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Original Article

Design of compositionally complex catalysts: Role of surface segregation



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ABSTRACT

Besides revealing excellent mechanical properties, compositionally complex alloys are also very promising candidates for applications in heterogeneous catalysis. The opportunity provided by the tremendously large composition phase space to explore new materials and tune the materials properties in the materials design cycle is, however, intrinsically coupled with the challenge of controlling surface segregation, which is generally more severe in multicomponent alloys as compared to simpler systems. We demonstrate this by computing the surface phase diagram of two candidate compositionally complex catalysts. Significant surface segregation is found even at very high temperature and this can strongly affect the catalytic properties of these alloys. We explain the observed phase stabilities in terms of segregation energies and rationalize the segregation trends with canonical models. Finally, we propose a set of descriptors accessible with first-principles calculations that allows to quickly incorporate the evaluation of the segregation during the alloy design process.

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1. Introduction

Materials for electrocatalysis are traditionally based on simple metals or bimetallic alloys. In contrast, compositionally complex alloys (CCAs, often termed high entropy alloys) [1–5] are complex metallic solid solutions with four, five, or more elements in concentrated compositions that, however, retain simple lattices (face-centered cubic, fcc, body-centered cubic, bcc, or close-packed hexagonal, hcp).

The principle that guides the design of materials for electrocatalysis is the optimization of the absorption energy

of the reactants and products on the surface of a catalyst (Sabatier principle or volcano plot principle) [6,7], i.e., the absorption energy must be high enough so that the reactants dissociate effectively at the surface, but low enough to let the products desorb.

Very recently, catalysts based on CCAs [8,9] were shown to outperform state-of-the-art metals for methanol oxidation [10–13], oxygen reduction [13–16], hydrogen evolution [13,17,18], ammonia splitting [19–21], oxygen evolution [16,22], and CO and CO₂ reduction [23] reactions. Possible explanations for this outstanding performance of CCAs are the

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possibility to better fine-tune the composition to obtain the optimal absorption energy, and the opportunity to perform this fine-tuning for more than one reaction step at once [8].

Despite the remarkable progress for this materials class, a potential issue that may impact the performance of CCA catalysts is surface segregation [24,25]. In contrast to simple metals, the composition of the surface of complex alloys can be rather different from the nominal composition of the bulk because some elements or element combinations may be thermodynamically favored or unfavored at the surface sites. Segregation may enhance or reduce the rate of certain reactions or reaction steps; having control of this phenomenon may turn out to be beneficial to boost some processes, but unwanted segregation shifting the surface composition away from a predetermined optimum could lead to a strong, detrimental decrease in the catalytic activity.

Although many new CCA catalysts were recently proposed [10–23], detailed analysis of surface segregation has often been lacking. The purpose of this work is to quantify the amount of surface segregation in typical noble-metal-based CCAs, to demonstrate that generally it is not negligible, and to present a robust strategy based on first principles calculations to evaluate segregation during the catalyst design process. To exemplify this, we calculate with Density Functional Theory (DFT) the surface phase diagrams of two candidate compositionally complex catalysts, namely Pt_{55.9}Ir_{22.6}Pd_{9.0}Ru_{8.9}Ag_{3.6} (Pt-rich alloy) and Ir_{47.0}Pt_{29.0}Ru_{12.9}Pd_{9.6}Ag_{1.5} (Ir-rich alloy) [26]. Similar compositions were recently studied in Refs. [15,27] in relation to the oxygen reduction reaction. We consider the possibility for oxygen to adsorb on the surface and we estimate the equilibrium coverage of the segregated and unsegregated surfaces as a function of temperature. We show that surface segregation is present at every temperature below melting. Indeed, strong Ru segregation at low temperature (when O can bind to the surface) and Ag segregation at high temperature up to the melting point (under vacuum conditions) are observed. We explain these observations by carefully analyzing the segregation energies of the constituent elements of the two CCAs derived from first principles. We also rationalize the segregation trends in terms of canonical models and suggest practical guidelines to incorporate surface segregation into the design process of multicomponent electrocatalysts.

