

Prediction of Vibrational Spectra of CO Adsorbed on PdPt(111) Using Machine Learning and Monte Carlo Simulations

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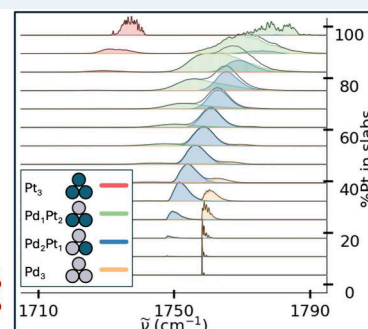
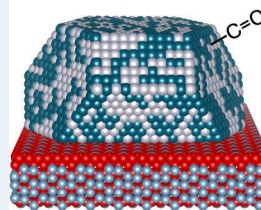


Supporting Information

ABSTRACT: In this work, we combine density functional theory (DFT), Gaussian Process Regression (GPR), and Monte Carlo simulations to investigate surface segregation and CO adsorption on Pd/Pt alloy surfaces. The DFT dataset is used to train a sparse GPR model that efficiently predicts formation energies, CO adsorption energies, and vibrational frequencies across a wide range of alloy configurations. Key structural features are encoded by local atomic descriptors, capturing both bulk and surface environments as well as adsorption sites for CO. Our simulations predict that Pd initially segregates to the surface at low temperatures, transitioning to a more random alloy configuration at elevated temperatures. CO adsorption strongly influences segregation, driving Pt toward the surface while altering the local environment and vibrational properties of adsorbed CO. The predicted surface segregation and the composition of the binding site can be connected directly to the observable vibrational spectrum and binding energy of CO. This allows us to predict central quantities in catalysis where the stretch frequency of CO is used for characterization, while the CO-adsorption energy acts as a central descriptor of catalytic activity when using BEP- or scaling relations. Many important processes involve CO, such as Fischer-Tropsch synthesis, steam reforming, the reverse water-gas shift, and oxidation reactions. Overall, the combination of GPR and Monte Carlo simulations not only provides a powerful framework for modeling large, complex systems under variable reaction conditions but also showcases a scalable, data-driven strategy for predicting segregation phenomena, adsorption energetics, and vibrational signatures in alloy materials.

KEYWORDS: density functional theory, machine learning, alloys, transition metal catalysis, emission control, vibrational spectroscopy, CO, carbon monoxide

CO-induced segregation and IR-spectra predicted with machine-learning



INTRODUCTION

The structure of a metal catalyst is pivotal in determining its activity.^{1–3} In situ and operando experiments have revealed that catalysts undergo significant structural reconstructions when exposed to changing gaseous environments.^{4–10} One example is the reshaping of metal NPs under reaction conditions, which has attracted considerable attention because it alters the number and nature of active sites during structural transformations.^{11–13} Additionally, recent studies have shown that adatoms, islands, step edges, and transient active sites can form on particles and extended surfaces to deviate significantly from the ideal situation of a low-index facet.^{14–17} Alloying allows the creation of a vast number of possible compositions and active site motifs, resulting in the discovery of many promising catalysts and catalyst candidates.^{18–22} Theoretical investigations, mainly using density functional theory (DFT), are increasingly used to predict the surface composition of alloyed nanoparticles.^{23,24}

PtPd catalysts are investigated for several reactions, involving oxidation in emission control,²⁵ the electrocatalytic oxygen reduction reaction, methanol decomposition, and hydrogenation reactions.²⁶ Besides affecting the reactivity, alloying also influences the

durability of a catalyst. In emission control catalysis specifically, alloying with Pd stabilizes Pt catalysts with respect to sintering^{27–29} and is also beneficial for regeneration of the catalyst.³⁰ It should be noted that in oxidation catalysis, particles are often partially oxidized^{31,32} and even the formation of Janus-shaped particles, being partially oxidic and partially metallic, has been reported.²⁸

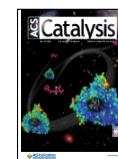
The advances in experimental methods, including operando investigations, have allowed detailed insights into the structure of PtPd catalysts under working conditions.^{28,33,34} While these investigations generate averaged information about the local environment of Pt and Pd atoms, theoretical investigations face the opposite challenge. Individual DFT calculations can only be performed for specific arrangements of Pd and Pt atoms in an alloyed surface.

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Such a calculation thus gives detailed results for this structure but provides only limited information about the average state and reactivity of the surfaces of a nanoparticle. Exhaustive sampling over all relevant structures of the alloys to compute ensemble averages can be performed with Monte Carlo simulations. Additional techniques to obtain ensemble averages are grand and semigrand canonical basin-hopping³⁵ and grand canonical genetic algorithms.³⁶ Monte Carlo simulations require a vast number of energy evaluations, which is generally elusive with DFT and instead requires a more efficient method to compute energies. As a result, different models have been used, involving simple analytical potentials, such as the modified embedded atom method (MEAM),³⁷ the Gupta potential,³⁸ and the Sutton-Chen potential.³⁹

A flexible approach that can be fit to the results of DFT calculations uses cluster expansion models.^{40–44} Cluster expansion models are based on the positions of the atoms within a crystalline structure, such as fcc. Here, local descriptors are used that describe the environment of an atom. Pairs and triples, quadruples, and so on of atoms, including the central atom, can be used to generate a systematically increasing and more complete description of the environment of said atom. Cluster expansion models have been used successfully to study bulk properties but also surface segregation, including the effects of adsorbates.^{45,46}

Machine learning (ML) approaches have gained popularity in recent years, also for the investigation of alloys. The most common approach to train and use ML models based on DFT calculations is to directly employ the atomic structure.^{47–57} An ML model trained in this way will thus be able to predict energies as a function of the atomic coordinates, as well as the derivatives of the energies, for example, forces. To do this, the Cartesian coordinates are usually converted into a representation, also called features or descriptors. This is because Cartesian coordinates are not well-suited as features since they are not rotationally or translationally invariant. Several features have been developed, and the most commonly used variants are similar to the Smooth Overlap of Atomic Positions (SOAP) descriptor.⁵¹ It is, of course, also possible to use ML with features that do not explicitly contain the atomic positions but only relate to the position in an idealized crystal, such as with cluster expansion models or only using coordination numbers.⁵⁸ Aside from the choice of representation of the atomic structure, mainly two types of ML models are used: Neural networks and Gaussian Process Regression (GPR). Neural networks have the advantage of being more flexible. The main advantage of GPR is its numerical simplicity; in particular, the training is simple. ML models have been used in a number of instances to study surface segregation of alloys.⁵⁹ Based on a machine-learned force field, vibrations can be computed, and this as well as other approaches have been explored to predict IR spectra using ML.^{57,60–63}

Bulk PtPd alloy formation is slightly exothermic (weaker than -0.05 eV/atom) with the most favorable composition predicted by DFT calculation at 50:50 composition as the $L1_1$ structure.⁶⁴ Surface segregation studies using Monte Carlo simulations and MEAM potentials showed that Pd tends to segregate to the surface layers in PdPt alloys.^{65,66} This enrichment is driven by the lower surface energy of Pd compared to Pt.^{65,67} Stronger segregation effects, i.e., more Pd enrichment, are found for more open facets, such as (110) and (100), as compared to (111).^{65,66} A monotonous decay of the Pd concentration from the first layer to the bulk was predicted at 1200 K,⁶⁵ while oscillations were found in a different study at 800 K.⁶⁶ Increased Pd concentration in the surface was also observed in Monte Carlo simulations with semiempirical potentials for large cuboctahedral and icosahedral particles.⁶⁸

Although DFT investigations of the PtPd surface are necessarily less detailed, they generally confirm the results obtained with semiempirical potentials quoted above. In ref 69, DFT was used to determine the optimal position of a single Pt layer in an otherwise pure Pd(111) surface. It was found that substitution into the surface layer is least favorable, also in the presence of oxygen coverages up to 0.75 monolayers.

