

# Predicting the Adsorption Behavior in Bulk from Metal Clusters

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The physicochemical properties of materials are directly related to their size. The ability to understand and eventually tailor the materials' properties over multiple length scales has always been of a primary research goal. Using quantum mechanical calculations and mathematical modeling, we establish a novel theoretical framework capable of predicting the catalytic behavior of bulk metals and alloys and specifically the adsorbate binding energy, using electronic structure information from sub-nanometer cluster models as input. These models demonstrate that bulk-phase concepts can be reproduced from clusters; a first step towards bridging the properties of materials at different length scales.

Highlights: • novel theoretical adsorption model on monometallic and bimetallic nanoparticles • calculation of d-band center on clusters • reproduction of bulk-phase concepts from nanoparticles • binding energy trends on metals and alloys

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# 1. Introduction

Understanding particle-adsorbate interactions has recently attracted significant attention[1-5] due to their importance in optimizing catalysts for clean and efficient energy production. Despite the accelerated pace of catalyst discovery, the physicochemical fundamentals of particle-adsorbate interactions are still not well understood. One of the reasons is the strong dependence of the nanoparticles' properties on their size. Such a dependence is exemplified by the catalytic behavior of Au, which is an inert metal in bulk[6], but becomes a surprisingly active catalyst at the nanoscale[7, 8].

Periodic density functional theory (DFT) has been instrumental in improving our understanding on how different metals affect the binding strength of adsorbates. In fact, the relationships developed based on periodic calculations allow us to predict optimal catalyst activity[9]. More specifically, Norskov's group related the chemisorption energy of CO on transition metals with the d-band center ( $d_C$ ) of the metal[10, 11]. The  $d_C$  is affected by the strain induced to the metal from the support, which in turn, affects the chemisorption of adsorbates[12]. Such concepts can also be used in analyzing the behavior of alloy catalysts[13] in order to engineer new materials that exhibit performance similar to that of commercially used metal catalysts, but are much less expensive. A successful example of this methodology was recently demonstrated by Hansgen et al.[4] The authors first predicted theoretically that the NiPtPt bimetallic surface is very active for the ammonia decomposition reaction and subsequently confirmed this finding experimentally.

In addition to providing a fundamental understanding of binding and catalytic activity, DFT can also serve as a search engine[2, 14] for catalyst selection. The latter can be accomplished by screening a large number of metal and alloy surfaces based on their adsorbate chemisorption energies and stability under working conditions. For example, out of a total of 736 materials tested for the hydrogen evolution reaction by Greeley et al.[2], the BiPt was found to exhibit better catalytic activity than pure Pt, a finding that was verified experimentally. Undoubtedly, modeling can provide valuable insight into catalyst behavior, thereby, minimizing tedious "trial and error" experimentation in the lab.

Despite their success, periodic DFT calculations are computationally expensive especially when simulating small nanoparticles. On the other hand, molecular orbital based, cluster DFT calculations can account for nanoparticle's structural characteristics and provide a firm understanding on the catalytic behavior of different sites[5]. The computational cost in these calculations increases with the

number of electrons of the system (for a given level of theory and basis set) and as result, these DFT calculations are limited to small nanoparticles (approximately reaching nanoparticle diameters of 1-2 nm).

Due to the computational cost just mentioned, there is currently a disparity in simulated length scales between the extremes of bulk metal and small clusters. Predicting the behavior of bulk metals from those at the nanoscale, or vice-versa, still remains a grand theoretical challenge, even though the first theoretical efforts date back to the 80's[15, 16]. This materials gap hinders our ability to understand and eventually control catalytic chemistry at various length scales.

In the present work we focus on the catalytic properties of metal and binary nanoscale alloy catalysts. Using computationally inexpensive, cluster DFT calculations on a 10-atom metal cluster and via appropriate mathematical modeling and computational analysis, we develop a framework that is able to predict adsorbate-nanocatalyst binding energies, is applicable to various scales, and eventually bridges the materials gap. This framework performs well for both single metal and alloy catalysts and demonstrates that traditional theoretical concepts pertaining to the bulk can be reproduced from nanoscale systems.