2. Calculation details

2.1. Surface phase diagram

To calculate the surface phase diagram of the two CCAs, we considered a slab with N_s surface atoms arranged in a random configuration (unsegregated slab, with free energy $G_{\text{slab}}^{(\text{ran})}$), and a corresponding slab having the surface atoms transmuted into type i (i -segregated slab, with free energy $G_{\text{slab}}^{(i)}$). For the surface we chose the (111) orientation. We also contemplated the possibility for O to adsorb on the surface, which is likely a stable configuration at low temperature, by modeling $\frac{1}{3}$, $\frac{2}{3}$, and 1 monolayer (ML) of O adsorbed at the hollow fcc sites. The interaction among the adsorbed O atoms is taken into

account. To quantify the tendency towards segregation for an element i , we evaluated the free energy difference

$$G_{\text{segr}}^{(i)} = \frac{1}{N_s} \left[G_{\text{slab}}^{(i)} - G_{\text{slab}}^{(\text{ran})} - \sum_j (n_j^{(i)} - n_j^{(\text{ran})}) \mu_j - n_O \mu_O \right], \quad (1)$$

where $n_j^{(i)} = N_s \delta_{ij}$ and $n_j^{(\text{ran})}$ are the number of atoms of type j on the i -segregated slab and the unsegregated slab, respectively. The number of O atoms adsorbed on the surface (0 , $\frac{N_s}{3}$, $\frac{2N_s}{3}$, or N_s) is denoted as n_O , and μ_j is the chemical potential of the element j that balances the energy cost associated with the transmutation of the surface atoms or the addition of O. By rearranging the terms, it can be shown that only chemical potential differences $\Delta\mu_{ij} = \mu_i - \mu_j$ between the constituent elements contribute to the third term in Eq. (1), which we determined in the bulk as [24,28].

$$\Delta\mu_{ij} = \lim_{c \rightarrow 0} \frac{1}{c} [G_{\text{bulk}}(A_{1-c}i_c) - G_{\text{bulk}}(A_{1-c}j_c)], \quad (2)$$

where G_{bulk} is the free energy of an fcc bulk structure and A denotes the Pt- or Ir-rich alloy. In practice, a finite value of $c = \frac{1}{54} \approx 1.85\%$ was chosen for the present work. The free energies and chemical potentials in the solid phase were considered based on the first-principles derived total energies and the configurational entropy of a random alloy:

$$G = E - TS + pV \approx E + k_B T \sum_j c_j \ln c_j. \quad (3)$$

Note that other finite-temperature contributions due to vibrations and electronic excitations are typically negligible as they largely cancel out in Eq. (1).

For estimating μ_O in the gas phase we instead took into account the vibrational, nuclear, rotational, and translational degrees of freedom, as suggested in Ref. [29]. We fixed the oxygen partial pressure in the gas phase to 0.2 atm.

Based on this, the free energy difference in Eq. (1) can be rewritten with Eq. (3) to explicit the temperature dependence as

$$G_{\text{segr}}^{(i)}(T) = G_{\text{segr}}^{(i)}(0) - k_B T \ln c_i - \mu_O(T), \quad (4)$$

where the temperature dependence of the chemical potential of oxygen $\mu_O(T)$ can be fitted from the data provided in Ref. [29]. We assumed a parabolic dependence of $\mu_O(T)$ and parametrized

$$\mu_O(T) = k_1 T + k_2 T^2 + \frac{1}{2} k_B T \ln 0.2, \quad (5)$$

with $k_1 = -9.44 \cdot 10^{-4}$ eV/K and $k_2 = -1.81 \cdot 10^{-7}$ eV/K² and the last term the ideal gas contribution at a partial pressure of 0.2 atm.

For each surface population (segregated with each of the five elements or unsegregated), we estimated the surface coverage at each temperature by fitting the free energies for the four considered coverages with cubic splines and then taking the numerical minimum of the free energy. At higher temperature, μ_O becomes lower and lower and competes with the binding energy, eventually triggering the desorption of oxygen from the surface.

We computed also the segregation energies at the sub-surface layer by fixing the configuration of the surface to the thermodynamically most stable one and calculating free energy differences as in Eq. (1).

