



Elucidating challenges of reactions with correlated reactant and product binding energies on an example of oxygen reduction reaction



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ABSTRACT

Using density functional theory (DFT), Pt-based sandwich catalysts have been studied to identify a strategy for improving the energetically unfavorable O hydration catalytic reaction ($O + H_2O \rightarrow 2OH$) in fuel cells. The challenge for this type of reaction is that the reactant, O, and product, OH, have correlated binding energies, making the improvement of the overall energetics of the reaction problematic. We screened 28 different transition metals as the Pt-M-Pt sandwich middle layer and developed a new index that specifically describes the difficulty of the reaction which involves adsorbed atomic O as the reactant and adsorbed OH as the product. This index is found to predict well the barrier of the O hydration. In order to understand how the index can be optimized, we further studied the electronic density of states (DOS) to elucidate the DOS changes for the different Pt-M-Pt sandwiches. This gives insight on strategies that might be applied to improve the catalytic reactions where the reactant and product have correlated binding energies, which is in fact a common challenge in heterogeneous catalysis.

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1. Introduction

Heterogeneous surface catalysis facilitates conversion of reactants to products. The overall reaction consists of individual reaction steps. The rate of each step and the overall reaction is significantly related to the binding energy of the reactant and product. A possible strategy for searching advanced catalytic surfaces may involve matching the binding energy for each reaction step, so that the largest, rate-determining barrier would be minimized. In this way, it would be ideal to tailor a catalyst that has an ideal binding energy for each species along the mechanism, and the overall mechanism contains as little “bumps along the road” as possible.

The common problem when researching an ideal catalyst, especially for multistep reactions, is that the intermediate species often have correlated binding energies. Selecting a catalyst that lowers or raises the binding energy of a particular intermediate may also lower or raise the binding energy of other intermediates (correlated binding energies). In this case, it will not improve a particular reaction step, since the binding energy of the product and reactant

changes by the same amount, resulting in the same overall energy of reaction (ΔE). Thus, new strategies need to be developed that would allow changing the binding energy of a particular intermediate without affecting the others in order to improve the individual reaction steps. The key here is to figure out ways to make the binding energies of intermediates that were previously correlated to become non-correlated.

An example of a well-studied reaction with correlated binding energies is the oxygen reduction reaction (ORR) in a proton-exchange membrane fuel cell (PEMFC). The ORR adsorbed intermediates, such as O and OH, have correlated binding energies [1,2], which makes it difficult to improve the efficiency of this reaction. We further examine this reaction to identify strategies for improving ORR catalysts.

The ORR can be broken down into eight fundamental reaction steps [1,3,4]:

- 1) H_2 dissociation: $H_{2ad} \rightarrow 2H_{ad}$
- 2) O_2 dissociation: $O_{2ad} \rightarrow 2O_{ad}$
- 3) Direct OH formation: $O_{ad} + H_{ad} \rightarrow OH_{ad}$
- 4) O hydration: $O_{ad} + H_2O_{ad} \rightarrow 2OH_{ad}$
- 5) OOH formation: $O_{2ad} + H_{ad} \rightarrow HOO_{ad}$
- 6) OOH dissociation: $OOH_{ad} \rightarrow OH_{ad} + O_{ad}$
- 7) H – OOH dissociation: $HOO_{ad} + H \rightarrow 2OH_{ad}$
- 8) H_2O formation: $OH_{ad} + H_{ad} \rightarrow H_2O_{ad}$

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By including these fundamental steps into an overall ORR mechanism, we distinguish three chemical processes:

- I O–O bond activation, which can occur via two reactions: O₂ dissociation (2) or OOH formation (5) followed by OOH dissociation (6)
- II OH formation proceeds via three reactions: Direct OH formation (3), O hydration (4), or H–OOH dissociation (7).
- III H₂O Formation: There is only one reaction (8).

Earlier we found that the O hydration step [4] in process II (OH formation) is probably the rate-determining step (RDS) for the ORR on Pt in solution with a barrier of 0.50 eV. O hydration has a lower barrier than direct OH formation (O_{ad} + H_{ad} → OH_{ad}) for pure Pt, making it the more relevant reaction to study. In the case of Pt alloys when the surface is 100% Pt but the second layer is not, the O hydration barrier was lower than direct OH formation (0.34 eV vs. 0.57 eV for Pt₃Ni) [3]. Therefore, O hydration is the more relevant reaction to study for the case of Pt-M-Pt sandwiches due to the 100% Pt surface which has shown a preference for O hydration over direct OH formation. It has been observed in experiments by Ertl et al. [5,6] and Campbell et al. [7]. It was also shown that the reactant, O_{ad}, dominates as the adsorbed intermediate above 0.7 V, while OH_{ad} dominates below [8,9], making this reaction more relevant at desirable potentials. This reaction does not have H_{ad} as a reactant, which makes it independent of potential. Calculations of potential dependent barriers require computationally expensive methods or complicated schemes that involve approximations of redox reactions and/or charged periodic systems [10–14]. This makes the O hydration step, an ideal barrier to focus on, as it is an experimentally relevant reaction that can be determined accurately.