## 2. Theoretical Methods

Spin unrestricted DFT calculations were performed using the Gaussian 03 program package[17]. The B3LYP functional along with the LANL2DZ basis set were applied to investigate the binding energy of O, OH, H, and CO on ten-atom  $d^9$  metal clusters (Cu, Ag, and Au) and their alloy combinations. The ten-atom clusters XY, X, Y = Cu, Ag, Au, consist of a seven-atom upper (surface) layer of the X-species and a three-atom lower (subsurface) layer of the Y-species, as shown in Figure 1. This setup allows for the central atom of the surface layer of the cluster to exhibit a coordination number of 9, and thus to mimic the (111) face of a face-centered cubic (fcc) metal (see Figure 1).

During the optimization of the metal clusters, the bond angles and dihedrals were frozen, whereas the bond distances were allowed to relax. This optimization scheme ensures that the cluster retains a 3D bilayer structure. The adsorbates (O, OH, H and CO) are allowed to interact with the clusters at three binding sites, the hollow (O, OH, H), the bridge (O, OH, H, and CO), and the top (O,

OH, and CO), as shown in Figure 1. To calculate the adsorbate–cluster interaction, the optimized bare cluster was frozen and the distance between the adsorbate and the cluster was relaxed. The three lowest spin states were investigated in every different calculation. The binding energy (BE) of the adsorbates was calculated as follows:

$$BE_A = E_{A-M} - E_A - E_M \quad (1)$$

Here,  $E_{A-M}$ ,  $E_A$  and  $E_M$  denote the total electronic energies of the metal-adsorbate system, the adsorbate A, and the metal cluster M, respectively. The aforementioned computational methodology is able to reproduce periodic DFT calculated adsorbate BEs. For example, the OH binding energy on Cu is -70.7 kcal/mole, which is in very good agreement with various periodic DFT calculations (binding energy range from -65.0 to -73.8 kcal/mole) presented in the work of Phatak et al.[18] (all adsorbate BEs are presented in Table 1 of the supplementary data).

### 3. Results and Discussion

Aside from CO, BEs of various adsorbates on extended (infinite size) transition metal surfaces correlate well with the  $d_C$ , and consequently with the factors controlling it[10-13]. Periodic DFT calculations on single metals have shown that  $d_C$  is proportional to the corresponding d-band width,  $d_w$ [13]. The latter is approximately related to the number N of the nearest neighbors and the hopping integral V between them, i.e.,

$$d_C \sim d_w \sim (N-1)^{1/2} \cdot V \quad (2)$$

The dependence of the BE on  $d_C$  can be understood in the simple case of an adsorbent (metal) with one electron per site within the single d-band tight binding (TB) approximation. In this picture, the  $d_C$  is identified as the onsite energy,  $\epsilon_i$ , which describes the adsorbent. That is,  $d_C$  describes the location of the d-band with respect to the Fermi energy,  $E_F$ , and therefore is a measure of the density of states (DOS) near  $E_F$ , which in turn determines the bonding with an adsorbate.

The interaction of an adsorbate with a binary alloy  $A_xB_{1-x}$  is characterized by the composition parameter x and the constituent metals' onsite energies  $\epsilon_A$  and  $\epsilon_B$ , hopping integrals  $V_A$  and  $V_B$ , and

coordination numbers  $N_A$  and  $N_B$ . In this case, there is no single relation, like Eq. (2), for the functional dependence of  $d_C$  on the  $N$ s and  $V$ s. An approximate picture, however, can be obtained within the Bethe lattice approximation, according to which the alloy develops two bands extending over the energy ranges given by Eqs. (3) and (4)[19]:

$$0.5 \cdot (\varepsilon_A + \varepsilon_B) - X \leq E \leq \varepsilon_B \quad (3)$$

$$\varepsilon_A \leq E \leq 0.5 \cdot (\varepsilon_A + \varepsilon_B) + X \quad (4)$$

where  $E$  is the energy.  $X$  is given as:

$$X = \sqrt{0.25 \cdot (\varepsilon_A - \varepsilon_B)^2 + 4 \cdot (N-1) \cdot V^2} \quad (5)$$

and it has been assumed that  $\varepsilon_A > \varepsilon_B$ ,  $V_A = V_B = V$  and  $N_A = N_B = N$