Adsorbates affect surface segregation as they change the stability of the clean surface. The effect of adsorbates on surface segregation has been studied in a number of cases with DFT: For oxygen on AgPd(111),⁷⁰ oxygen on RuPt(111),⁴⁵ and acrolein on AgPd(111).⁷¹ There are a number of studies for CO-adsorption on PtAg(111) and PdAg(111) surfaces, where CO preferentially binds to either Pd or Pt.^{24,72–75} H₂-induced surface segregation on PdAu(111) and PdCu(111) has been studied with Monte Carlo simulations, where H₂ was found to promote segregation of Pd to the surface due to the more favorable binding energies.⁷⁶

In addition to determining the stability of structures and eventually the equilibrium state, an additional question is how fast the equilibrium is reached based on the initial state. This question is difficult to address both experimentally and theoretically. In experiments, it is difficult to investigate whether or not the observed state is thermodynamically stable or just metastable. Determining kinetics for rearrangements of surfaces and particles theoretically is generally complicated and becomes more complicated with the complexity of the system when adsorbates are involved or alloys instead of monometallic systems. Insights can be gained from DFT investigations of the mechanism for reconstruction of specific systems, for example, surface segregation of PdPt through vacancy migration.^{77–79} The full complexity of rearrangements of surfaces and particles can be addressed using kinetic Monte Carlo (kMC) simulations,⁸⁰ which require parametrization of models for large systems using either lattice-based approaches or ML.^{14,81–85}

The precise properties of alloyed nanoparticles depend on their morphology, specific composition, number of atoms, particle/support interface, and likely also their history, i.e., how they were prepared. All of these aspects are, of course, important in determining catalytic reactivity, but they make it difficult to study fundamental aspects of chemical reactivity. Low-index facets, mainly 111 and 100, have for decades been used as well-defined systems to study the behavior of transition metals under more controlled and reproducible conditions. In particular, CO-adsorption has been the focus of many studies on the common 111 and 100 surfaces, not only of Pd and Pt.^{86–94} Although experimental and computational methods have advanced and allow us to study more complex systems, we believe that studying low-index facets, such as PtPd(111), is important. Keeping the structural motif simple allows us to focus more on other aspects, such as alloy composition, adsorbate binding sites, and adsorbate properties, and to do that with high precision.

CO-adsorption is of central importance in catalysis for two reasons. First, CO is widely used as a probe molecule to characterize catalysts. Besides determining surface area, the stretch vibration of CO is also used to identify active sites, also in situ and operando experiments.⁶ Second, CO plays a central role in many industrial processes. One large application is exhaust after gas treatment catalysts, where CO is an intermediate in the combustion of hydrocarbons.^{95,96} Another field of catalysis is the transformation of syngas ($H_2 + CO$), for example, the generation of syngas with steam reforming and dry reforming.⁹⁷ Syngas is used for methanol synthesis⁹⁷ and for the formation of hydrocarbons in Fischer-Tropsch synthesis.^{98,99} In these catalytic

processes, the CO-adsorption energy is a central quantity, which not only determines the extent of surface coverages. Through the application of scaling relations,¹⁰⁰ or the related Bell-Evans-Polanyi (BEP) relations,^{101,102} the barrier of rate-limiting steps can be related to the CO-adsorption energy. Eventually, catalytic activity can thus be predicted with CO-adsorption as one of the descriptors in so-called volcano plots to improve catalysts.^{103–106} Scaling relations involving CO-adsorption on transition metal surfaces as a descriptor were employed for CO-oxidation,¹⁰⁷ for methanol synthesis.¹⁰⁸ In many examples that involve splitting the C–O bond, the adsorption energies of carbon and oxygen are used instead, for example, for methanation,¹⁰⁹ synthesis of higher alcohols,¹¹⁰ and Fischer-Tropsch.¹¹¹

In this work, we study the composition of PdPt(111) alloyed surfaces under the influence of CO-adsorbates. We first describe the DFT-computed data that we use for training and validation. Next, the representation used in our ML model, as well as the model itself, is explained. Finally, we discuss the Monte Carlo simulations and the results that we obtain for surface segregation with and without CO, as well as the results obtained for vibrational frequencies and binding energies.

COMPUTATIONAL DETAILS OF DFT CALCULATIONS

All DFT calculations were performed with VASP in version 5.4.1^{112,113} and the ASE¹¹⁴ using the BEEF–vdW functional^{115,116} and the PAW method.^{117,118} The lattice constants of Pd/Pt alloys were optimized using an energy cutoff of 600 eV, while slab calculations were performed with a cutoff of 400 eV and a Γ -centered k-point grid with a $6 \times 6 \times 1$ mesh for a (2×2) surface unit cell. All the slabs are separated by 28 Å of vacuum to eliminate artificial interactions due to periodic boundary conditions. The expansion of the density includes reciprocal lattice vectors with a norm up to $3/2$ times larger than for the wave function, $|G_{\text{cut}}|$ (PREC = Normal in VASP). The calculations were performed with real-space projectors (LREAL = AUTO), and the self-consistent field (SCF) procedure was converged to a threshold of 10^{-8} eV for the total energy. A 0.01 eV/Å criterion for the maximum forces on individual atoms was used for geometry convergence. Gaussian smearing with a 0.1 eV width was applied.

The slab used the lattice constant of the L_{10} 50%Pd alloy, $a = b = 3.972$ Å, $c = 3.994$ Å. The vibrational frequencies of adsorbed CO were calculated within the harmonic approximation based on a partial numerical Hessian including only carbon and oxygen as free atoms. The numerical differentiation was performed using central finite differences with four displacements per Cartesian degree of freedom ($n_{\text{free}} = 4$) and a displacement of 0.02 Å.

RESULTS AND DISCUSSION

Model to Simulate Surface Segregation

Data Set. The training set for surface formation energies contains 650 $(4 \times 4 \times 9)$ slabs and 500 $(2 \times 2 \times 4)$ slabs, see Figure 1d. These were generated to consist of some important structures, like pure Pt, pure Pd, and pure Pd or Pt top layers. The remaining structures were generated first of all with a random composition and then with random atom ordering to obtain a training set covering all possible configurations as well as possible. The trained quantity for clean surfaces is the formation energy of the slabs,

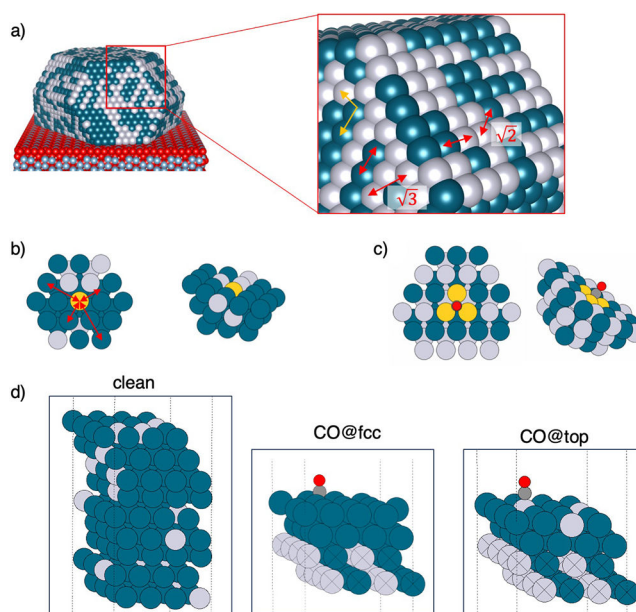


Figure 1. (a) Illustration of nanoparticle surface and pairwise descriptors. (b) Cluster for a surface atom for surface stability and on-top adsorption. (c) Cluster for the fcc site. (d) Slab models used for DFT calculations.

relative to the bulk energies of Pd(fcc) and Pt(fcc), which are -1.949 and -3.129 eV per atom. For CO adsorption energies and vibrational frequencies at the fcc-site, the training set contains 497 $(4 \times 4 \times 4)$ slabs, with the bottom two layers frozen, see Figure 1. In this data set, only one CO molecule per unit cell ($\theta[\text{CO}] = 1/16$) was adsorbed at the fcc-site. The dataset for adsorbate-adsorbate interaction included is based on 256 $(2 \times 2 \times 4)$ slabs, which are then repeated 2×2 times. This allows us to assess the binding energy of $\theta[\text{CO}] = 1/16$ vs $\theta[\text{CO}] = 1/4$ in the same local alloy composition, thus singling out the adsorbate-adsorbate interaction unambiguously. For binding on top of a Pt atom, 200 structures with $\theta[\text{CO}] = 1/16$ were employed, i.e., higher coverage was not considered.

