Molecular bonding-based descriptors for surface adsorption and reactivity

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A B S T R A C T

Descriptors, quantities that correlate with catalytically interesting quantities, are widely used in computational catalyst screenings. For example, adsorption energies of atomic species (O, C, etc.) are often employed as descriptors of catalytic activity, in conjunction with appropriate scaling and Brønsted–Evans–Polanyi relations. While very successful in terms of their predictive value, the reaction-specific *mechanistic* insight gained from such relations can be limited since adsorption energy descriptors often correlate indirectly with catalytic activity. To this end, we have developed a novel class of descriptors based on molecular bonding, characterizing the intramolecular bonding of adsorbed reactants in terms of two-center bonding derived on the basis of Natural Bond Orbital analysis. We demonstrate this approach by examining a diverse set of reactions across a variety of transition metal surfaces. We find that these bonding-based descriptors have a direct connection with the surface–adsorbate interactions that mediate catalysis, explicitly treating the bond breakage/formation that accompanies the rearrangement of atomic contacts. In many cases, we can interpret these interactions in terms of adsorbate "pre-activation", reflecting the intrinsic locality of surface reactions. We anticipate that this molecular bonding-based approach can help elucidate more comprehensive mechanistic insight into surface-catalyzed reactions and facilitate the unification of concepts from homogeneous and heterogeneous catalysis.

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1. Introduction

Efficient screening procedures play a critical role in the discovery of new heterogeneous catalysts due to the substantial cost (in both time and money) of traditional catalyst discovery and optimization. Consequently, substantial progress has been made to enable both high-throughput experimental [1–3] and computational [4–6] approaches. This screening is facilitated by models that relate difficult-to-obtain properties (e.g., turnover frequency) to simpler "descriptor" properties. Generation of these descriptors relies on mechanistic insight into adsorbate–catalyst interactions at the atomic level [7,8]. The resulting descriptor-based models enable rapid identification of promising candidate materials, which can then be studied with more quantitative approaches.

Use of descriptors in modern computational modeling relies upon the existence of surface correlations relating the descriptor quantity to some other quantity of interest. An important example of one such correlation is the scaling relationship between adsorption energies of variably hydrogenated species of a given atom on metal surfaces [9]; such scaling relations have also been found for

various metal carbides and oxides [10,11] and polyatomic adsorbates [12]. Recent studies have even found correlations between adsorbates bound to the surface via different atom types [13,14]. These correlations enable the prediction of the potential energy along a complete reaction path based on a handful of (usually atomic) adsorption energies [15].

Other correlations seek to establish relations between reaction thermodynamics and kinetics. Most notably, the Brønsted–Evans–Polanyi (BEP) relation [16–20] linearly correlates the activation energy, E_a, of a reaction to the reaction energy, ΔE, via

$$E_a = \alpha \Delta E + \beta, \qquad (1)$$

where α and β are reaction-specific, fitted parameters. Coupling BEP and scaling relations enables calculation of catalytic activity (via E_a) and a complete treatment of a reaction network based on a small number of adsorption energy descriptors [21,22].

These surface relationships also provide at least some *mechanistic* insight, beyond the minimum energy reaction pathway (MEP) that results from subsequent kinetic modeling. While the MEP identifies key intermediates for catalytic activity and selectivity, it often fails to highlight the relevant adsorbate–surface interactions that mediate each constituent elementary reaction, which (if understood) would paint a far more complete picture of the

catalytic process. In the case of BEP, the unitless α term modulates the similarity of adsorption contacts in the transition state and product structures, with larger values of α indicating later transition states [20]. The β term informs the structural sensitivity (e.g., varying effects of open- and close-packed faces) of the reaction [23]. The BEP α and β terms are thus seen to capture respectively the two traditional roots of surface catalytic activity, electronic and structural effects [23]. Electronic effects reflect the ability of surface atoms to bond to atoms that would be otherwise bare in the gas phase; changing this bonding will variably affect the energy of both transition and product states. Structural effects arise from the relative positions of surface atoms and their resulting capacity to satisfy the valency of the various atoms of the transition state [24]; a surface with a relative positioning of atoms uniquely capable of coordinating the transition state would give a distinct BEP relation with a lower β value.

Unfortunately, additional reaction-specific mechanistic insight is often difficult to obtain. Studies have shown a wide level of universality in BEP relations [25]. For example the dissociations of O_2, CO, NO, and N_2 on all close-packed metallic faces [fcc(111), fcc(100), bcc(110), hcp(0001)] can be modeled with a single BEP relationship [26]. While advantageous from a screening point of view, such universality hints at the challenge in extracting specific chemical or mechanistic insight. Similar universality has been found among dehydrogenation reactions of a vast array of molecular species [27], indicating that BEP relations are only capable of distinguishing broad reaction classes [25]. It should be noted that reactions over transition metal oxides show a variety of distinct BEP relations dependent on surface structure and reactant, indicating the possibility of reaction-specific information [28].