It is easily verified that for  $\varepsilon_A = \varepsilon_B$ , Eq. (2) is recovered. From Eqs. (3-5), it is clear that the location of  $d_C$  is a function not only of  $\varepsilon_A$ ,  $\varepsilon_B$ ,  $V_A$ ,  $V_B$ ,  $N_A$  and  $N_B$ , but also of the filling factor of the d-band which specifies which of the two bands is occupied. It is worth noting that in the case of a binary alloy-diatomic molecule, the bands described by Eqs. (3) and (4) are the analogue of the bonding and anti-bonding orbitals. From Eqns. (3)-(5) we obtain that the  $d_C$  is approximately restricted in the energy range:

$$0.5 \cdot (\varepsilon_A + \varepsilon_B) - X \leq d_C \leq 0.5 \cdot (\varepsilon_A + \varepsilon_B) + X \quad (6)$$

For  $\varepsilon_A \approx \varepsilon_B$ , it becomes apparent that

$$\varepsilon_A - 2 \cdot V \cdot \sqrt{N-1} \leq d_C \leq \varepsilon_A + 2 \cdot V \cdot \sqrt{N-1} \quad (7)$$

Eqs. (6) and (7) indicate that the onsite tight binding matrix elements are crucial factors for  $d_C$  in a single metal or an alloy. Additional factors affecting the  $d_C$  are the hopping integrals and the coordination numbers. Eqs. (6) and (7) relate the position of the  $d_C$  with fundamental properties of the elements as well as with the composition  $x$  and the symmetry of the adsorption points, the latter specifying the coordination number of the adsorption site. These dependencies imply that in a bulk or cluster alloy, concentration-dependent strain effects, charge transfer and structural reconstructions should play a dominant role in specifying the onsite energies and the hopping integrals (as well as the coordination numbers in the case of reconstruction), and thus, the BE of the adsorbate. These

considerations rationalize the conclusions reached by Norskov and co-workers[10-13] who related “*ab-initio*” computed BEs with the corresponding  $d_C$  for a series of metal and alloy surfaces.

Our objective is to identify the physical attributes of a cluster that correlate with the binding energies of the adsorbates. In lieu of the bulk-phase physics, we expect that the electronic properties, and specifically the  $d_C$  of a cluster, should be related with the binding affinity of the adsorbates[10-13]. Thus, our first task is to introduce a method to calculate the  $d_C$  of a cluster, since a cluster exhibits molecular orbitals of discrete energy, consisting of mixed atomic orbital characters. As the size of the cluster increases, the number of the molecular orbitals (MOs) also increases, and eventually, the discrete-energy MOs of small clusters will turn into bands of the bulk. In a MO-based cluster calculation, the MOs are represented as a linear combination of atomic orbitals  $\phi$  (LCAO) in the form:

$$\psi_i = \sum_j c_{ij} \cdot \phi_j \quad (8)$$

where  $\psi_i$  is a MO,  $\phi_j$  an atomic orbital (AO) and  $c_{ji}$  is the contribution of the  $j^{\text{th}}$  AO to the  $i^{\text{th}}$  MO (to be denoted as  $\text{MO}_i$ ). These coefficients, along with the energy  $E_i$  of each  $\text{MO}_i$  are output by Gaussian 03[17]. We compute the total DOS as a superposition of Gaussian distributions ( $\mathcal{G}$ ) with means  $E_i$  and standard deviation  $\sigma$ , which is related to the half width  $h$  as:  $\sigma = h/(\ln 4)^{1/2}$  ( $\approx 0.0578$  Hartrees; half width is 0.0025 Hartrees):

$$\text{DOS} = \sum_i \mathcal{G}(E_i, \sigma) \quad (9)$$

For the calculations of the partial DOS, the normalized contribution of the  $k^{\text{th}}$  AO to the character of  $\text{MO}_i$  is computed as:

$$\lambda_{ki} = \frac{c_{ki}^2}{\sum_j c_{ji}^2} \quad (10)$$

where  $j$  ranges over all atomic orbitals (in the case of a normalized  $\text{MO}_i$ , the denominator of Eq. 10 is equal to 1 since every MO is occupied by one electron). Subsequently, the partial density is calculated as:

$$\text{pDOS} = \sum_i \sum_k \lambda_{ki} \cdot \mathcal{G}(E_i, \sigma) \quad (11)$$

where index  $k$  ranges over the desired atomic orbitals. For example, if we were to calculate the partial DOS of the d-orbitals, then  $k$  would range over the d-orbitals of all atoms in the structure. Note that if all atomic orbitals are included in the summation over  $k$ , Eq. (11) gives the overall DOS, Eq. (9). Once the d-orbital DOS is known, the  $d_C$  is calculated as the median of that distribution, namely the energy value that splits the area under the distribution into two equal parts (or equivalently the energy for which the cumulative d-DOS is equal to  $1/2$ ).