2.2. Computational setup

The DFT calculations were conducted with the plane-wave projector augmented wave (PAW) method [30,31] as implemented in VASP 5.4 [32–34] with the generalized gradient approximation (PBE) [35]. We employed the same setup as in Ref. [24]. We modeled fcc(111) surfaces with $3 \times 3 \times 9$ slabs with 20 Å of vacuum and used a k -mesh of $6 \times 6 \times 1$. To compute the chemical potentials we used $3 \times 3 \times 6$ supercells with a k -mesh of $6 \times 6 \times 4$. To estimate the statistical uncertainties on the segregation free energies, due to the finite size of the supercells, we took into account 5 different random slabs and 100 different random supercells for each composition and for each element to compute surface energies and chemical potentials, respectively. The equilibrium lattice parameters (3.932 Å and 3.899 Å for the Pt-rich and Ir-rich CCAs, respectively) were found by a Birch-Murnaghan fit [36,37] of energy-volume points. We arranged the adsorbed oxygen atoms for the partial coverages of $\frac{2}{3}$ and $\frac{1}{3}$ ML on a honeycomb pattern and its complementary, respectively, to minimize the lateral interactions between the oxygen atoms.

3. Results

3.1. Segregation at finite temperature

Fig. 1 presents the relative stability of the different surface configurations as a function of temperature for a) the Pt-rich alloy and b) the Ir-rich alloy. The free energy differences (solid lines) are calculated with respect to the random configuration of the surface. The equilibrium coverage for each configuration, resulting from the minimization of the free energy interpolated from the data at 0, $\frac{1}{3}$, $\frac{2}{3}$, and 1 ML, is also

reported in Fig. 1. In agreement with previous investigations [38], we find that elements with a low affinity to oxygen, especially Ag, tend to prefer low coverages at low temperature, while a whole ML is instead favored on the Ru-rich surface at low temperature. As expected, the behavior of the random surfaces is intermediate between these two scenarios.

The surface phase diagram of the two CCAs is very similar: in both cases, 1 ML O is absorbed at the surface at low temperature, promoting the segregation of Ru. At temperatures higher than roughly 1100 K and 750 K for the Pt-rich and Ir-rich CCAs, respectively, the segregation of Ag with little or no oxygen is instead preferred. Despite the low concentration of Ag, which tends to lower the chemical potential of this element at finite temperature and hence would hinder the segregation (see Eq. (4)), this element is favored at the surface sites even up to the melting point (here roughly estimated as a weighted average of the melting temperatures of the single elements). Segregation happens because the main driving force towards disorder, the configurational entropy $-k_B \sum_j c_j \ln c_j$, is not strong enough to contrast the large segregation energies of Ru (in the presence of O) and Ag (in vacuum). Consequently, the composition of the surface is predicted to be markedly different from that of the bulk. As already mentioned, due to the limited supercell size, we considered multiple random configurations of the surface and the bulk structures; from these, we obtained statistical errors which result in an uncertainty on the derived transition temperatures of about 150 K but do not qualitatively alter the observed tendencies.

To explain the observed segregation trends, we analyze in detail the segregation energies of the constituent elements of the two CCAs at 0 K in the next subsection.

3.2. Segregation energies

Fig. 2 shows the segregation energies of the constituent elements in the Pt-rich and Ir-rich CCAs in vacuum (Fig. 2a and c) and with 1 ML O absorbed on the surface (Fig. 2b and d). The upper panels refer to the segregation at the outermost layer (surface), the lower panels at the layer immediately below (subsurface).

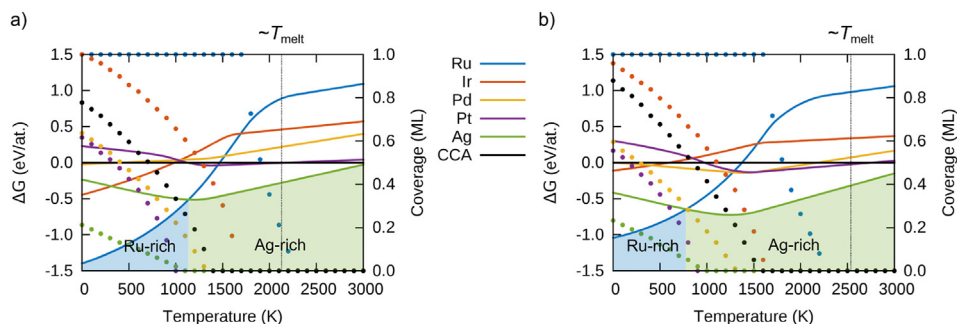


Fig. 1 – Free energy difference with respect to the random state (left scale, solid lines) and surface coverage (right scale, points) of the studied surface configurations as a function of temperature for a) the Pt-rich alloy and b) the Ir-rich alloy. Results are obtained by averaging 100 random bulk supercell configurations and 5 different slab configurations for each composition and for each segregating element. The reported coverages for each temperature are those that minimize the free energy at that temperature. The indicated melting temperature T_{melt} is estimated as a weighted average of the melting temperatures of the constituent elements.