Alternatively, one can envision descriptors based on the *local electronic structure* of the catalyst and/or adsorbate. Such descriptors have been applied to a variety of surface processes: electrocatalytic perovskite reactivity based on cation d-orbital occupancies [29,30], bulk metal catalytic activity related to Slater-type orbital characteristics [31]. Ideally, one may expect these descriptors, motivated by intuition regarding the underlying chemistry, to have a more fundamental and direct connection with reactivity. Deployment of such descriptors would necessarily rely on new surface relationships that are purely chemical in nature and should yield additional reaction-specific mechanistic insight. The value of such localized relationships has actually been demonstrated by recent analysis of the localized bonding basis of scaling relations [13]. The original bond order conservation explanation [9] of scaling relationships was applied to different atoms with the same valency [13], for example O and S. Since each atom has the same number of valence electrons, the propensity of each to bond to a given metal surface will be related, which was interpreted in terms of the 8- and 18-electron rules common in molecular chemistry [13]. This insight then enabled the use of metal atom valency as a descriptor for adsorption energy [32].

We thus propose and apply surface relationships based on the *intramolecular bonding* of adsorbed reactants, utilizing the "Lewis-like" language of localized chemical bonds obtained via Natural Bond Orbital (NBO) analysis [33]. These bonding-based correlations have a direct (and in some cases perhaps even *causal*) connection with the surface–adsorbate interactions that mediate catalysis, explicitly treating the bond breakage/formation that accompanies the rearrangement of atomic contacts and reflecting the intrinsic locality of surface reactions. In this way, it is possible to obtain "electron-pushing" mechanistic insight, commonplace in homogeneous catalysis, for surface-catalyzed reactions. Such relations facilitate a natural quantification of adsorbate "preactivation," weakening of intramolecular bonding upon adsorption, and the elucidation of its role in subsequent reactions [34,35]. If paired with future kinetic modeling, such relations will provide explicit

molecular bonding-based descriptors. While these bonding-based descriptors will most likely not supplant atomic adsorption energies for high-throughput catalyst screening, they should prove valuable in providing a clearer description of surface reaction mechanisms.

While many algorithms exist to quantify chemical bonding [36,37], NBO analysis provides an explicit Lewis-like representation of the molecular electron density by analyzing the results of standard electronic structure calculations in terms of a localized bonding representation [33]. Delocalized molecular orbitals are converted to a picture of lone pairs and two-center bonds, quantified by associated electron occupancies. NBO analysis thus provides an ideal lens through which to view and analyze the bonding of reactants adsorbed on catalytically active surfaces. A comprehensive description of the NBO algorithm can be found in Ref. [38].

In the present manuscript, we propose and explore a novel class of molecular bonding-based surface activity relations, developed on the basis of NBO analysis. Using this approach, we examine the adsorption and dissociation of CH_3 and CO on the close-packed faces of bulk metals as example reactions with industrial relevance. These reactions serve as ideal test cases due to an established literature base and their varied chemical nature; the dehydrogenation of CH_3 involves σ-bond cleavage and preactivation via bond depletion, while CO dissociation centers on π-bonding that is weakened by donation of charge from the surface into adsorbate antibonding orbitals. CO dissociation on various fcc crystal faces is also studied to explore the effects of structural morphology. In both cases, our bonding-based approach offers a chemically intuitive description of adsorbate preactivation and paints a clear, insightful picture into the adsorbate–surface interactions that mediate catalysis. These diverse examples illustrate the generality and promise of such bonding-based descriptions of catalysis.

2. Computational details

All calculations were performed at the density functional level (DFT) of theory with a plane wave basis using the Vienna Ab Initio Simulations Package (VASP) [39–42]. The Perdew–Burke–Ernzerhof exchange correlation functional [43,44] was used for all calculations in conjunction with projector–augmented wave (PAW) pseudopotentials from the VASP database [45,46]. A plane wave cutoff of 400 eV was used for all calculations. In structural optimizations, forces on all atoms were minimized to within 5 meV/Å. Transition state searches were initiated using a nudged elastic band calculation of eight beads to approximate the reaction path [47,48] and subsequently refined using the dimer method until the forces on all atoms were below 5 meV/Å [49].

The $3d$ and $4d$ elements of groups VIII to XI served as the test set. These industrially relevant materials represent a chemically varied set with different crystal structures and magnetization. Since these factors may affect the observed trends [50], an additional non-spin polarized fcc treatment of Fe, Co, Ni, and Ru was also included. The resulting fcc set was used for all fits, although similar results are obtained in either case. This uniform treatment also enables analysis of specific fcc crystal faces with a wide range of materials. Optimized lattice constants were used for all metals to allow for a consistent treatment of all systems. Additional computational details can be found in the Supplementary Information.

Finite width slabs were used to model bulk metal surfaces. The bottom layers were fixed at their bulk position and the top layers relaxed under vacuum. The relaxed structures were then frozen for all calculations with adsorbates. For the fcc(111) and fcc(100) faces, four layers were used, with the top two free to