Having established a methodology to calculate the  $d_C$  of clusters (Eqs. 8-11), our next step is to correlate the BE of the adsorbates with the  $d_C$  and identify descriptors that control  $d_C$ . The results are shown in Figure 2. Figure 2a portrays linear trends between the BE and the  $d_C$ , consistent with bulk-phase results [10, 13], and demonstrates that through the computation of the cluster's  $d_C$  bulk-phase concepts can be reproduced from nanoscale systems. **In addition, Figure 2a demonstrates that the d-band center can be used as a BE descriptor for metals with filled d-bands. This is due to the fact that the  $d_C$  determines to some extent the energy level of the metal's sigma orbitals which were found to play an important role in adsorption (results not shown here). As a result, the  $d_C$  can act as an indirect descriptor of the BE (through the energy level of s orbitals).**

While the BE of monomer clusters scales linearly with  $d_C$ , the BEs of binary clusters consisting of Cu on the top layer are shifted to higher values (-7.8 to -7.4 eV). This shift can be attributed to two possible reasons. The first one is the difference in the electronegativity between the  $d^9$  metals, with the Cu being the least electronegative (Pauling scale electronegativity: Cu 1.90, Ag 1.93, Au 2.54). The second reason pertains to the size of the metal atom, since Cu is the smallest in the  $d^9$  column. Clearly, electronegativity and strain effects are important as discussed next.

Figures 2b and 2c show that the BE scales linearly with the difference in the Pauling electronegativities between the two metal layers of the cluster and the strain of the clusters, respectively. The strain is calculated as  $(a-a_0)/a_0$ , where  $a$  is the average bond length of the top layer of the alloy and  $a_0$  is the average bond length of the top layer of the corresponding single-metal cluster. The results of Figure 2b indicate that the difference in electronegativities of the two metals is crucial, as it determines the charge transfer on the surface which, in turn, affects the BE of the adsorbates (due to electrostatic interactions). This charge transfer, which we identified to be of sp electron character, was shown to be important in developing models capable of capturing the BE trends on metals with

nearly fully occupied d-bands[20]. The results of Figure 2c indicate a dependence of the BE on the size of the metal atoms because the strain affects mainly the mean distances of the top layer. A metal is subject to strain due to lattice mismatch with another metal or the support. Specifically, an expansive strain on the metals shifts their  $d_C$  towards the Fermi level[12]. This is also found in our study of clusters (Figure 2d).

The strong correlation between the charge transfer (as modeled by the electronegativity difference) and the strain, observed in Figures 2b and 2c (similar linear trends of BE vs.  $\Delta(\text{Electronegativity})$  and BE vs. strain), indicates that these factors are interdependent, both affecting mainly the onsite energies. In fact, the strain on bimetallics depends on the size of the constituent metals, which in turn, defines the radii and energies of d-orbitals. Finally, the electronegativity of a metal depends on its d-orbital energies.

The above analysis and results rationalize the empirically obtained relationship between BE and a key property of the adsorbents and indicate that the  $d_C$  could be a reasonable descriptor of BE for clusters as well, since it incorporates explicitly or implicitly primary parameters, Eqs. (3-7). However, the charge transfer and strain effects are implicitly incorporated and cannot be adequately reflected by the gross descriptor  $d_C$ . For this reason, we investigate whether the strain or the charge transfer can stand for an independent descriptor for BE, i.e., we are looking for descriptors of the form

$$\text{BE} = f_1(d_C, S) \text{ or } \text{BE} = f_2(d_C, \Delta E) \text{ or } \text{BE} = f_3(\Delta E, S) \quad (12)$$

