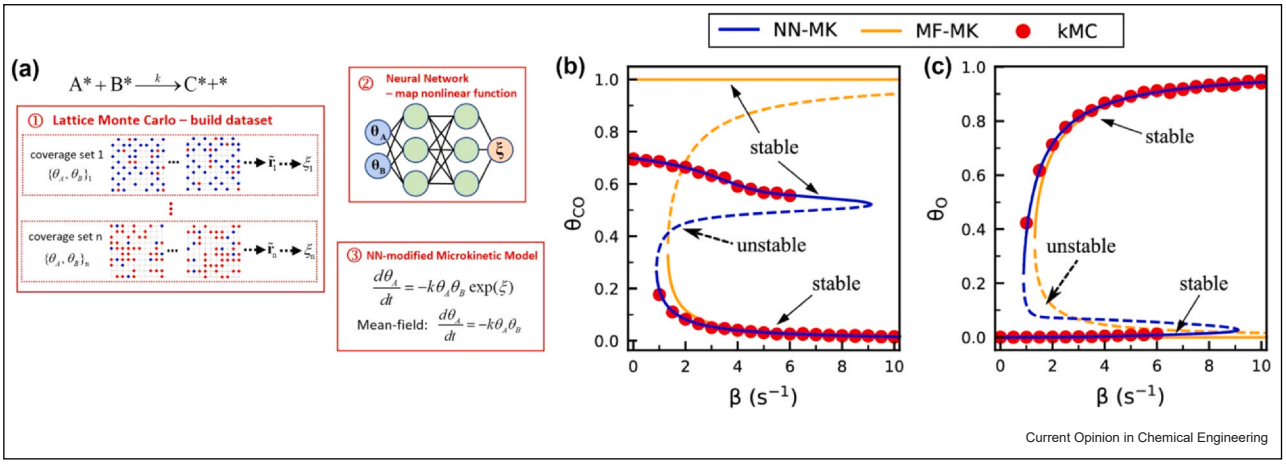
$$r_{MC} = r_{MF} \times \exp(\xi) \quad (1)$$

A neural network (NN) was then employed to determine a continuous relationship between the coverages of adsorbates and correction terms (ξ). The traditional mean-field MKM was then modified by adding the correction to the reaction rates of elementary steps, and activation barriers, in the same fashion. Therefore, the MKM was modified by considering the lateral interactions computed by MC models, which improved the accuracy of the MKM model. The model was applied to an example of CO oxidation reaction, and they showed that NN-MKM captured the phenomenon as shown in Figure 3b and c, in which the MKM completely failed, particularly for the *CO coverage. This work has improved the MKM to have similar performance compared to kMC simulations. The modified mean-field model is still in the form of deterministic ordinary differential equations, allowing various numerical operations which are difficult to implement in stochastic kMC simulations.

Deep learning models

When aiming for kinetic studies of more complex surface reactions such as CO methanation, partial methane oxidation, or the Fischer-Tropsch reaction with diverse surface species and adsorption modes, the cluster expansion approach is fundamentally limited by the number of required calculations, since the number of surface configurations grows exponentially with the number of adsorbate species. Even a simple case with *NO and *O adsorbates on Pt(111) have enormous configurations [33]. For low symmetry surfaces with various types of active sites, such as kinks and steps [12,13,49,50], and multielemental alloys [51], the loss of