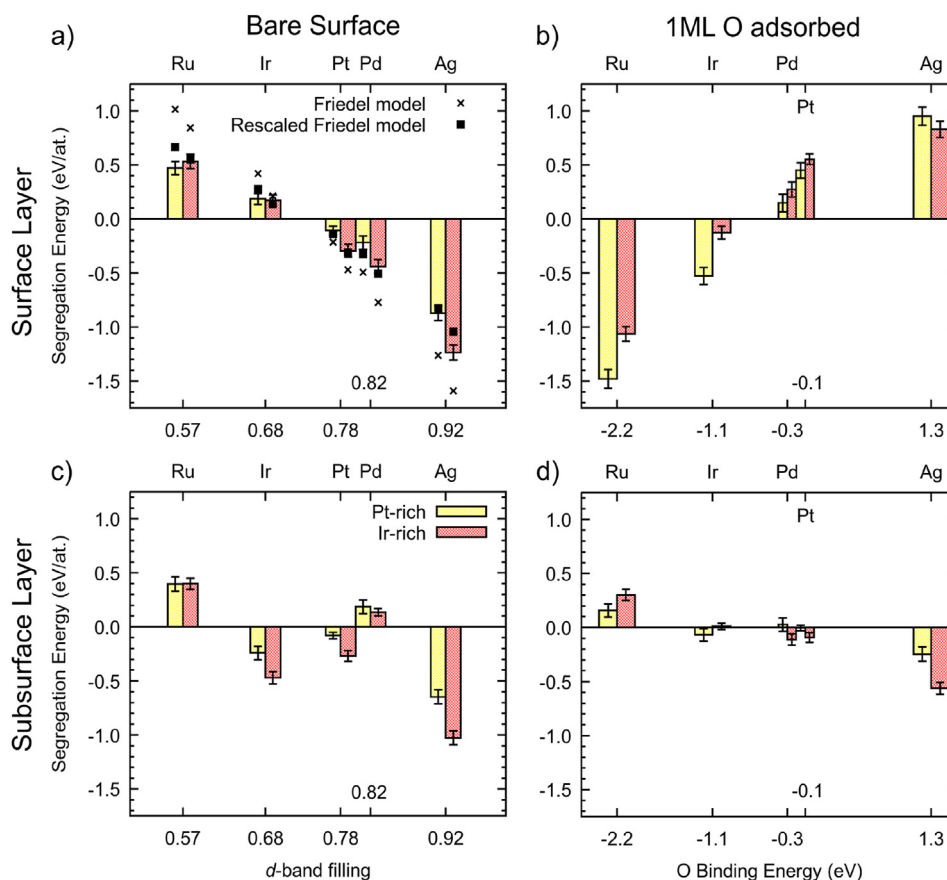


Fig. 2 – Surface segregation for the constituent elements in Ag-Ir-Pd-Pt-Ru: a) for the surface layer in vacuum, b) for the surface layer with 1 ML O, c) for the subsurface layer if the surface layer is occupied by Ag, d) for the subsurface layer if the surface layer is occupied by Ru. The x-axes are common descriptors that correlate with the segregation energies: the *d*-band filling of the elements for segregation in vacuum and the oxygen binding energy to the surface of the elements for segregation with O. The statistical error bars account for different atomic configurations. Crosses are the predictions by the Friedel model (see Sec. 3.3), squares are the same values rescaled by 0.655 (see text for details).

In vacuum conditions (Fig. 2a), as already evident from the surface phase diagram, Ag strongly segregates at the surface for both compositions, whereas Ru strongly antisegregates. This result is largely expected, given that Ag and Ru have the lowest (722 mJ/m²) and highest (2537 mJ/m²) surface formation energies among the five elements, respectively. Furthermore, Ag has a significantly larger lattice parameter than that of the two CCAs (+5.5% and +6.4% with respect to the Pt-rich and Ir-rich CCAs, respectively), which favors the migration of this element to the surface to release internal strains. The opposite holds for Ru, with a smaller lattice parameter than the two CCAs (−3.1% and −2.3%, respectively).