Representation of Atomic Structures with Local Descriptors. We chose a local representation of the atomic structure similar to a cluster expansion model. We use clusters up to three atoms (triples). The different types of pairs and triples are classified by the distance that they have in an ideal crystal, based on the nearest-neighbor distance d ($d \approx 2.818$ Å in our DFT data set). We thus consider pairs separated by d , $\sqrt{2}d$, $\sqrt{3}d$, and $2d$, see Figure 1a,b. For triples (atom 1–atom 2–atom 3), we consider only those where the central atom is a nearest-neighbor of the terminal atoms, i.e., $d_{1-2} = d$ and $d_{2-3} = d$. There are then several types of triples that differ by the distance between the terminal atoms: d (triangle), $\sqrt{2}d$, $\sqrt{3}d$, and $2d$.

Based on the pairs and triples, the representation of an atom contains the following data:

1. Its identity (Pd or Pt)
2. The number of pairs or triples of each type, irrespective of the identity of the involved atoms (Pd, Pt). This number is normalized by its maximum possible value, which is achieved in the bulk, so that the normalized descriptor varies between 0 and 1. For example, the number of nearest-neighbors is divided by 12.

3. The composition of pairs also varies between 0 and 1. The composition is described by the fraction of heteroatoms around the reference atom, i.e. fraction of Pd atoms in descriptor for a central Pt atom and fraction of Pt atoms in descriptor for a central Pd atom.
4. For triples, six compositions are possible (Pd–Pd–Pd, Pd–Pd–Pt, etc.) and four for a triangle, where some of these are equivalent. The composition of the triples is given in terms of the fraction of a certain elemental composition (for example Pd–Pd–Pd) of all triples of that type

For pairs, there are thus eight descriptors per atom, the four pairs (d , $\sqrt{2}d$, $\sqrt{3}d$, and $2d$) and the corresponding four compositions. For triples, there are four descriptors for the triples (d , $\sqrt{2}d$, $\sqrt{3}d$, and $2d$ distance between the terminal atoms) and four or six descriptors for their composition.

To describe the fcc site (consisting of the three surface atoms of this site), the pairs and triples of the three atoms are combined, discarding the duplicates that would result from just adding up the atomic descriptors, see Figure 1c. For adsorption on top of a Pt atom, the atomic descriptors of that atom were used, see Figure 1b. The descriptors are determined not based on the crystal lattice positions, but actually simply according to the distances of the idealized fcc crystal. For DFT data used for training, surface relaxation, of course, leads to deviations from that. To obtain the ideal fcc-crystal lattice distances with sufficient accuracy, structures are simply re-optimized with a short-range Lennard-Jones potential that has the minimum where desired and excludes interactions beyond the nearest neighbor ones.

Modeling Stability and CO-Vibration with GPR. We use GPR with a 'squared exponential' (Gaussian) kernel:

$$k(\mathbf{x}_i, \mathbf{x}_j) = \exp\left(-\frac{1}{2} \sum_{d=1}^D \theta_d^2 (\mathbf{x}_i^d - \mathbf{x}_j^d)^2\right) \quad (1)$$

Here, θ_d are the hyperparameters and $\mathbf{x}_i^d$ are the values of the features for each dimension d . For formation energies, we found that it is sufficient - and much more efficient - to include only pairs. Here, we used $\theta_d = 0.5$ for all pairs and all pair compositions. For CO-adsorption on both the fcc and on-top sites, $\theta_d = 0.04$ is used for the descriptor that gives the number of Pd or Pt atoms (out of three). For all descriptors for CO-adsorption on fcc sites, $\theta_d = 3 \times 10^{-6}$ is used. CO-vibration uses the same descriptors as CO-adsorption, but for fcc sites with $\theta_d = 1$ for the number of Pd or Pt atoms and $\theta_d = 10^{-3}$ for all other descriptors. For on-top sites, we used $\theta_d = 0.83$ for the number of Pd or Pt atoms and $\theta_d = 10^{-3}$ for all other descriptors.

To describe formation energies of surfaces, we use the common approach of atomic references.⁵⁶ In this approach, the kernel function that compares systems A and B is written as a sum over atomic kernels that include the descriptors for each atom:

$$K(A, B) = \sum_{t \in \tau} \sum_{\mathbf{x} \in A_t} \sum_{\mathbf{y} \in B_t} k_{\text{atomic}}(\mathbf{x}, \mathbf{y}) \quad (2)$$

where τ is the set of atomic types (here Pd or Pt) and A_t or B_t represents the set of descriptor vectors of type t for structure A or B .

Due to the high dimensionality and large number of local descriptors per structure, directly computing a full kernel matrix across all descriptors is computationally expensive. To address this, a sparse GPR framework is employed. In this framework, a subset

of representative descriptors (inducing points) is selected using a custom reduction function. This function reduces the total number of descriptor sets (for example, to 50) by computing a kernel matrix among the descriptors and then selecting a subset that minimizes redundancy (i.e., off-diagonal elements in the kernel matrix).

To ensure scale invariance, the off-diagonal elements are normalized by the geometric mean of the corresponding diagonal elements, so that the normalized similarity between descriptors i and j is given by:

$$\tilde{k}(\mathbf{x}_i, \mathbf{x}_j) = \frac{k(\mathbf{x}_i, \mathbf{x}_j)}{\sqrt{k(\mathbf{x}_i, \mathbf{x}_i)k(\mathbf{x}_j, \mathbf{x}_j)}} \quad (3)$$

Once the inducing points are determined, two key kernel matrices K_{mm} and K_{mn} are constructed. K_{mm} is the kernel matrix among the inducing points, which describes their mutual similarities. K_{mn} is the kernel matrix between the inducing points and the training structures.

The training process then proceeds by solving a regularized linear equation system. Under the assumption of Gaussian noise with variance σ^2 , the weights $\mathbf{w}$ associated with the inducing points are computed by solving:

$$\mathbf{w} = (K_{mm} + K_{mn} \sigma^{-2} K_{nm})^{-1} (K_{mn} \sigma^{-2} \mathbf{y}) \quad (4)$$

where $\mathbf{y}$ is the vector of training target values (after subtracting the training mean). This equation effectively combines the information from the inducing point kernel with the training data, thereby enabling a low-dimensional representation of the full Gaussian process model. We use $\sigma^2 = 10^{-5}$ for formation energies and $\sigma^2 = 10^{-6}$ for adsorption energies and vibrations.

Once the model has been trained, predictions for new structures are made by first computing the kernel vector between the new structure and each of the inducing points:

$$\mathbf{k}_* = \begin{bmatrix} k(\mathbf{x}_*, \mathbf{z}_1) \\ k(\mathbf{x}_*, \mathbf{z}_2) \\ \vdots \\ k(\mathbf{x}_*, \mathbf{z}_m) \end{bmatrix} \quad (5)$$

where $\mathbf{x}_*$ represents the descriptor of the test structure and $\mathbf{z}_i$ that of the inducing points. The final prediction is then obtained by a linear combination of these kernel values weighted by the previously determined weight vector, with the training mean added back to restore the original scale:

$$\hat{y}_* = \mathbf{k}_*^T \mathbf{w} + y_{\text{mean}} \quad (6)$$

Finally, predictions for the test set are made using the trained GPR model, and the performance is evaluated by comparing predicted values with actual target values, visualized through plots of mean absolute errors (MAEs, shown in Figure 2). The model is shown to be very accurate, giving formation energies of clean ($4 \times 4 \times 9$)-slabs with a mean-absolute error of 0.025 eV (per entire slab, not per atom). MAEs for adsorption at the fcc site are in the meV range, and the MAE for predicted frequencies is below 1 cm^{-1} . The cross-validation results are shown in the SI. For binding at the top site, the corresponding plots are shown in Figure S3. Here, we observe larger errors for binding energies (MAE = 0.01 eV), but similar performance for frequencies.