Figure 3



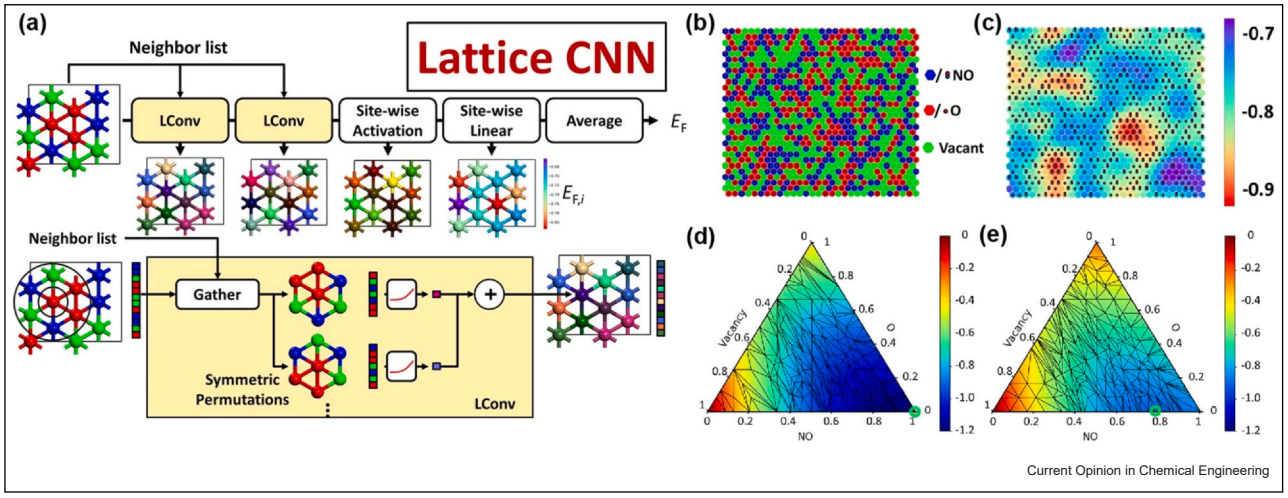
(a) The schematic illustration of the neural network-modified microkinetic (NN-MK) framework [48•]. It contains three modules: lattice kinetic MC to build a dataset, NN to map nonlinear relationships, and microkinetic model with a modified reaction rate term. The coverages of *CO and *O when varying the dissociative adsorption rate of O_2 (β), which is proportional to the partial pressure of O_2, are predicted by different modeling formalisms (NN-MK, mean-field microkinetic (MF-MK), and kMC) as shown in **(b)** and **(c)**, respectively [48•]. The solid and dashed lines represent stable and unstable steady states, respectively. The kinetic MC simulations are shown for reference as red-filled circles.

translational symmetry causes a drastic increase of configurations and clusters needed to determine model Hamiltonians. The problem is exacerbated when multidentate species adsorb on surfaces since current CEs applications are only limited to simple adsorbates that can be directly mapped to individual active sites. Thus, researchers introduced surrogate models by using ML methods, which rely on flexible and often non-linear models that are trained from reference material data to predict desired material properties. Many ML models employing neural networks and various algorithms have been developed to estimate adsorbate interactions [52–54]. As a subset of ML models, graph-based convolutional NN frameworks can directly learn material properties from crystal structures. The reference structures are converted into crystal graph features, and then connected with convolution, pooling layers, and the fully connected network to predict the target properties. Graph-based deep learning methods have huge advantages when dealing with low symmetry surfaces and multidentate adsorbates compared to CEs since the featurization automatically learns the structural information, and the nature of non-linearity improves the accuracy.

Several graph-based deep learning frameworks have been developed for lateral adsorbate interactions. Lym et al. [55] developed a novel lattice convolutional neural network (LCNN) that improved the formation energy prediction compared to state-of-the-art CE methods by 20–30% (Figure 4a). Featurization process extracts features of each site's neighbor lists using one-hot encoding. The extracted information then undergoes lattice convolutional (LConv) layers which are built to construct the local environment by considering the nearest neighbors and including permutations to account for the symmetry of the lattice. Activation and summation are followed for new site features. Once all convolution operations are performed, the representation of the lattice is obtained. Followed by the site-wise activation and linear multiplication, the formation energy of each image can be predicted. They applied the LCNN model to study the coverage of O and NO adsorption on Pt(111) surface, the model captures the local environment of adsorbates, and a one-hot encoding input and the predicted site formation energy distribution are shown in Figure 4b and c, respectively. Compared to CE models, the LCNN achieves the best performance with a test root mean squared error of 4.4 meV/site using less training data. The effect of van der Waals (vdW) forces on lateral interactions have also been studied by comparing the formation energy with and without vdW forces for an example of all unique configurations in a unit cell containing up to 12 adsorption sites (1 581 607 in total). The convex hull diagrams of LCNN computed formation energies trained using Perdew–Burke-Ernzerhof-D3 (PBE-D3) (with vdW forces) and PBE (without vdW forces) datasets are shown in Figure 4d and e, respectively. They found that the trend in the convex hull has changed by the vdW interactions. Particularly, the global ground state configuration for PBE is observed at 0.78 monolayer (ML) of NO, whereas it is 1.0 ML of NO for PBE-D3.