When Ag segregates to the surface, we observe an enrichment of Ag and Ir at the subsurface layer, with the subsurface segregation of Ag larger than that of Ir (Fig. 2c). At thermodynamic equilibrium, we therefore expect Ag to form a film on the surface, despite the content of this element is only a few at.% for both CCAs.

As anticipated from the surface phase diagram, the situation changes drastically in the presence of O (Fig. 2b). In this case Ru strongly segregates at the surface, whereas Ag strongly antisegregates and Ir, Pd, and Pt take intermediate

values for the segregation energy. However, at the subsurface layer (Fig. 2d), Ag is again favored, possibly due to strain-induced contributions, i.e., the small lattice parameter of Ru at the surface needs to be compensated by that of Ag below.

Overall, the results show that surface segregation is very prominent in both CCAs (segregation energies are higher than 1 eV in magnitude) and explain why the resultant surface composition is predicted to be considerably different from the nominal bulk composition even at high temperature. For these systems, strong segregation is typically undesirable, as it may substantially decrease the catalytic performance of the candidate alloys and ultimately invalidate the whole design protocol. To overcome this issue, in the next subsection we propose descriptors that can be used to take into account surface segregation during the alloy design process.

3.3. Descriptors that correlate with the segregation energy

Besides surface formation energies and lattice parameters, the trend of the segregation energies in vacuum and in the

presence of reactants can be rationalized using canonical models and/or simple descriptors that can be calculated straightforwardly from first-principles and which can be easily implemented in an alloy design protocol. As detailed in Ref. [24,28], the segregation energy of an element in an alloy in vacuum depends mainly on the d -band filling of the element, f^* , and of the alloy f . This dependence can be accounted for using the canonical Friedel model [39], that assumes a rectangular d -density of states with bandwidth w . For the fcc(111) surface, the Friedel model gives [24,28].

$$E_{\text{segr}} = 0.670 w(f) [f^* (1 - f^*) - f (1 - f)]. \quad (6)$$

We obtained f^* by integrating the d -densities of states of the constituent elements and f and w by a weighted average of the corresponding quantities for the pure elements. w is 6.98 eV and 7.47 eV for the Pt-rich and Ir-rich CCAs, respectively, and the d -band fillings for the elements are Ru: 0.57, Ir: 0.68, Pt: 0.78, Pd: 0.82, and Ag: 0.92.

As can be seen in Fig. 2a, the surface segregation energies correlate very clearly with the d -band filling (x -axis) and the Friedel model (crosses in Fig. 2a) captures qualitatively the segregation trend, despite this simplistic approximation overestimates the magnitude of segregation/antisegregation. Employing an empirical rescaling of the Friedel model predictions (by a factor of 0.655) though provides good agreement (root-mean-squared error of only 0.102 eV) with the DFT segregation energies (squares in Fig. 2a). This rescaling may be interpreted as a homogeneous shrinkage of the d -bandwidth, that compensates the crude assumption that the density of states is rectangular in the Friedel model. Although we do not expect this factor to be the same for any arbitrary alloy, we already observe that it is reasonably well transferable between the two compositions and likely applicable to the present alloy family.

Using the Friedel model, some peculiar features in the calculated segregation energies can be explained. For instance, the lower segregation energy of Ag in the Ir-rich alloy can partially be ascribed to the fact that this alloy has a smaller lattice parameter, and partially to the fact that it has also a smaller f .

The reason why canonical models such as the Friedel model can make reasonable predictions for CCAs is that the densities of states of these complex alloys are indeed very similar to those of the constituent elements and trends can often be qualitatively explained by considering bandwidth adjustments and rigid shifts of the Fermi level. For instance, Fig. 3 displays the projected densities of d -states (PDOS) of Ag, Pd, Pt (upper panel), Ir, Ru, and the Pt-rich CCA (lower panel). The densities of states of the $4d$ elements Ag, Pd and Ru, and the $5d$ elements Pt and Ir can clearly be obtained from each other by dilatation of the bandwidth and shift of the band filling, and the PDOS of the CCA presents intermediate features between the five elements: as the alloy is rich in Pt, the corresponding PDOS is very similar to that of Pt, but distinctive attributes of the PDOSs of the other elements, such as the broadening of the peak at the Fermi level due to Pd and the higher energy peak due to Ir and Ru, can be recognized as well.