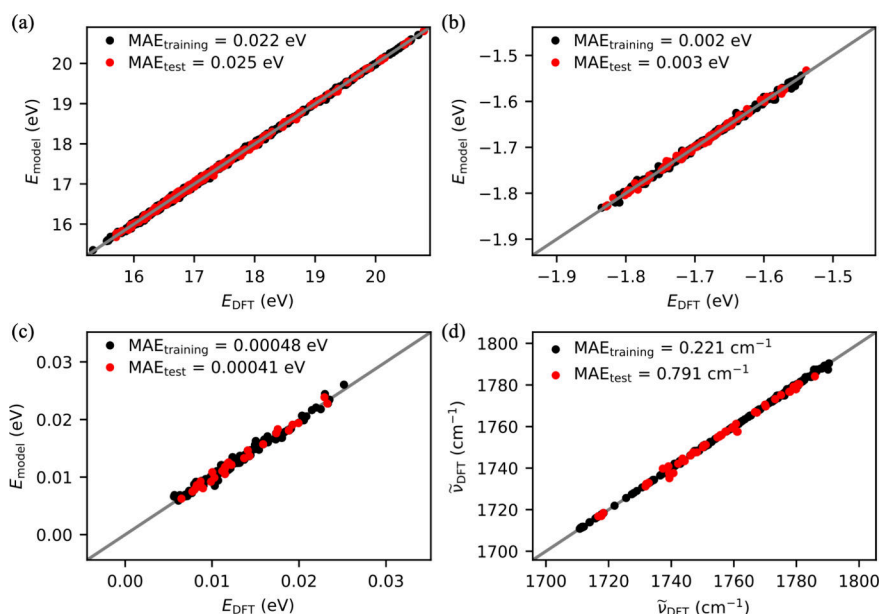


Figure 2. Performance of the models in 5-fold cross-validation, with training data shown in black and test data in red. Only the adsorption at the fcc site is included in the dataset. (a) GPR model for the formation energy of the clean slab. (b) GPR model for the CO-adsorption energy at $\theta[\text{CO}] = 1/16$. (c) Linear model for adsorbate-adsorbate interaction per CO and next-nearest neighbor derived from the difference between $\theta[\text{CO}] = 1/16$ and $\theta[\text{CO}] = 1/4$. (d) GPR model for the vibrational frequency of CO at $\theta[\text{CO}] = 1/16$.

Adsorbate-Adsorbate Interaction. To compute the final formation energy, including CO-adsorption at the fcc-site, we use a multicomponent energy model:

$$E = E_{\text{clean}}(\mathbf{X}^{\text{atoms}}) + \sum_i^{n_{\text{CO}}} E_{\text{ads}}^{\theta=1/16}(\mathbf{X}_i^{\text{site}}) + \sum_i^{n_{\text{CO}}} E_{\text{rep}}^i(\mathbf{X}_{\text{all}}^{\text{site}}) \quad (7)$$

Here, $E_{\text{clean}}(\mathbf{X}^{\text{atoms}})$ is the energy of the clean alloy slab without any adsorbates. $E_{\text{ads}}^{\theta=1/16}(\mathbf{X}_i^{\text{site}})$ is the adsorption energy of a single CO molecule at a specific site i when the coverage is low ($\theta[\text{CO}] = 1/16$), where $\mathbf{X}_i^{\text{site}}$ represents the set of descriptors for site i .

Adsorbate-adsorbate interaction at the fcc-site per adsorbed CO molecules is described by the term $E_{\text{rep}}^i(\mathbf{X}_{\text{all}}^{\text{site}})$, which includes contributions from repulsive interactions between CO molecules. We have limited our investigation to maximum coverage of $\theta = 1/4$. Relative to the low-coverage adsorption at $\theta = 1/16$, we thus consider adsorbate-adsorbate interaction with a distance of $2d$, i.e., the next-nearest neighbors. As the adsorbate-adsorbate interaction is relatively small, we found it sufficient to employ linear models:

$$E_{\text{rep}}^i = \sum_j^{d(ij)=2} \mathbf{C}^T (\mathbf{X}_i^{\text{site}} + \mathbf{X}_j^{\text{site}}) \quad (8)$$

where $\mathbf{C}$ are the coefficients from the least-squared fit. For the fitting of the adsorbate-adsorbate interactions, we use the $(2 \times 2 \times 4)$ slabs with one CO per unit cell, which give adsorption energies at $\theta = 1/4$. Repeating these cells to $(4 \times 4 \times 4)$ and again using one CO per unit cell, gives as the adsorption energy at $\theta = 1/16$ and thus the adsorbate-adsorbate interaction for next-nearest neighbors. As shown in Figure 2, the fit is good with an MAE of about 0.5 meV, while the adsorbate-adsorbate interac-

tion per next-nearest neighbor is mostly between 0.01 and 0.02 eV. In the case of $\theta = 1/4$, there are six next nearest neighbors, and the repulsive interaction per CO, i.e., the difference in adsorption energy relative to $\theta = 1/16$, is thus between 0.06 and 0.12 eV. Adsorption at the on-top site was treated analogously, using the same correction model for adsorbate-adsorbate interaction.

Monte Carlo Simulations. We performed Monte Carlo simulations utilizing the Metropolis algorithm to investigate the adsorption behavior of CO on a Pd/Pt alloy surface. The simulation was conducted on a $4 \times 4 \times 9$ Pd/Pt alloy slab, where the bottom two layers were fixed to represent the bulk material, leaving 112 unfrozen atoms on the surface that could participate in dynamic processes. Additionally, four potential adsorption sites for CO molecules were considered on the surface. For the simulation of the adsorption of CO at the on-top site, the identity of the four corresponding Pt atoms was kept fixed throughout the simulation. Comparison with simulations on a $8 \times 8 \times 9$ supercell show that the $4 \times 4 \times 9$ cell is sufficiently large (see Figure S7b).

The simulation encompassed three primary types of stochastic processes:

1. Atom type exchange with flexible composition: A randomly selected unfrozen atom on the surface changes its elemental type from Pd to Pt or vice versa. This process allows the overall composition of the alloy to vary during the simulation, enabling the exploration of different alloy compositions.
2. Atom swap with fixed composition: Two randomly selected unfrozen atoms swap their elemental types (Pd and Pt). This process keeps the overall composition constant but allows for different atomic arrangements and distributions of Pd and Pt atoms on the surface.
3. Adsorption/desorption of CO molecules: A CO molecule is either adsorbed onto or desorbed from a randomly selected adsorption site among the four available on the surface. The simulation considered CO coverages (θ_{CO}) ranging from $\frac{1}{16}$

to $\frac{1}{4}$, corresponding to one to four CO molecules adsorbed on the surface.

If only atom swaps according to process type 2 are considered, then the Monte Carlo simulation is performed in the canonical ensemble. If additionally the number of CO molecules or Pt and Pd atoms can change, then a semi-grand canonical Monte Carlo (SGCMC) simulation is performed.⁷¹ In contrast to a grand canonical Monte Carlo simulation, this has the limitation that the total number of metal atoms remains constant, such that the slabs do not grow or shrink. One of the aforementioned processes was randomly selected at each simulation iteration based on a uniform probability distribution. The Gibbs free energies required for the Monte Carlo simulations are approximated by energies predicted by the ML model ($\Delta G \approx \Delta E$), with an additional correction for the free energy of CO in the gas phase. We will therefore explicitly refer to energies ΔE below, although in general, Gibbs free energies are the appropriate quantity. For the adsorption event, the energy change ΔE associated with adding a CO molecule to an unoccupied site was calculated. For the desorption event, the energy change ΔE associated with removing a CO molecule from an occupied site was calculated similarly.