Ghanekar et al. [56•] developed a workflow called Adsorbate Chemical Environment-based Graph

Figure 4



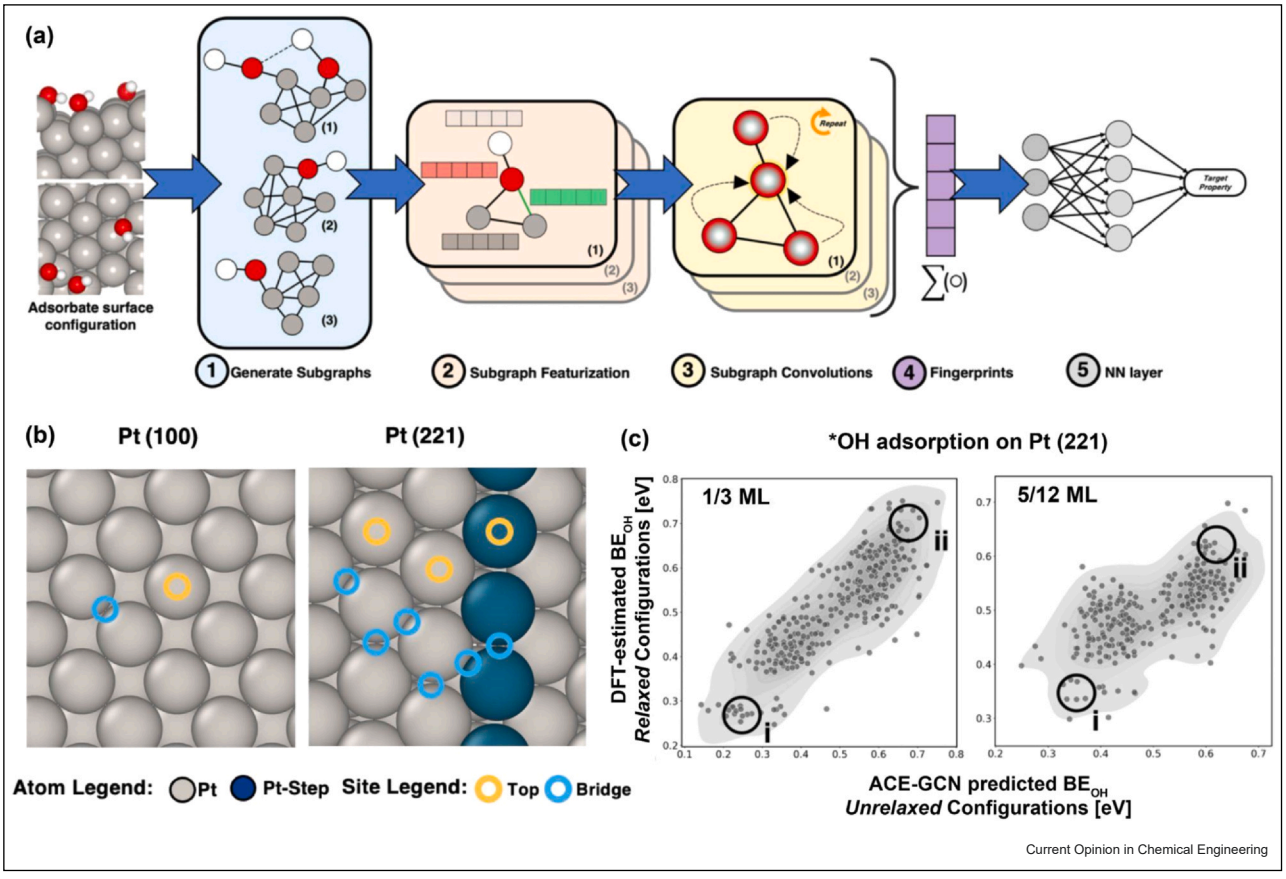
(a) Overall design of the lattice CNN model with the 2D hexagonal lattice as an example [55]. The model contains featurization, LConv layers, and site-wise activation and linear multiplication layers to predict the average formation energy. **(b)** Visualization of the site layer of adsorbates for each adsorption site after one-hot encoding of site species, that is, *NO, *O, or vacant [55]. **(c)** Visualization of the site layer shows the formation energies for each adsorption site (eV/site), where color in red means a more exothermic formation energy [55]. The convex hull of LCNN-computed formation energies (eV/site) trained using **(d)** PBE-D3 and **(e)** PBE [55]. The green circle indicates the configuration with the global minimum formation energy.