where S denotes the strain of the adsorbent and  $\Delta E$  the electronegativity difference of the two layers of the alloy-cluster, which quantifies the charge transfer. For this purpose, we constructed a bi-quadratic model to fit the DFT calculated values. Three different descriptors were considered, namely, the strain ( $x_1$ ), the difference in the electronegativity values between the metals of the two layers ( $x_2$ ), and the  $d_C$  ( $x_3$ ). The BE of the most stable binding configuration of each adsorbate was fitted. The results are presented on Table 1. The best fits (parity graphs) are shown in the supplementary data. The high cross-correlation terms (Table 1) indicate the dependence of  $d_C$  and  $\Delta E$  or S discussed above. The coefficients of the O BE are 1.2-1.4 times larger than those of the OH BE (a rough approximation is  $\text{BE}_O(d_C, \Delta E) = 1.3 \cdot \text{BE}_{OH}(d_C, \Delta E)$ ), indicating similar adsorption of O and OH on the  $d^9$  metals. Such a behavior clearly shows that scaling-energy correlations, found originally on bulk systems (e.g.,  $\text{OH}_n$ ,  $\text{CH}_n$ ,  $\text{NH}_n$ ) using periodic DFT calculations[21], also exist on metal and alloy clusters. This finding



underscores the possibility of predicting BEs of complex adsorbates from atomic binding energies. Moreover, the fact that a bi-quadratic model is essential to describe the BE of the adsorbates, relies on the physics behind these descriptors. For example, the determination of the atomic electronegativities in a chemical bond by Pauling, is a square mathematical expression[22].

The BE of O, OH and H are best described using  $d_C$  and  $\Delta E$  as descriptors, whereas the BE of CO using  $d_C$  and S. A possible explanation is that the adsorption of O, OH and H is strong, with a partial electrostatic character, affected by the total charge transferred between the two layers of the cluster (represented with  $\Delta E$ ). On the other hand, the adsorption energy of CO is weak and affected by the presence of point charges localized on the atoms constituting the upper layer of the cluster (mainly with the peripheral atoms of the 7-atom, upper layer). As a result, such interactions are affected by the CO-metal distances, which in turn, depend on the metal's strain. Even though the descriptors S and  $\Delta E$  are interdependent, as already mentioned, we do not expect their BE models ( $BE(d_C, \Delta E)$  and  $BE(d_C, S)$ ) to show similar behavior, since the values of S and  $\Delta E$  (scale) differ.

Each model (Table 1) describes the BE of an adsorbate (O, H, OH, CO) onto a  $A_xB_y$  (A, B = Au, Ag, Cu) binary cluster surface in terms of two independent parameters ( $d_C$  and  $\Delta E$  or S). Having constructed these bi-quadratic models, the question is whether they can be extrapolated to other metals. The answer lies in the fact that the coefficients of the model depend strongly on the chemical nature of the substrate. It is therefore expected that each model can describe particular substrates i.e., binaries of metals from the same column or period of the periodic table. Our approach can be extended by constructing a relationship of the form  $d_C = g_C(A, B, x, y)$  for each pair of metals A and B with respect to their composition x and y in the cluster. Similarly, one can obtain relationships for  $\Delta E = g_{\Delta E}(A, B, x, y)$  and  $S = g_S(A, B, x, y)$ . Even though all descriptors ( $d_C$ , S  $\Delta E$ ) can be calculated by first principles, values thereof can be found in tables and an estimation of the  $d_C$  of an alloy can be obtained within the virtual crystal approximation.

Furthermore, cluster-size dependence ( $\lambda = g_\lambda(A, B, x, y)$ ,  $\lambda = d_C, \Delta E, S$ ) can be incorporated in these relationships by fitting results obtained for a range of cluster sizes. Additionally, it has to be considered that the cluster size determines the number of different adsorption sites (i.e. corners, planes, etc.) and the average coordination of the surface atoms, factors which control the adsorption energy[5]. **The calculated BEs within this methodology refer to equivalent adsorption sites, i.e., to sites with the**

same number of first nearest neighbors. Adsorption on the peripheral atoms of the cluster model used in this study could correspond to adsorption on peripheral defect-atom sites of bulk materials. A generalization of our model to include adsorption site (coordination number) dependence is straightforward through the use of coordination number dependent adsorption models [5]. With all this information, models for binary systems ranging from the nanoscale to the bulk-phase can be constructed. Finally, to direct future efforts we would like to mention some important aspects for bimetallics catalyst design that the present model does not account. Such binding energy models work well if the reactions are driven by thermodynamics and not by kinetics and since the metal clusters were partially constrained in this study (to mimic bulk) they do not take into consideration adsorbate induced metal reconstruction.

