

Towards the development of single atom alloy catalysts as a means of escaping linear scaling relations

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The rational design of heterogeneous catalysts remains a formidable task, though if successful will pave the way to more efficient and effective catalysts. Linear scaling relations have provided important steps in advancing rational design, significantly facilitating the task faced. For example, the Brønsted-Evans-Polanyi (BEP) relationship correlates the binding energy of a species with its activation energy for a given chemical reaction, allowing for deductions to be made about a variety of catalytic surfaces based on fundamental surface adsorption properties.[1][2] The Sabatier principle connects the BEP relation to catalytic activity yielding Volcano plots which demonstrate that the most active catalysts must bind substrates strongly enough to dissociate reactants but weakly enough to allow for desorption.

Ab initio calculations, using for instance density functional theory (DFT), allow for the simulated study of important catalytic materials. Many such studies on metal surfaces have demonstrated the validity of BEP relationships for numerous simple chemical reactions, allowing for extrapolations and inferences to be made about more complicated, yet related systems. [3-6] The apparent universality of the BEP relation could on one hand be extremely useful in predicting the activity of a catalytic surface, though on the other hand will inevitably limit the prospects of catalyst due to the linearity between activation energy and binding strength.

Many of the catalysts that adhere to BEP type linear models often exhibit spatial homogeneity. Moving away from such surfaces, stepped or kinked surfaces as well as metal alloys have much greater spatial heterogeneity and in many instances still show BEP type trends, for example in the cases of pseudomorphic monolayers and near surface alloys. [7] In this study, we focus on alloys consisting of single, isolated metal dopant atoms dispersed in the surface layer of a host metal; these materials are referred to as single atom alloys (SAAs). High single atom dispersity in the surface of a SAA leads to unique strain and ligand effects unseen in pure metal analogues and many other alloy structures, giving rise to some counterintuitive surface binding properties. In addition, the high degree of spatial heterogeneity in the surface of a SAA may limit the description of its behaviour by simple BEP relations. It has been shown in several systems that SAAs can adsorb and

dissociate reactants at one site before facile spillover to the host metal allows for further reaction to occur [8-11].

We present a DFT-based study of nine SAAs formed from Au, Ag and Cu hosts doped with individual surface atoms of Ni, Pd and Pt. We investigate the chemistries of catalytically relevant bond dissociation reactions such as in the scission of C-H, N-H, H-H, O-H, C-C, N-N and O-O. Our results illustrate how strain and ligand effects contribute to the reactivity of the dopant atom, showing that different host metals can result in reduced or increased reactivity compared to the pure dopant metal surfaces. We demonstrate that isolated single atoms are sufficient for such chemistries and also allow for facile spillover onto host metal facets. Moreover, we rigorously evaluate the validity of the BEP relationship on each SAA for each process, determining the cause of any alloys not following a simple linear correlation.

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