Convolution Neural Network (ACE-GCN) (Figure 5a) to overcome some challenges: high adsorbate coverages, the local morphology of the catalysts, and variations in the catalysts' surface composition induced by adsorption. Systematic enumeration of surface configurations can be efficiently performed using graph-based representations [57]. ACE-GCN utilizes the chemical and structural environment of a given adsorbate surface configuration as the input, and first splits each configuration into multiple subgraphs, each of which represent one adsorbate and local environmental properties. Each subgraph is featured and expressed in a vector representation based on the elemental properties and spatial bond distance. Followed by convolutional, pooling, and fully connected NN operations, the target property of choice, such as the average adsorption energy, can be mapped and predicted. They applied their workflow to *OH adsorption on stepped or defected crystal surfaces with the consideration of lateral interactions. The datasets have around 200 configurations of *OH adsorption on Pt(100) at coverages from 1/8 to 5/8 ML, and around 400 configurations of *OH adsorption on Pt(221) at coverages from 1/12 ML to 1/4 ML (Figure 5b). With subsequently another ~800 configurations added during the training of ACE-GCN, this framework was able to explore a huge design space (~11500) for *OH on Pt(221) with different coverages (1/12 ML–1/2 ML), even including high coverage configurations (1/3 ML–1/2 ML of *OH on Pt(221)) that are not included in the training data. For example, Figure 5c shows the strong correlations of the ACE-GCN predicted average binding energies with unrelaxed structures and the corresponding DFT energies with relaxed structures for *OH on Pt(221) at both 1/3 ML and 5/12 ML coverages. The application of *OH adsorption on different surfaces demonstrates the possibility to employ the transfer learning approach to utilize multiple datasets with a moderate number of different configurations to describe the vast configurational spaces for the complex and low symmetry surfaces. The model can serve as a starting point for rational design of catalysts and potentially provide the structurally and chemically governing factors of heterogeneous catalysis.

Prospects and future challenges

Although ML of lateral adsorbate interactions has proved to be useful in modeling surface reaction kinetics, there are important challenges toward the development of highly accurate, data-driven models that can be flexibly generalized across the chemistry and materials space. For surface reactions involving simple adsorbates, for example, monatomic or diatomic species, CEs are highly promising for parameterizing interaction energies of effective clusters with limited training data. However, the use of deep learning as a generic framework in modeling complex surface interactions is clear for moving the catalysis field forward. The challenge of data generation can be partially alleviated by strategic sampling algorithms, for example, active learning [58]. In this aspect, uncertainty quantification of model predictions [59] is particularly important for not only refining model predictions but also providing meaningful statistics in kinetic modeling. While the purely data-driven models have advantages when tackling diverse surface

Figure 5



(a) The ACE-GCN algorithm to encode adsorbate configurations, which undergoes generating subgraphs, subgraph featurization, subgraph convolutions, fingerprints and NN layers to predict the target property [56•]. **(b)** *OH adsorption on two surface structures (Pt(100) and Pt(221)) with possible sites (top and bridge) [56•]. **(c)** Parity plots show the average *OH binding energies of unrelaxed configurations for coverages of 1/3 ML and 5/12 ML, as predicted by ACE-GCN (x-axis), with DFT-relaxed energies of the corresponding structures (y-axis) [56•].

configurations, they lose interpretability of adsorbate–adsorbate interactions which are valuable for rationally designing catalysts with promoters or surface modifiers. In this aspect, physical models have some merits by considering the electronic structure of adsorbates and adsorption sites to obtain an analytic expression, which can reduce the number of data samples needed for parameterization [60]. Physical understanding of adsorbate–adsorbate interactions often starts from the change of surface *d*-band characteristics upon the perturbation from adsorbate frontier orbitals [61]. Xin and Linic [5] interpreted complex interactions on metal surfaces in terms of tractable energy contributions, that is, one-electron interaction, electrostatic interaction, and polarization, all of which can be evaluated independently to identify the dominating mode of interactions that governs surface reactivity trends. Hoffmann et al. [60] developed a general framework that predicts the magnitude of adsorbate-adsorbate interactions based on the precalculated electronic structure properties, such as the *d*-band center and the Bader charge. The framework is able to predict differential adsorption energies of adsorbate at different coverages without explicitly sampling a large amount of surface configurations, which makes the kinetic studies feasible even with multiple adsorbate species. Although these studies provide valuable insights toward understanding lateral interactions, physical models have limited accuracy and typically need electronic structure information that adds to the computational overhead. Improving the interpretability of purely data-driven models by the consideration of physically meaningful interactions [62•] could be a potential solution to accurately predict lateral adsorbate interactions in surface reaction kinetics. Leveraging physics-based models and knowledge in deep learning might prove to be fruitful but appears difficult at this stage because of the complexity of adsorbate-adsorbate interactions across the chemistry and materials space. Its realization will likely need new developments of the high-level featurization of surface configurations [63],

integrated architecture design of deep neural networks [62•], and theoretical advances of chemical interactions at solid surfaces [64].

Declaration of Competing Interest

Nothing declared.

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- •• of outstanding interest.

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