For an atom exchange with a flexible composition, a single unfrozen atom was randomly selected, and its elemental type was changed from Pd to Pt or vice versa. For an atom swap with a fixed composition, two unfrozen atoms were randomly selected, and their elemental types were swapped. The formation energy E_{form} of the new alloy configuration was calculated. The adsorption energies E_{ads} for any occupied adsorption sites were recalculated, considering the new local atomic environment. The total energy change ΔE was computed as:

$$\Delta E = (E_{\text{form}}^{\text{new}} + \sum E_{\text{ads}}^{\text{new}}) - (E_{\text{form}}^{\text{old}} + \sum E_{\text{ads}}^{\text{old}}) \quad (9)$$

The acceptance probability P_{accept} for the adsorption or desorption event was determined using the Metropolis criterion:

$$P_{\text{accept}} = \min\left(1, \exp\left(-\frac{\Delta E - \mu_{\text{CO}}}{k_{\text{B}}T}\right)\right) \quad (10)$$

where k_{B} is the Boltzmann constant. The chemical potential of CO (μ_{CO}) was calculated based on the temperature T and CO partial pressure p_{CO} , using standard thermodynamic relations, see Table S1. E_{form} is the formation energy of the alloy slab without any adsorbed CO molecules. $\sum E_{\text{ads}}$ is the sum of the adsorption energies of all CO molecules currently adsorbed on the surface.

To determine whether the step has been accepted, a random number r in the range (0, 1) was generated. If $r \leq P_{\text{accept}}$, the event was accepted, and the system state was updated accordingly. If $r > P_{\text{accept}}$, the event was rejected, and the system remained in its current state.

The acceptance probability P_{accept} for affecting the Pd/Pt atoms was equivalently calculated using the Metropolis criterion:

$$P_{\text{accept}} = \min\left(1, \exp\left(-\frac{\Delta E}{k_{\text{B}}T}\right)\right) \quad (11)$$

The chemical potential for Pd and Pt was chosen as their bulk chemical potential at 0 K. In practice, this is achieved by computing ΔE directly using the formation energies as predicted by the

ML model, which are referenced to fcc Pd and Pt. A simulated annealing process was employed to improve convergence by initially permitting extensive exploration and subsequently refining the search. This approach commenced with a high temperature (1500 K), which increases the likelihood of accepting a diverse range of solutions, including suboptimal ones, thereby allowing the system to avoid local minima. As the temperature decreases, the acceptance probability for less favorable solutions declines, concentrating the search on the most promising solutions. In our implementation, the initial 60% of the steps are allocated to the annealing phase, which is critical for preventing the system from becoming confined to local minima.

RESULTS OF THE MONTE CARLO SIMULATIONS

Surface Segregation of Surface in Vacuum and in CO Environment

The segregation behavior of a clean surface was simulated with a $4 \times 4 \times 9$ slab, starting with a stoichiometric surface of 50% Pt L1₀ crystal structure. The composition of the slab was allowed to vary freely. This type of simulation will be referred to as a variable composition simulation (SGCMC), as opposed to a fixed composition simulation (canonical Monte Carlo), where the number of Pt and Pd atoms remains fixed throughout the simulation. Figure 3a shows the average composition (%Pt) of each atom in the slab obtained after a Monte Carlo simulation using a color code. The results were obtained as an average over 20 Monte Carlo simulations of 200,000 steps each. At low temperatures, such as 100 K, the surface layer consists entirely of Pd. From the second layer onwards, the substructure will change from L1₀ to L1₁. Since the L1₁-order, where Pd and Pt alternate in different 111-planes, can be realized in different ways, this order is not very apparent in Figure 3a. Figure S3 shows the result of a single Monte Carlo trajectory, where the ordering at 100 K is more apparent. As the temperature increases, the amount of Pt on the surface increases gradually. The average composition of the first four layers as a function of temperature is also shown in Figure S5. It can be seen that the average composition of the third and fourth layers is close to 50%, irrespective of temperature. The first and second layers, however, show a clear deviation, and the first layer has an increased Pd content even at higher temperatures. Figure 3a furthermore shows that at temperatures of 300 K or higher, there is no ordering in the layers when looking at the averaged compositions.

To study the effect of CO, we have first introduced a single adsorbed CO-molecule per simulated slab, which stays adsorbed in a fixed position. This type of simulation will be referred to as a fixed-coverage simulation with $\theta = 1/16$. Temperature-dependent CO-adsorption and desorption will be discussed later. Introducing just a single CO allows us to study its isolated effect. Furthermore, a fixed coverage allows to differentiate between intrinsic temperature effects on the distribution of Pd and Pt and between the secondary effect of CO-desorption at high temperatures. Figure 3b shows that adsorption of CO into the highlighted position introduces some local ordering that persists even at 300 K.

The simulations with variable composition of the slabs are motivated by the limit of large nanoparticles, which will have a large reservoir of bulk-like atoms. In such a case, variation of the surface composition through surface segregation will not change the bulk-composition significantly. Therefore, surface segregation in the limit of infinitely large particles can be described as changing the surface composition at unchanged bulk composition.

As described in the method section, our model allows us to describe CO-adsorption at the fcc- or on-top-site up to a coverage of $\theta = 1/4$, where CO-adsorption in the $4 \times 4 \times 9$ slabs occurs in four designated sites. Figure 4a shows the simulated CO-coverage as a function of temperature for 1 mbar of partial pressure of CO. It can be seen that coverage goes from its maximum value of $1/4$ to zero within a temperature range of 600–800 K for 1 mbar. Effectively, all simulations below 600 K thus have a coverage of $\theta = 1/4$. Figure 4b shows the average composition of the first two layers in the presence of CO, in addition to the results for the clean surfaces. For the clean surface, the first layer composition converges towards 0%Pt as the temperature approaches 0 K. Even at 1000 K, there is still a decreased amount of Pt, 40% in the top layer. In the presence of CO, significant deviations are observed, which are also larger than those discussed above for a fixed coverage of $\theta = 1/16$ at the fcc site, because a coverage of $\theta = 1/4$ is reached at low temperature (see Figure 4a). The average composition of the surface layer remains more or less constant at 25% Pt until desorption starts to take place at around 600 K. The same applies to the composition of the adsorption sites itself, which remains in the range of 35% Pt at all coverages. This is because both the preferred fcc-site (Pd_2Pt) and the on-top Pt site lead ideally to four Pt atoms in the surface per 16 surface atoms in total, corresponding to the observed 25% Pt. The trend in the composition of the second layer differs significantly depending on CO-adsorption. For the clean surface, an increase in %Pt is observed, which counteracts the Pt-depletion, starting with 50% Pt initially at 100 K and then decreasing towards the limit of the clean slab, 40% Pt. Similar results are obtained when studying fixed overall slab compositions (Figure S6). For CO binding at the on-top site, the second layer shows a composition somewhat larger than 60% Pt initially, which

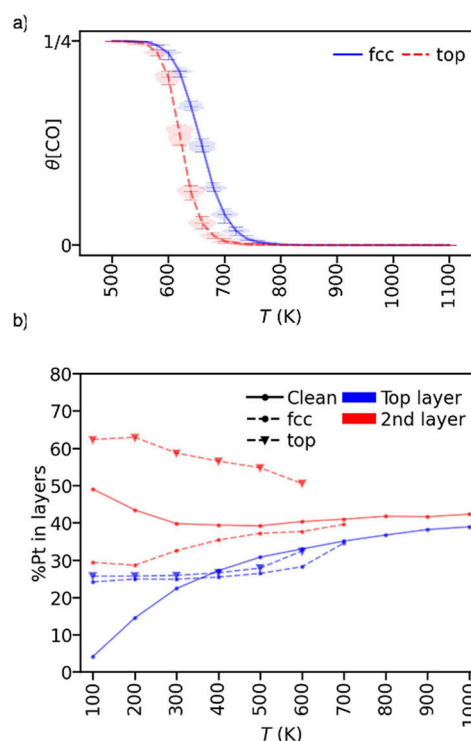


Figure 4. CO-adsorption on surfaces with variable composition (semi-grand canonical Monte Carlo). (a) Coverage obtained as a function of temperature and partial CO-pressure. (b) Average composition of first and second layers.

can be explained by the preference of having three Pt atoms below the Pt atom in the first layer that binds CO. With increasing temperature, the Pt-composition decreases. Figure 4 does not show the composition for the on-top simulations beyond the point of close-to full coverage (600 K), because the analysis would be ambiguous since the Pt-binding sites were fixed. For CO binding at the fcc-site, a Pt-depletion is observed, with around 30% initially at 100 K, then converging toward the limit of the clean slab with increasing temperature.