The barriers for process I and III of the ORR connect well with the binding energy, whereas the process II shows poor coupling for pure metals due to the correlated binding energies [1,2] of the reactant (O) and product (OH). In our previous paper [1], we showed for very noble metals (Ag, Au), process I (O–O bond activation) is rate-limiting due to the large binding energy of the product (atomic O) compared to the reactant (O₂). On the other hand, for easily oxidized metals (Cu, Ir, Rh, Ni, Os, Ru, Co, Fe), process III (H₂O formation) is rate-limiting due to the large binding energy of the reactant (OH) compared to the product (H₂O). Process II is rate-limiting for Pt, because it has intermediate binding energy which makes both Process I and Process III very fast. Although Pt is the best pure metal catalyst for ORR, it can still be improved further by alloying it with metals in the 2nd layer that affect the binding characteristic of the surface Pt, so that Process II becomes faster.

As shown previously, the degrees of oxo-philicity (relative binding energy of O and OH) of pure metal catalysts are similar and their binding energies have been demonstrated to scale linearly. It is desirable to find an oxo-asymmetry index that specifically predicts the difficulty of process II. In this way, each of the three processes of the ORR can be improved by focusing on the following criteria:

- O₂ activation: High O binding energy.
- OH formation: High oxo-asymmetry index
- H₂O Formation: Low OH binding energy.

We have tested our hypothesis on 28 Pt-M-Pt (M is a transition metal) sandwich catalysts which consist of Pt on the surface layer, a transition metal in the second, and Pt in the bulk. Such catalysts display unique properties that improve the sluggish ORR in fuel cells [15,16]. It was shown for Pt-M-Pt (M = Ru, Rh, Pd, Re, Os, Ir, Pt) that the O and OH binding energies could possibly be non-correlated for these materials [1,17]. Thus, we seek to find cases of high oxo-asymmetry, and this class of catalysts was shown to display this property. In our previous work, we also found that a

position of the surface d-band center poorly estimates the binding energy of O and OH on pure metal surfaces [1]. Here, we would like to determine how well the d-band center correlates with the binding energy for the 28 Pt-M-Pt sandwiches.

2. Computational methods

Periodic QM calculations were carried out using the SeqQuest code [18,19] which employs Gaussian basis functions at the optimized double- ζ plus polarization level (rather than the plane-wave basis often used in periodic systems). We use DFT with the Perdew-Burke-Ernzerhof [20] (PBE) approximation of the generalized gradient approximation [21] (GGA) exchange-correlation functional. The up-spin orbitals are allowed to be optimized independently of the down-spin orbitals (spin-unrestricted DFT). The small core pseudopotentials with angular momentum projections are applied in our calculations.

The DOS structures were analyzed using the SeqQuest post-analysis code [19]. The bands are further broadened by convolution with a 0.5 eV FWHM Gaussian function to approximate the experimental Gaussian broadening and Lorentzian lifetime broadening. We applied the Nudged Elastic Band [22] (NEB) function of SeqQuest to calculate energy barriers of the intermediate reactions for the best and worst Pt-M-Pt sandwiches as determined by the index.

The calculated lattice parameter (3.97 Å) of the bulk Pt was used for all 28 Pt-M-Pt sandwiches. Surfaces are modeled as two-dimensional infinite periodic slab with four atoms per cell. The thickness of the slabs were three, four, or five layers with the top two layers relaxed. For the three slabs, the energy convergence was tested against thicker slabs to see that it was sufficient. Because of the Gaussian basis functions, a vacuum layer is not necessary for two-dimensional calculations. The real space grid density is 5 points per angstrom while the reciprocal space grid is $5 \times 5 \times 0$. The coverage for atomic O is 0.25 monolayer (ML) following experimental results [23]. The initial state of O hydration is 0.25 ML coverage atomic O with 0.25 ML coverage water co-adsorbed. The 0.50 ML OH coverage of the final O hydration state corresponds to the experimental coverage of 0.67 ML [24].

3. Results and discussions

Based on the binding energies (BE) of our previous calculations on pure metal surfaces (Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt, Au) [2], an oxo-symmetry linear dependence, $BE_{OH} = 0.667 \cdot BE_O - 8.17 \times 10^{-4}$, might be proposed to best fit the O and OH binding energies of these metals. Since the barrier for the OH formation does not significantly vary with different pure metals [4], the line plotted for the twelve pure metals with BE_O as the x-axis and BE_{OH} as the y-axis, is the baseline for correlated binding behavior of pure metals. This line is a combination of both the O and OH binding energy difference ($BE_O - BE_{OH}$) and ratio (BE_O/BE_{OH}). The small 8.17×10^{-4} eV y-intercept shows that the BE_O/BE_{OH} ratio is the dominant correlation. To measure the degree of non-correlated O/OH binding energy in the Pt-M-Pt sandwiches, we plotted the O and OH binding energies of each Pt-M-Pt sandwich (Fig. 1 and Table 1) to determine how far it is from the line for the pure metals. From Fig. 1, we can conclude that the previously observed non-correlated O and OH bindings for some Pt-M-Pt sandwich catalysts [1,17], are not a universal trend. Although there exist several catalysts that are far from the main line, the general trend is that the O and OH binding energies of all 28 Pt-M-Pt sandwich catalysts average out to the main line. This differs from our previously published result that compared just seven Pt-M-Pt sandwich catalysts with Pt-group metals (Ir, Os, Pd, Pt, Re, Rh, Ru) in the cen-

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