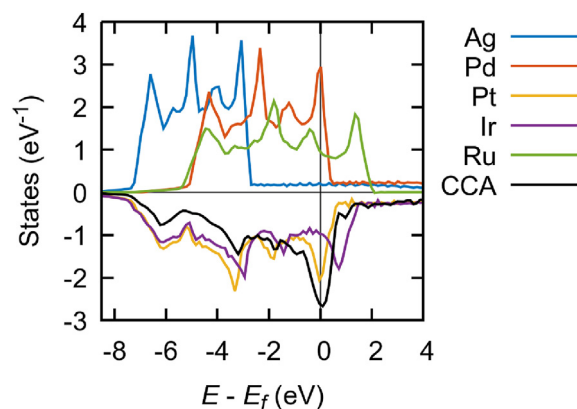


Fig. 3 – Projected density of d -states of the $4d$ elements (upper panel) and $5d$ elements and of the Pt-rich alloy (lower panel).

In the presence of O, an intuitive descriptor that correlates with the segregation energy is instead the binding energy of O on the surface of the pure elements, here computed as

$$E_{\text{bind}} = \frac{E_{\text{slab-O}} - E_{\text{slab}} - E_{\text{O}_2}}{2}, \quad (7)$$

where $E_{\text{slab-O}}$ and E_{slab} are the energies of slabs with and without O adsorbed on the two surfaces, respectively, and E_{O_2} is the total energy of a O_2 molecule.

As observed in Fig. 2b, the segregation energy is approximately linear with respect to E_{bind} (on the x -axis). Although it is difficult to predict the magnitude of the segregation energy solely from E_{bind} , during the alloy design process one may limit the choice of the elements to those whose E_{bind} differ by less than a given threshold (a reasonable estimate may be, for instance, 1.5 eV).

It should also be noted that generally reactants bind on the surface of noble metals only at relatively low temperature. In these conditions, diffusion from the bulk to the surface may be kinetically hindered, hence the most stable configuration at high temperature could be retained, even if thermodynamically unstable. This is also the reason why accurately assessing the segregation in vacuum may sometimes be more important.

4. Discussion

Even if the constituent elements of the two alloys studied here were initially chosen close to each other in the periodic table to avoid demixing and precipitation of new phases, our results prove that surface segregation does take place, potentially affecting the functionality of the designed electrocatalysts. The design of new multicomponent materials for electrocatalysis should therefore take segregation effects into account. We propose two alternative strategies: (i) the optimal composition should be chosen to boost the reaction kinetics but also under the constraint of minimizing segregation; (ii) selective segregation could be enhanced and actively exploited to achieve the target composition on the surface, different from the bulk.

To incorporate the evaluation of the segregation energy inside the computational materials design protocol, efficient descriptors from first-principles can be used to boost up the theoretical predictions. The segregation in vacuum can be estimated from bandwidths and band fillings, that both can be very efficiently computed as weighted averages of the bandwidths and band fillings of the individual constituents. The segregation in the presence of reactants such as O can be related to the binding energy of the reactants on the surface of the pure metals. It is found that canonical theories, such as the Friedel model, work well for the considered CCAs because the mixing of the constituent elements in these systems is almost ideal and, as a first approximation, the first few moments of the densities of states can be interpolated from those of the pure elements.

In summary, we calculated the surface phase diagrams of two candidate CCAs for electrocatalysis of the oxygen reduction reaction. At low temperature, when the absorption of O is favorable, Ru tends to segregate at the surface, whereas at high temperature, when O prefers the gas reservoir, Ag segregates. We predict that segregation is thermodynamically favorable even up to the melting point. This is due to the very strong segregation energies of Ru and Ag, that can be rationalized in terms of the *d*-band filling. We propose to take segregation into account during the materials design cycle by exploiting the computationally very efficient Friedel model, that only needs the densities of states of the constituent elements as an input, and the binding energies of the reactants on the pure elements. These findings pave the way for exploiting more active and stable catalysts, crucial for a plethora of applications ranging from energy production and storage over processing of chemicals to sequestration of harmful substances.

Data availability

Derived data supporting the findings of this study are available from the corresponding author upon request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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