To get more insights into the interplay of the composition of the surface and active site composition and the effect of adsorption, we performed a series of simulations with a fixed overall composition of the slabs. This allows us to steer the average composition of the binding sites while also changing the composition of the remaining slabs. Figure 6a shows the binding energy of CO as a function of the slab composition. Binding at the fcc-site starts at around 1.7 eV, remains more or less constant, with a small maximum around 40% Pt, and drops sharply at around 80% Pt. This behavior can be explained by the composition of the fcc-site and the corresponding binding sites. Figure 5e shows how often the possible fcc sites, Pt_3 , Pd_1Pt_2 , Pd_2Pt_1 , and Pd_3 are observed as a function of overall composition. At Pt content $<20\%$, Pd_3 is the main site. In the intermediate range of 20–70% Pt, it is Pd_2Pt_1 , and for $>70\%$ Pt, it is Pd_1Pt_2 . Binding to Pt_3 is rather unfavorable, and this site becomes occupied only at overall compositions of $>80\%$ Pt. The adsorption energy maximum for the fcc-site is thus observed because Pd_2Pt_1 binds strongest, but it is only a small maximum in a mostly flat curve because the binding energies of Pd_3 , Pd_1Pt_2 , and Pd_2Pt_1 differ only by about 0.1 eV.

For the on-top site, a clear maximum of the binding energy is observed at around 80% Pt in Figure 5a. This can again be explained

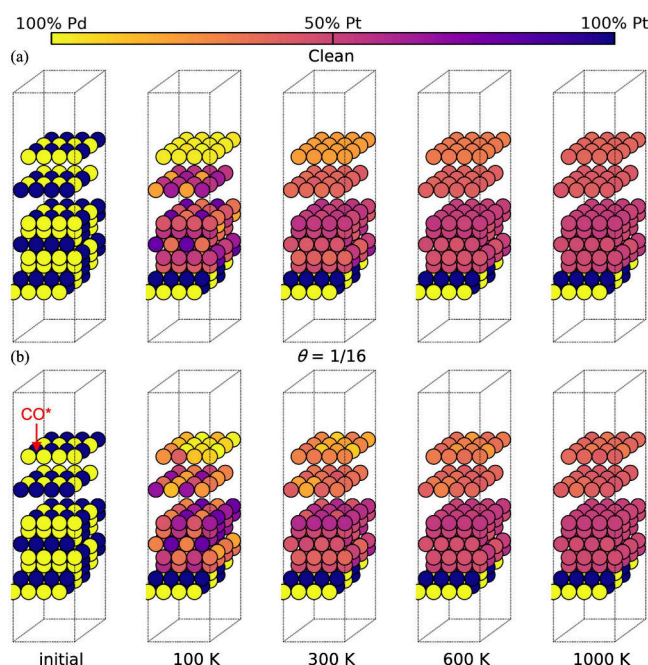


Figure 3. Surface segregation for (a) clean surfaces (b) $\theta[\text{CO}] = 1/16$. Variable composition simulation (semi-grand canonical Monte Carlo). The first two layers are lifted from the others for ease of display. The closer the atom is to yellow, the more likely it is to be Pd, and conversely, the closer it is to blue, the more likely it is to be Pt.

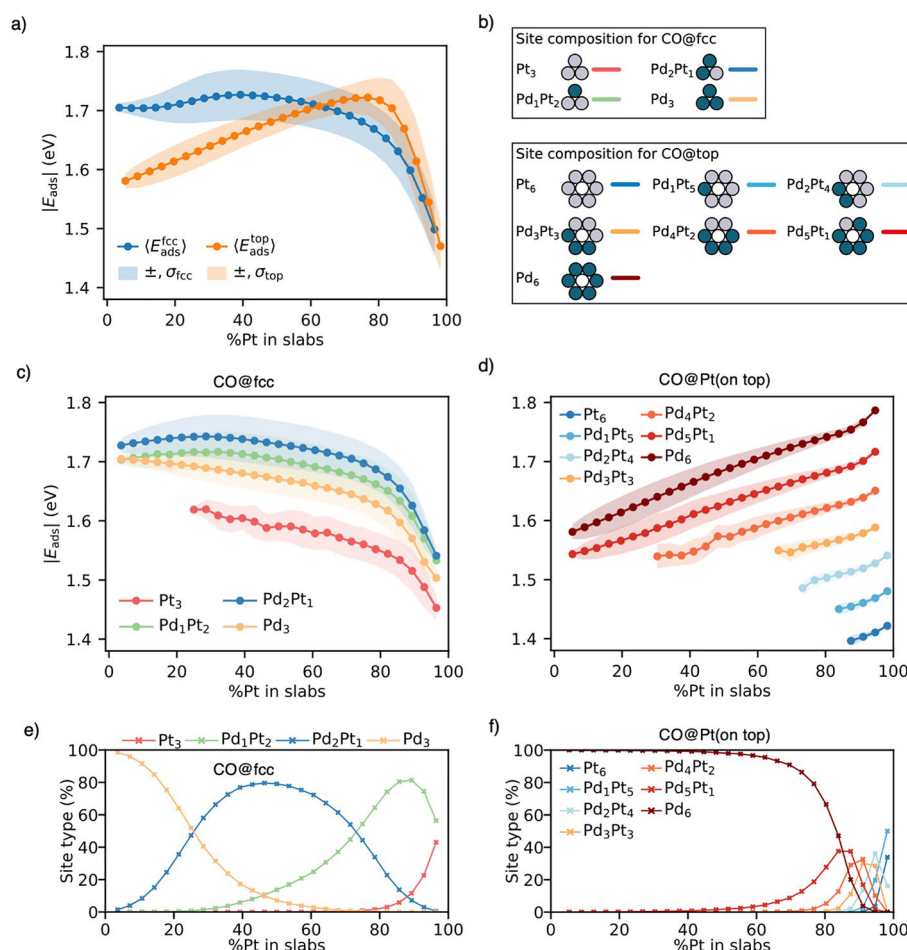


Figure 5. CO-adsorption as a function of the composition of the slabs. MC simulations at 300 K and 1 mbar CO with fixed composition of the slab. (a) For fcc and on-top, binding energies averaged over all sites are shown as a function of overall composition. (b) Illustration of the site composition. For the six atoms around the on-top site, only one configuration is shown in each case, but all were considered. (c) Average binding energy of fcc-site shown separately for different site compositions. (d) same as (c) for on-top. (e) Occurrence of different active site compositions for fcc. (f) same as (e) for on-top.