## 4. Conclusions

To conclude, Figures 2a-d underscore that the adsorbate's BE on small clusters is not a single function of the metal's d-band center,  $d_C$ . Despite charge transfer and strain being implicitly included in the determination of  $d_C$ , two descriptor models (Table 1) with explicit dependence on  $d_C$  and  $S$  or  $\Delta E$  are necessary to obtain the correct trends and achieve better accuracy (the form  $BE=f[d_C(S,\Delta E)]$  is unable to provide an accurate description of binding).

The present work demonstrates that with the appropriate computational modeling, catalytic concepts (e.g., d-band center, linear scaling relations) pertaining to the bulk can be reproduced from clusters, bridging the behavior of materials at different length scales. Moreover, our study provides a framework for estimating the BE of adsorbates on single metals and alloys. by calculating only the  $d_C$  on a small cluster (calculations with little computational expense) and using tabulated electronegativity values of metals. Finally, this methodology opens up new horizons in the theoretical catalysis field, as one can take into account for the first time, the electronic properties of the monometallic and alloy nanoparticles, captured in  $d_C$ , as well as their physical and structural characteristics(e.g., electronegativity, strain, coordination number [5]), in the development of theoretical models capable of predicting the adsorbate binding at every site of the structure.

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Appendix A. Supplementary data

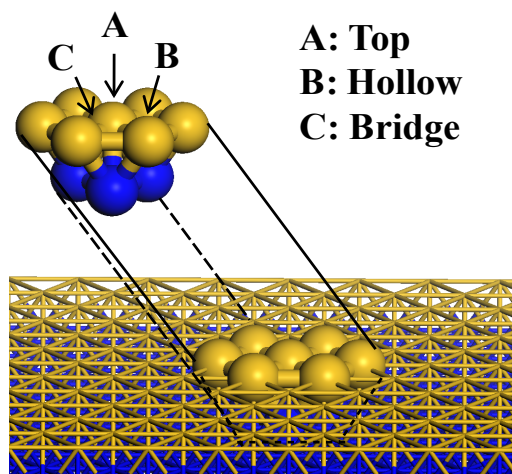
Supplementary data associated with this article can be found, in the online version.

## References

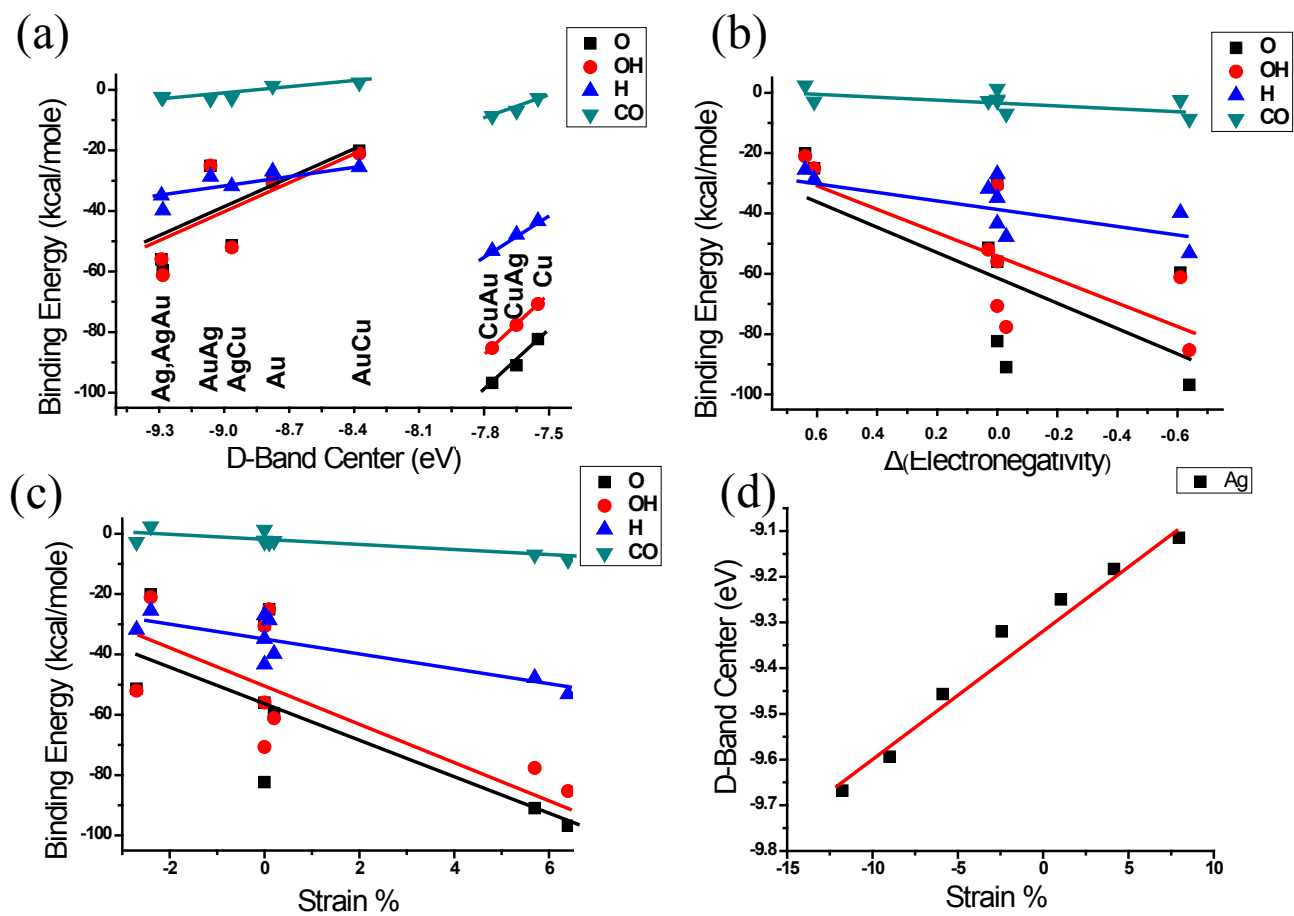
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## Figures and Tables:



