Benchmarking computational alchemy for carbide, nitride, and oxide catalysts

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Computational catalysis plays a growingly important role in guiding the design of new and improved materials for catalysis.[1] Candidates for catalyst sites are regularly screened for using high level quantum chemistry calculations,[2] [3] [4] [5] and Kohn-Sham density functional theory (KS-DFT) is normally applied because it brings a favorable balance of accuracy, transferability, and computational efficiency. However, even the simplest KS-DFT calculations can be relatively computationally intensive, and their computational expense limits their utility in very deep searches through hypothetical materials space.

One way to expedite catalyst discovery is with the d-band model,[6] which relates an adsorbate’s binding energy (BE) with the position of the catalyst surface’s d-band center. If a shift in the d-band center from a reference state to a hypothetical one is known, that shift would correlate with the difference between an adsorbate’s BE in the two cases. While elegant and useful, the d-band model does not satisfactorily predict trends in calculated BEs for electronegative adsorbates such as OH, F, and Cl on materials having mostly filled d-states.[7] Furthermore, the d-band model can only be used on systems that have significant adsorption energy contributions that arise from d-orbitals, i.e. transition metal systems. For other classes of materials, extensions to the d-band model have been developed.[8] [9] [10]

Analogous to the d-band model, computational alchemy correlates an adsorbate’s BE to the material’s electrostatic potentials,[11] [12] [13] which in effect reflects an amalgam of the
material’s full band structure. When given a known adsorbate BE as well as the alchemical derivative that reflects how electrostatic potentials of the system change upon adsorption, one can intuit a BE by approximating the alchemical derivatives for a hypothetical material.\textsuperscript{[14]} \textsuperscript{[15]} A key advantage of alchemy is that no additional information is needed besides a single DFT-quality adsorbate BE, and once this is obtained, large numbers of adsorbate BES for hypothetical surface structures can be obtained \textit{with effectively no computational cost}.

Other references provide more detailed descriptions of this method,\textsuperscript{[16]} \textsuperscript{[17]} \textsuperscript{[18]} \textsuperscript{[15]} \textsuperscript{[14]} \textsuperscript{[19]} \textsuperscript{[20]} but a brief description of our approach is summarized here. DFT calculations were used to obtain a reference BE. We then made a list comprised of individual differences in electrostatic potentials between atoms in the slab due to adsorbate binding. We then constructed a second list that reflects the change in nuclear charge represented by net isoelectronic transmutations to generate a hypothetical material. We then take the dot product of these two lists to compute a first order approximation for the binding energy, $\Delta \text{BE}$, which is essentially a first order perturbation of the reference state BE. The values of $\Delta \text{BE}$ from alchemy were then benchmarked to $\Delta \text{BE}$ values from single point DFT calculations on the identical structures used for the alchemy predictions.

We previously showed that computational alchemy schemes can predict BES of oxygen reduction reaction intermediates on alloys of Pt, Pd, and Ni within 0.1 eV of DFT results.\textsuperscript{[14]} Computational alchemy performed reasonably well for OH intermediates as well as for skin alloys that are known to be problematic for the d-band model.\textsuperscript{[7]} Alchemy errors are highest when alchemical derivatives are high. These are highest when transmutations occur nearest to the adsorption site, or when net isoelectronic transmutations span multiple groups of the periodic table, or when more and more atoms are transmuted.

It remains unclear if computational alchemy can be trusted for predicting binding energies on other material surface besides transition metals. Rocksalt TiC (111), TiN (100), TiO (100), as well as rutile TiO$_2$ (110) were considered due to these surfaces being of interest
We considered pristine surfaces as well as those containing a main group element vacancy. The carbon vacancy was at the three-fold site in TiC, nitrogen and oxygen vacancies were under the four-fold site in TiN and TiO, respectively, and the oxygen vacancy in TiO$_2$ was a bridging oxygen. We chose H* and OH* as adsorbed species since they are oxygen reduction reaction intermediates. Both intermediates are bound on the three-fold site with a metal atom directly underneath in TiC and the four-fold site of TiN. For TiO, H* is also bound to the four-fold site, but OH* binds on top of a metal atom. For TiO$_2$, H* binds on top of a bridging oxygen atom, and OH* binds on top of a metal surface atom. These binding sites are favorable for both the pristine slabs and the slabs with a vacancy.