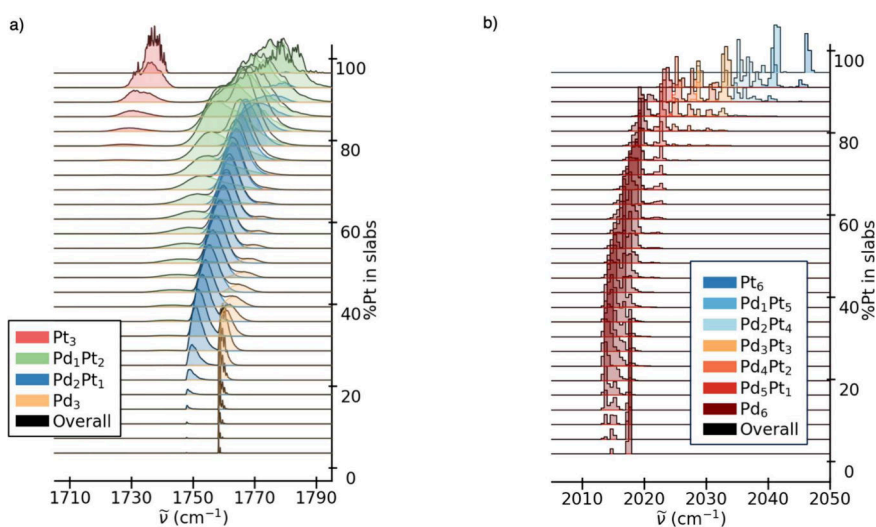


Figure 6. Vibrational spectrum of CO adsorbed at 300 K and 1 mbar partial pressure as a function of overall composition, split into the contribution by the different binding sites. (a) fcc (b) on-top. The spectra were computed as histograms of the individual frequencies predicted for bound CO-molecules, which depend only the site CO is bound to.

by the behavior of the binding site, which is mainly controlled by the six surface neighbors of the central Pt atom to which CO binds. Figure 5d shows that for all sites, binding generally gets stronger with increasing overall Pt-content. At the same time, the binding gets weaker with increasing Pt-content in those six neighbor atoms in the surface, see Figure 5b. The composition of the neighboring atoms remains dominated by Pd₆ up until 80% Pt in the slab, see Figure 5f. Only at higher Pt-fractions is the system forced to include also Pt in those neighboring atoms, leading to a sharp drop in CO-binding energies. In the limit of high Pt-concentration, the CO-binding energy converges to the limit of pure Pt(111), where the binding energy was reported previously at 1.39 eV using the BEEF-vdW functional.¹¹⁹ Finally, we note that the specific dependence on %Pt shown in Figure 5 is a function of the size of the slabs and is thus not transferrable when considering surfaces or particles of different sizes. However, we expect the trends to be transferrable, i.e., that there will be the competing effects of overall composition and binding site composition. We note in passing the issues of common density functionals with getting the correct adsorption energy for CO on top of Pt (CO-puzzle).^{120,121} BEEF-vdW is among the better functionals for this problem.¹¹⁹ For the PdPt(111), our calculations predict that both adsorption on-top of Pt as well as in the fcc position (with some Pd content) are competitive. This agrees with the experimental results, where both of these adsorption sites were observed.¹²²

Prediction of IR-Spectra

IR-spectra are simulated as histograms over the vibrational frequencies predicted with our model for all structures sampled during the MC simulation. The observed broad peaks are due to the distribution of the predicted frequencies and contain no other source, such as natural broadening or coverage-dependent coupling between neighboring adsorbed CO molecules. We focus here on simulations at 300 K. Simulations at higher temperatures lead to a broadening of the spectrum, which is simply due to the fact that more and more structures become accessible, which also differ in terms of the CO spectrum from the most stable structures (see Figure S7).

Figure 6 shows the CO-spectra predicted for binding on fcc and on-top sites as a function of composition based on the same simulations evaluated in Figure 5. For the fcc site, Figure 6a shows the spectra separated by the constituting binding sites. The predicted frequencies generally follow the order Pt₃ < Pd₁Pt₂ < Pd₂Pt₁ < Pd₃, i.e., the wave number decreases with Pt-content in the binding site. It can also be seen that the overall Pt-content has an opposite effect. For any given binding site, the corresponding peak shifts to higher wave numbers with increasing Pt-content. This is in line with our previous calculations, which were based only on a few structures.¹²² Experiments showed no monotonous trend for the CO-frequency with the overall composition, which can be explained by the competing effects of site- and overall composition.¹²² Figure 6b shows the CO-spectra predicted for the on-top Pt-site. In the range up to around 60% Pt that is dominated by Pd₆-surrounding the central Pt-atom, the spectrum does not shift significantly and is also rather narrow with a width of around 5 cm⁻¹. At higher Pt-compositions around the active site, a shift to higher wave numbers occurs, leading to a spectrum that is a superposition of different compositions and is also spread across a broader range of around 20 cm⁻¹. This is in agreement with previous experimental work that showed a shift of the frequency of on-top bound CO by about 20 cm⁻¹ with increasing Pt content.¹²² The

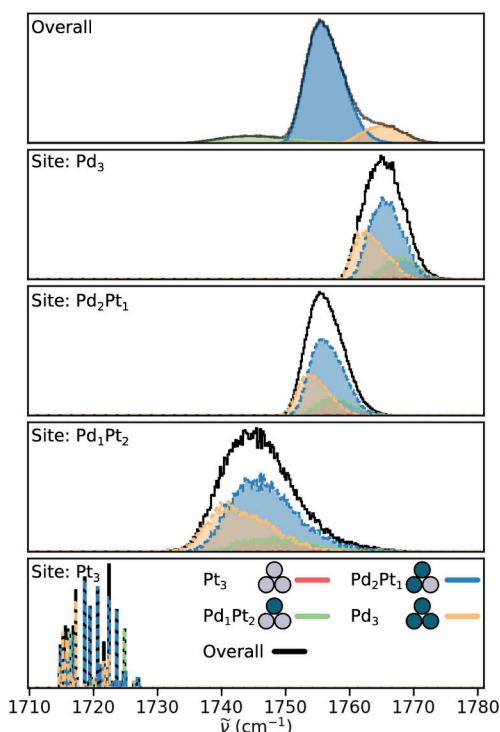


Figure 7. Effect of subsurface composition on the vibrational frequency distributions of CO adsorbed on various sites at 300 K and 1 mbar partial pressure of CO. Simulations were performed with a variable slab composition, which is on average 46% Pt, somewhat lower than the optimal bulk value (50%) due to the increased Pd-content in the surface. The top panel shows the overall distribution (black solid line) and the four contributions from the possible binding site compositions: Pd₁Pt₂ (blue), Pd₂Pt₁ (orange), Pd₃ (beige), and Pt₃ (green). Each colored curve is normalized so that their sum reconstructs the overall distribution. The lower four panels break down the contribution from each binding site into the contributions from different sub-site compositions (same color code).

shift with the composition observed experimentally occurs more gradually, while in Figure 6b, the frequency changes initially slower and then more rapidly with %Pt. Here, it is important to note that it is not clear how the experimental overall composition affects the composition of the surface and the binding site. A limitation of our simulations is the maximum coverage of $\theta = 1/4$ at an ordered structure, which allows all six surrounding surface atoms to be Pd. This is not possible at higher coverages or more random adsorption positions, which would favor an earlier transition to binding sites with a higher concentration of Pt on the surface.