**Figure 1.** Alloy, ten-atom AuAg cluster approximating the (111) surface of a slab (top layer: Au, bottom layer: Ag). The arrows show the different adsorption sites on the cluster; top (A), hollow (B) and bridge (C).



**Figure 2.** Binding energy of the adsorbates vs. (a) the  $d_C$  of the clusters, (b) the electronegativity difference between the two metal layers and (c) the strain of the surface layer of the cluster; (d) relationship between the  $d_C$  and the strain on a monometallic cluster.

**Table 1.** Model expressions for adsorption of O, OH, H and CO on the most stable binding site of the cluster. Fit model is:  $g(x_i, x_j) = b_1 \cdot x_i^2 + b_2 \cdot x_j^2 + b_3 \cdot x_i \cdot x_j + b_4 \cdot x_i + b_5 \cdot x_j + b_6$ . All pairwise combinations of descriptors were tested ( $BE = f_1(d_C, S)$ ,  $f_2(d_C, \Delta E)$ ,  $BE = f_3(\Delta E, S)$ ), using the MATLAB fitting function LSQCURVEFIT.

Adsorbate/site	Descriptors Used	Binding Energy Expression (kcal/mole)	R <sup>2</sup>
O/hollow	$\Delta E (x_2)$ , $d_C (x_3)$	$BE_O = 12.20 \cdot x_2^2 - 38.75 \cdot x_3^2 + 16.62 \cdot x_2 \cdot x_3 + 172.39 \cdot x_2 - 673.10 \cdot x_3 - 2963.26$	0.949
OH/hollow	$\Delta E (x_2)$ , $d_C (x_3)$	$BE_{OH} = 10.27 \cdot x_2^2 - 31.47 \cdot x_3^2 + 11.64 \cdot x_2 \cdot x_3 + 128.54 \cdot x_2 - 543.23 \cdot x_3 - 2384.52$	0.934
H/hollow	$\Delta E (x_2)$ , $d_C (x_3)$	$BE_H = -5.55 \cdot x_2^2 - 13.79 \cdot x_3^2 + 6.83 \cdot x_2 \cdot x_3 + 69.01 \cdot x_2 - 239.26 \cdot x_3 - 1066.68$	0.956
CO/top	$S (x_1)$ , $d_C (x_3)$	$BE_{CO} = -0.08 \cdot x_1^2 - 5.81 \cdot x_3^2 - 0.85 \cdot x_1 \cdot x_3 - 7.18 \cdot x_1 - 97.24 \cdot x_3 - 405.11$	0.909



# Supplementary Data for “Predicting the Adsorption Behavior in Bulk from Metal Clusters”

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Table 1S: Binding Energies of O, OH, H and CO (most stable binding configuration) on mono and bimetallic clusters (kcal/mol). (Test calculations where the adsorbate is bound on top and the central metal atom was allowed to fully relax (vertical motion), showed that the difference in the calculated BEs was less than 2 kcal/mol when compared to the completely frozen cluster.)