Figure 1 shows the performance of alchemy with low-energy facets of three different rock salt materials: TiC(111), TiN(100), and TiO(100) without and with a main group element vacancies. Consistent with our previous study on transition metal alloys, alchemy can reasonably calculate adsorbate BEs for H* and OH* intermediates when two, four, and six atoms have been transmuted. Deviations from the parity line correlate with systems having higher alchemical derivatives and/or systems where adsorption results in more significant polarization near the site where transmutations occur. In some cases including when H* is found near a vacancy, the presence of a vacancy results in smaller alchemical derivatives and thus lower errors. Overall, alchemy can capably model H* and OH* binding energies on these three materials within a range of 0.01-0.33 eV depending on the material, even when a vacancy is present. In all of these cases, there is a significant density of states at the Fermi level of all of these systems as would be expected for any transition metal alloy system (see supporting information).
Figure 1. Parity plots comparing the accuracy of alchemy for predicting binding energy (BE) against DFT (in eV) for H* and OH* on pristine slabs (a-c) and slabs with the presence of a vacancy (d-f): TiC, TiN, and TiO. $\Delta B_{\text{alc}}$ is the alchemical derivative of BE between the hypothetical and reference slab. $\Delta B_{\text{DFT}}$ is equal to $B_{\text{alloy}} - B_{\text{ref}}$ calculated from DFT. The hypothetical materials were obtained by alchemical transmutations to one (red), two (blue), and three (green) pair(s) of Ti atoms. Mean absolute errors (MAEs) are listed in each figure and given in eV.

We then evaluated computational alchemy when used on non-conducting materials (Figure 2). Interestingly, the performance of alchemy for approximating adsorbate BEs was rather poor even for just H*, and so other calculations involving OH* and vacancies were not pursued. For ZnO(100), there is a linear trend between alchemy and DFT, but the slope does not show parity. For SnO$_2$(110), there correlation is parallel to the parity line but consistently
offset. The MAE for ZnO(100) is as high as the upper limit of errors seen in Figure 1, and MAEs were even greater for SnO2 and TiO2. As expected, the density of states for these materials all show a bandgap. Alchemy exhibits very poor agreement with DFT in TiO2, but there is somewhat better agreement with DFT in SnO2 and ZnO. We presently attribute this issue to the bandgaps in the materials. A significant density of states crossing the Fermi level signifies a conductive material that would also have a relatively high degree of shielding. High shielding makes atom-centered electrostatic potentials less sensitive to other nearby atoms, and this corresponds to the situations where first order approximations with alchemy would be most valid. This hypothesis will be validated in future work by testing second order alchemy approximations.

Figure 2. (a) Parity plots comparing the accuracy of alchemy for predicting binding energy (BE) against DFT (in eV) for H* on pristine slabs of semiconducting materials: (a-c) ZnO, SnO2, and TiO2. ΔBE_{alc} is the alchemical derivative of BE between the hypothetical and reference slab. ΔBE_{DFT} is equal to BE_{alloy} – BE_{ref} calculated from DFT. The hypothetical materials were obtained by alchemical transmutations to one
pair of Zn, Sn, or Ti atoms. Mean absolute errors (MAEs) in each plot above are given in eV. (b) Density of states (DOS) for (d-f) ZnO, SnO₂, and TiO₂. The Fermi level is zero for each plot.

To further test that problems with alchemy approximations relate to bandgaps, we considered modified systems where 50% of the Ti atoms in the top layer or the second layer were replaced with Pt atoms. Placing Pt atoms in the TiC(111), TiN(100), or TiO(100) structures was expected not to significantly impact these systems since each was already electronically conducting. Indeed, alchemy in these systems with Pt atoms included led to similar errors as cases shown in Figure 1.

However, by placing Pt atoms in the second layer (Pt@2L) or top layer (Pt@1L) of TiO₂(110), we expected to tune the density of states near the Fermi level. We hypothesized that Pt atoms in the second layer do not directly interact with the vacuum layer, and so fewer states were expected to arise at the Fermi level, while Pt atoms in the first layer interact directly with vacuum, and so more states were expected to be found at the Fermi level. Figure 3 confirms this hypothesis and shows a dramatic improvement in alchemy predictions when there is a greater density of states at the Fermi level. Alchemy becomes significantly more reliable when Pt is in the first layer and predicts H* and OH* binding energies within the range of 0.16-0.29 eV.
Figure 3. Parity plots comparing the accuracy of alchemy for predicting binding energy (BE) against DFT (in eV) for H* and OH* on (a-c) TiO\(_2\) pristine and with 50% Pt-substituted in the second layer (Pt@2L) and first layer (Pt@1L). ΔBE\text{alc} is the alchemical derivative of BE between the hypothetical and reference slab. ΔBE\text{DFT} is equal to BE\text{alloy} – BE\text{ref} as calculated from DFT. The hypothetical materials were obtained by alchemical transmutations of one (red), two (blue), and three (green) pair(s) of Ti atoms (pristine) or Pt and Ti atoms (Pt-substituted). Mean absolute errors (MAEs) in each plot above are given in eV. Density of states (DOS) for (d-f) TiO\(_2\) pristine, Pt@2L, and Pt@1L. The Fermi level is zero for each plot.