In addition to steering the site-composition by changing and fixing the overall composition, we will now analyze the results for adsorption at the fcc site from a variable composition simulation in detail. Figure 7 shows the spectrum obtained for a simulation of a slab with variable composition at a partial pressure of 1 mbar and a temperature of 300 K. The average slab composition is 46% Pt, close to the expected 50% value for the bulk. The difference can be explained by the enrichment of Pd in the surface layer. The top panel of Figure 7 shows the overall spectrum with the main contributions from the sites Pd₁Pt₂, Pd₂Pt₁, and Pd₃ highlighted in color. In agreement with the trends found above, the peak positions shift to lower wave numbers with increasing Pt-content in the binding site. To analyze the influence of the subsurface, the peak corresponding to each site is furthermore decomposed

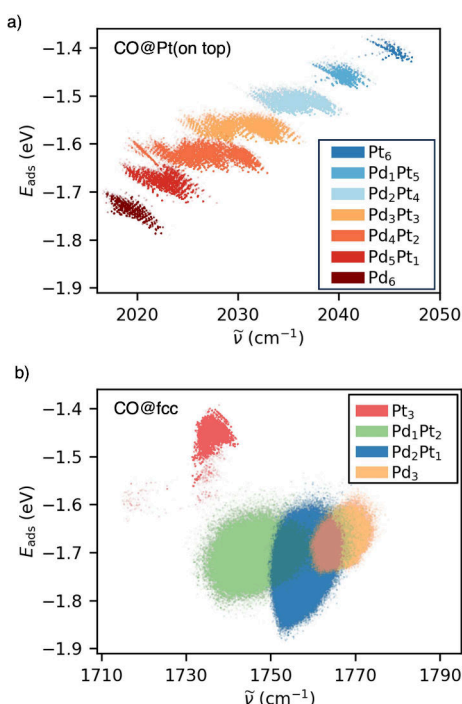


Figure 8. Correlation between binding energies and frequencies sampled during the Monte Carlo simulations in Figures 5 and 6. The data for each type of site analyzed was extracted at an overall composition where it occurs frequently: (a) All on-top sites were averaged over simulations at 83.9, 91.1, 94.6, and 98.2 Pt%. (b) fcc simulations at 96.4 Pt% were used for Pt_3 and at 46.4% for all other sites.

into the contributions from the three subsurface atoms below the active site. Again, we find the opposite trend here, that for a given fcc binding site, an increasing amount of Pt in the subsurface shifts the peak to lower frequencies. Binding to a Pt_3 -site is so rare in a variable-composition simulation that statistics are very poor and are displayed only in a bar-histogram with coarse resolution. Nevertheless, despite the poor sampling, the trends are also reproduced for Pt_3 , i.e., a peak at high wave numbers and the effect of the subsurface atoms to shift the peak to lower wave numbers with increasing Pt content.

Figure S8 shows the distribution of binding energies for the same simulation as discussed above for Figure 7 and using the same analysis. The trend in terms of binding energies and site-distribution is similar to that observed in Figure 5 for a simulation with fixed composition at around 50% Pt. From Figure S5, it is clear that Pd_2Pt_1 is the most frequently observed site because it typically leads to stronger binding. Pt_3 clearly binds the weakest and is therefore rarely observed. PdPt_2 binds second-strongest after Pd_2Pt_1 , followed by Pd_3 . When it comes to the effect of the subsurface atoms, Pd_3 leads to stronger binding, followed by Pd_2Pt_1 and PdPt_2 .

We will now investigate how vibrational frequencies on fcc and on-top sites are related to binding energies. Figure 8 shows data extracted from Monte Carlo simulations, where the adsorption energy is plotted as a function of the corresponding CO-frequency. For binding on top of the Pt-atom, there is a clear correlation between frequency and energy when comparing different compositions of the six surface atoms surrounding the central Pt atom. The trend follows the expected direction that stronger binding leads to red-shift (lower frequency), which can be explained by increased back-donation of electron density into the π^* -orbitals of

CO. However, for a given composition of the surface neighbors, the correlation between frequency and energy is opposite and can be attributed to changes in the subsurface. For fcc, no clear correlation between adsorption energy and the vibrational frequency of CO is observed. The fcc site constituted of Pt_3 is clearly an outlier because of its very weak binding. For fcc-sites, frequencies generally follow the order $\text{Pt}_3 < \text{Pd}_1\text{Pt}_2 < \text{Pd}_2\text{Pt}_1 < \text{Pd}_3$, while binding energies increase as: $\text{Pt}_3 < \text{Pd}_3 < \text{Pd}_1\text{Pt}_2 < \text{Pd}_2\text{Pt}_1$.

CONCLUSIONS AND OUTLOOK

In this work, Monte Carlo simulations were performed to sample the structure of alloyed $\text{PdPt}(111)$ surfaces. This allowed us to extract equilibrium properties of both clean and CO-covered surfaces. To be able to evaluate the required large number of energies for different alloyed surfaces, an ML model was trained using GPR, based on the position of the metal atoms in the fcc-lattice. Monte Carlo simulations were performed in a canonical ensemble, where the number of adsorbed CO and Pd/Pt atoms is fixed, and in a semi-grand canonical ensemble, where only the total number of metal atoms was fixed.

For clean surfaces with variable composition, bulk-like behavior was found for the third layer and below, which converges to a Pd:Pt ratio of about 50% in SGCMC simulations. The first and second layer tends to be enriched in Pd. In particular, the Pd-content of the first layer tends toward 100% when approaching 0 K. At elevated temperatures, this effect is diminished by configurational entropy, but the enrichment in Pd in the first layer remains significant, for example, with 69% Pd at 500 K.

For CO-adsorption, we performed separate simulations to study adsorption on the fcc-site and on top of Pt atoms. The fcc-site is the most favorable site for $\text{Pd}(111)$ and is also observed experimentally for $\text{PdPt}(111)$. Structures with a maximum CO-coverage of $\theta = 1/4$ were considered. For $\text{Pt}(111)$, binding on top of Pt is known to be the most favorable binding site for CO. The GPR models were found to reproduce both adsorption energies and vibrational frequencies of CO very well with MAEs < 0.01 eV and < 1 cm^{-1} . Using these models, the equilibrium composition of binding sites and the overall effect of CO on surface composition were evaluated. For the fcc-site, CO-adsorption is stronger on mixed adsorption sites, in particular Pd_2Pt_1 , and thus favors a surface layer that is at lower temperatures less enriched in Pd than the clean surfaces.

Vibrational spectra were simulated as histograms of the vibrational frequencies predicted for the sampled structures with adsorbed CO. In SGCMC simulations with variable PdPt -composition, the spectrum of CO adsorbed at the fcc-site is dominated by the Pd_2Pt_1 -site, with small contributions from Pd_3 and Pd_1Pt_2 , while the Pt_3 -site is too unfavorable to form. The predicted wave number for CO-vibration generally decreases with Pt-content in the fcc site in the order: $\text{Pt}_3 < \text{Pd}_1\text{Pt}_2 < \text{Pd}_2\text{Pt}_1 < \text{Pd}_3$. The effect of the composition of the three atoms below the fcc-sites is opposite: Here, the wave number for CO-vibration generally increases with Pt-content in the subsurface.

For CO binding in the on-top position on a Pt-atom, the binding energy is mainly dominated by the six surface atoms surrounding the binding site. Binding energies decrease with increasing Pt-content, and this correlates with an increasing wavenumber for the CO stretching vibration. The effect of subsurface atoms and the overall Pt-content is contrary to that of the nearby atoms, leading to stronger binding energies with higher Pt-content. This leads to competing effects of the composition of the binding site and the

overall composition. When changing the overall composition, we observe a clear maximum at the point where the overall Pt-content is high, but atoms surrounding the binding site are still mainly Pd.

We have thus demonstrated the prediction of a spectroscopic quantity over an ensemble of different alloy structures obtained with Monte Carlo simulations. This was made possible with an ML model that accurately reproduces the DFT computed energies for surface segregation, CO-adsorption, adsorbate-adsorbate interaction, and CO-vibrations. CO is not only used as a probe molecule for characterization using IR-spectroscopy. It is also an important reactant, intermediate, or product in many catalytic processes, ranging from exhaust after gas treatment to Fischer-Tropsch synthesis. The adsorption energy of CO is a central descriptor for the prediction of catalyst activity, and our investigation has shown how the binding energy is related to active site composition and stability. Challenges for future work include the effect of support, different facets, such as PdPt(100), different binding sites, bridge and hcp-sites, as well as high coverage structures with mixed site-occupancies. Furthermore, adsorbates can also induce structural changes through surface reconstruction and the formation of adatoms, islands, step edges, and transient active sites on the surface.^{14–17} An additional challenge is the prediction of the kinetics of alloy-rearrangement through diffusion and surface segregation.^{14,83,85}

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.6c01908>.

Total energies, vibrations and further analysis, and Cartesian coordinates uploaded to a repository¹²³ (PDF)

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Notes

The authors declare no competing financial interest.

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