Cluster	O-Hollow	OH-Hollow	H-Hollow	CO-Top
CuAu	-96.80	-85.31	-53.19	-8.63
CuAg	-90.98	-77.64	-47.81	-6.92
Cu	-82.32	-70.72	-43.35	-2.66
AgAu	-59.60	-61.19	-39.80	-2.41
Ag	-56.00	-55.94	-34.87	-2.28
AgCu	-51.41	-52.02	-31.84	-2.72
Au	-30.02	-30.64	-26.96	1.35
AuAg	-25.08	-25.06	-28.68	-2.92
AuCu	-20.12	-21.05	-25.54	2.45

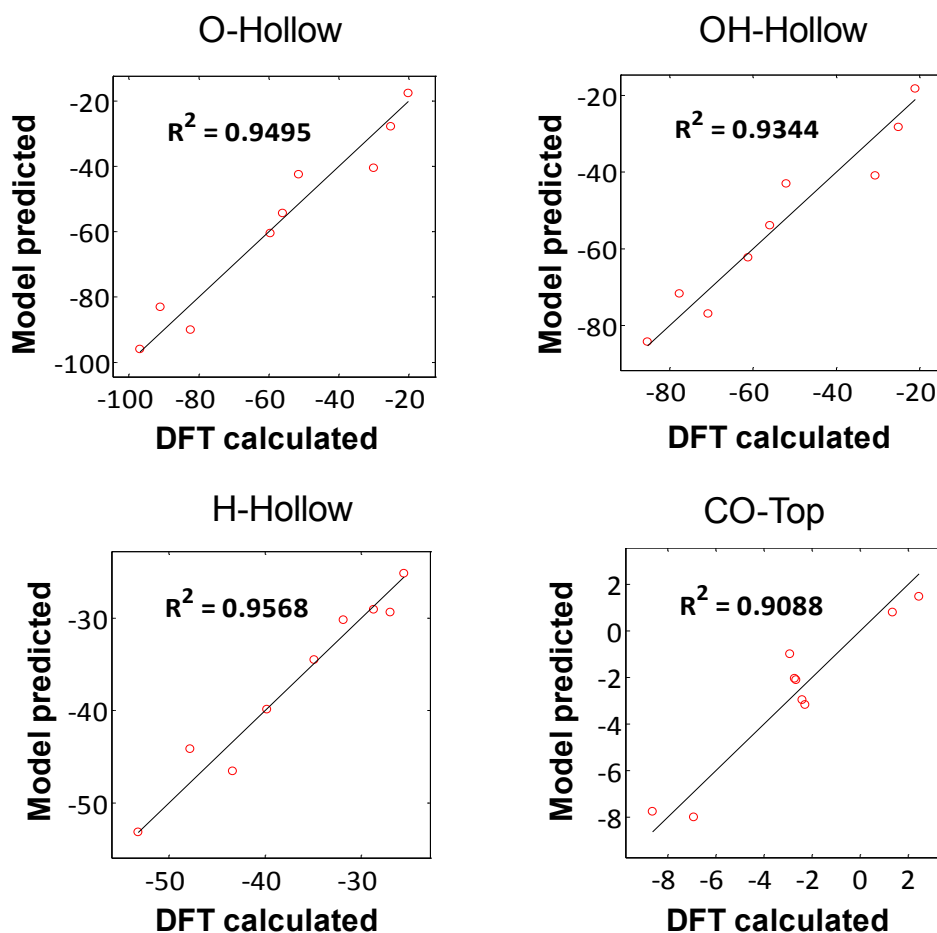


Figure 1S. Parity graphs of model predicted vs. DFT calculated binding energy values of O (hollow), OH (hollow), H (hollow) and CO (top) interaction with  $d^9$  metals and alloys XY, X,Y=Cu, Ag, Au. The model is a two parameter fit having the expression  $y = b_1 \cdot x_i^2 + b_2 \cdot x_j^2 + b_3 \cdot x_i \cdot x_j + b_4 \cdot x_i + b_5 \cdot x_j + b_6$  where  $x_i$  is the electronegativity difference ( $\Delta E$ , for O, OH and H adsorption) or the strain (for CO adsorption) and  $x_j$  is the d-band center of the cluster ( $d_C$ ).