In conclusion, we have demonstrated the utility of computational alchemy for approximating thermodynamic descriptors for catalysis for non-transition metal alloy systems.

Computational alchemy performs reasonably well when predicting binding energies for H* and OH* on carbide, nitride, and oxide systems that have no band gap. Significant errors in
this computational scheme arise when used on systems that have a band gap. The present explanation for this is that first order approximations using alchemy are most valid for systems having high electronic shielding, which have been used to test alchemy in cases of transition metal alloys\cite{14} and BN-doped graphene\cite{30}. Results from alchemy can become more reliable by ensuring that the materials of interest have a substantial density of states at the Fermi level (which we did via in silico alloying with Pt in the top layer of the system). This shows a practical path forward to leverage computational alchemy for high-throughput searches of catalyst sites though broad regions of materials space.

**Computational Section**

Kohn-Sham density functional theory (DFT) calculations were conducted using PBE\cite{31} exchange correlation functional with projector augmented wave pseudopotential representations of core electrons as implemented in VASP\cite{32} [33]. A plane wave basis set was used to represent valence electrons where 350 eV energy cutoff was chosen for rocksalt TiC, TiN, and TiO, 400 eV for rutile SnO$_2$, and 450 eV for rocksalt ZnO and rutile TiO$_2$. A $4 \times 4 \times 1$ Monkhorst-Pack sampling of the k-point grid was employed for all materials except SnO$_2$, which used $5 \times 5 \times 1$. The minimum energy configuration of each reference surface was determined iteratively with conjugate gradient algorithm until the difference in steps was less than 0.1 meV. Each surface is modelled as a $2 \times 2$ slab extended to 4 layers, and bottom two layers are fixed, while the top layers and adsorbates are relaxed. We note that TiC, TiN, TiO, and ZnO unit cells contain four Ti atoms in each layer whereas TiO$_2$ and SnO$_2$ contain eight.

**Supporting Information**

Projected density of states for structures mentioned in the main text and instructions for accessing structures using an ASE database.

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References


Supporting Information

Benchmarking computational alchemy for titanium carbide, nitride, and oxide catalysts

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1. Projected Density of States for Reference Material Slabs

![TiC(111) Density of States](image)

**Figure S1.** Atom-projected density of states (DOS) for TiC (111) shown for all atoms (black), Ti d-states (red), and C p-states (green). The Fermi level is zero.
Figure S2. Atom-projected density of states (DOS) for TiC (111) with a carbon vacancy shown for all atoms (black), Ti d-states (red), and C p-states (green). The Fermi level is zero.

Figure S3. Atom-projected density of states (DOS) for TiN (100) shown for all atoms (black), Ti d-states (red), and N p-states (green). The Fermi level is zero.
Figure S4. Atom-projected density of states (DOS) for TiN (100) with a nitrogen vacancy shown for all atoms (black), Ti $d$-states (red), and N $p$-states (green). The Fermi level is zero.

Figure S5. Atom-projected density of states (DOS) for TiO (100) shown for all atoms (black), Ti $d$-states (red), and O $p$-states (green). The Fermi level is zero.
Figure S6. Atom-projected density of states (DOS) for TiO (100) with an oxygen vacancy shown for all atoms (black), Ti d-states (red), and O p-states (green). The Fermi level is zero.

Figure S7. Atom-projected density of states (DOS) for ZnO (100) shown for all atoms (black), Zn d-states (red), and O p-states (green). The Fermi level is zero.
Figure S8. Atom-projected density of states (DOS) for SnO$_2$ (110) shown for all atoms (black), Sn $p$-states (red), and O $p$-states (green). The Fermi level is zero.

Figure S9. Atom-projected density of states (DOS) for TiO$_2$ (110) shown for all atoms (black), Ti $d$-states (red), and O $p$-states (green). The Fermi level is zero.
Figure S10. Atom-projected density of states (DOS) for 50% Pt substituted in the second layer (Pt@2L) of TiO$_2$ (110) shown for all atoms (black), Ti $d$-states (red), O $p$-states (green), and Pt $d$-states. The Fermi level is zero.

Figure 11. Atom-projected density of states (DOS) for 50% Pt substituted in the first layer (Pt@1L) of TiO$_2$ (110) shown for all atoms (black), Ti $d$-states (red), O $p$-states (green), and Pt $d$-states. The Fermi level is zero.