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Heterogeneous catalysis: Optimal performance at a phase boundary?

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Summary

Most of the industrially used heterogeneous catalysts have been discovered by trial-and-error, and, despite decades of experience, discovery of new catalysts continues to be extremely challenging. The drive to uncover guiding principles in catalyst design is more present than ever. We share a series of observations indicating that optimal catalysts typically function at characteristic phase boundaries (e.g. abrupt changes in adsorbate coverage, catalyst structure, etc.) accessed in the reaction conditions. The catalyst exploits the associated instability – the desire to exist in multiple states simultaneously - as a driving force for chemical transformations. In other words, phase boundaries are good places to start the catalyst search, and indeed we should focus on at least two phases at once, rather than just one. We substantiate this claim with several studies that combine statistical *operando* modeling and experiment. Transpiring from these observations is a hitherto unrecognized vector in catalyst discovery.

1. Introduction

Catalyst discovery is hard. Trends relating catalyst structure or composition and function can be developed using experiments and theory, including on model systems. However, industrial catalyst formulation, together with the promoters and reaction conditions, have been mostly discovered by chance and optimization. Our favorite example is the discovery of PPM amounts of chlorine as a promoter for ethylene epoxidation catalysis on Ag, which occurred in the 1930's.¹ It was found as the plant used O₂ breathed from air and was upwind of a vinyl chloride plant, so in the right wind days selectivity went up from ~50% to ~80%. After a long search for reasons behind the boosted performance, the wind direction was found to be the only correlating factor, which then led to the finding of Cl in the air, which is used to this day in ethylene oxide production. Interestingly, the function of Cl promoters is still a subject of scientific debate, suggesting that the *a priori* identification of Cl promoters (had they not serendipitously been found) would still not be obvious, even with current theoretical tools.

While serendipity has been arguably the most successful strategy in catalyst discovery to date, machine learnt models predicting catalyst performance (based on experimental or theoretical data, or both) have recently gained interest. If enough appropriate descriptors are given to the model, along with training data sets, these strategies might uncover completely new catalysts. Much like we put effort into trying to understand the operational principal of a catalyst discovered via an experimental accident, we will then be interpreting the outcome of the ML model. Indeed, interpretable models are of the highest value to the scientific community as a matter of principle and basic curiosity. Undoubtedly, ML approaches are going to be useful in catalyst discovery or optimization, even though brute force in the computational sense. However, still, we do not believe it is time to give up on chemical logic and fundamental principles governing catalysis and guiding catalyst discovery. Despite the fact that it has been a difficult journey so far, we propose here that we might have been looking in a slightly wrong place or at least through the wrong lens all along.

We suggest that new catalysts should be identified not by looking at stable materials phases, but at phase boundaries, and at reaction conditions that can force the catalyst to exist at those

boundaries. We will illustrate this idea through several systems, where through realistic modeling of the catalysts and comparison to experiment, the optimum performing catalysts are not found in the middle of a stable phase on a phase diagram, but always at or near the region of particular instability, which furthermore is important for the given reactivity. With this perspective, it then seems most important for computational catalyst design to identify the correct phase boundary descriptors and the theoretical approaches needed to sample the boundaries.

2. Defining and Classifying “Boundaries”

We mean “boundary” or phase transition in a broadest sense. From the perspective of the system free energy, the chemical potential of reactive environments dictates the most stable/reactive active site state: structure, composition, electronic structure, and adsorbate coverage. Boundaries are where catalytic sites preferably co-exist in multiple states, and the rapid interconversion may drive turnovers. The boundaries are various forms of first order phase transitions, where an abrupt rather than gradual change in the system state occurs. Macroscopically, the change may seem gradual, because local conditions at the interface will vary.

We classify the boundaries as coverage boundaries (e.g. the preference of one adsorbate over another, or an optimum coverage allowing for labile adsorbates), stoichiometric (e.g. redox states or phase transitions), structural boundaries (2D vs 3D structure preference, or reconstruction onsets), and purely electronic boundaries (e.g. spin cross-overs, or topological phase transitions). More classifications of “phase boundaries” likely exist. Below we highlight examples of these types of boundaries and draw connections between the catalyst behavior at the boundary and why this provides optimum performance. We note that while researchers who study each of these case examples may recognize the boundaries and their coincidence with optimum catalyst performance – here we aim to bring these seemingly disparate examples under one umbrella to highlight this as a general perspective for catalyst design.

3. Adsorbate coverage boundaries

The influence of adsorbate coverage on catalytic chemistry and kinetics is ubiquitous.^{2,3} Rate laws derived for surface reaction mechanisms based on Langmuir Hinshelwood mechanisms and quasi-equilibrium assumptions result in adsorbate coverage dependent apparent activation barriers and reaction orders. In this picture, when there is a particular and constant rate limiting step, a high coverage of an adsorbate decreases the reaction order in the reactant that the adsorbate derived from (e.g. high CH^* coverage would decrease reaction orders in CH_4).⁴ In this scenario, the optimum catalytic rate is achieved over a material and at a reaction condition where the surface is on average $\sim 50\%$ covered by adsorbates, indicating the vicinity of a phase boundary.⁵

More interesting scenarios exist when finite coverage of multiple adsorbates is needed for optimal catalytic rates. In the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) the formation of a surface carboxyl intermediate (via $\text{CO}^* + \text{OH}^* \rightleftharpoons \text{COOH}^* + *$) has been proposed as a kinetically relevant elementary step. This requires finite coverage of both CO^* and OH^* , which derive from CO adsorption and dissociative H_2O adsorption.⁶ Coverage dependent microkinetic modelling demonstrated that Cu and Pt surfaces sit at either side of the boundary between optimum oxophilicity and carbophilicity, which are both required to enable finite coverage of CO^* and OH^* intermediates at relevant reaction conditions. A similar balance between CO^* and H^* adsorption coverage and structure have been proposed as crucial to enable CO insertion and chain growth during Fischer Tropsch synthesis on Co.² In a more

complicated example, catalysts that are optimal for vinyl acetate monomer synthesis from ethylene and acetic acid exhibit simultaneously high coverage of adsorbed ethylene and acetate.⁷ In each of these examples, catalyst design requires identifying surfaces that exist at the phase boundary that defines high coverage of 2 different adsorbates under the required reaction conditions.

In a final example, studies of the reactivity of multifunctional molecules (e.g. furfural or 1-epoxy-3-butene) have shown that selectivity in molecular activation can be influenced by coverage due to adsorption geometry.⁸ Furfural adsorbed on Pd(111) at low coverage results in decarbonylation to produce furan due to an adsorption geometry where both the ring and aldehyde bind to the surface. However, at saturation coverage an adsorption geometry with only aldehyde-surface interaction dominates (to maximize coverage) and thus furfural activation results in methyl furan (the desired product). Under catalytic conditions the reactant chemical potential controls coverage, and the understanding of coverage dependent furfural activation has been used to design catalysts that exist at this boundary in coverage.

4. Stoichiometric and redox phase boundaries in catalysis

Linked to the previous section is a very well-known concept in heterogeneous catalysis - a catalytic volcano relating the optimal adsorption energy of the key intermediate to the optimal catalyst performance. This concept typically assumes that materials spanning both overbinding and underbinding sides of the volcano do not change phase, but instead only coverage changes. For example, on the strong binding side of an oxidation reaction, it is simply assumed the surface would become “poisoned” by O, although this is typically derived from calculations on clean slabs.⁹ In reality, the strong binding side of the volcano plot will actually represent the transition in phase for an oxidation chemistry to a surface or bulk oxide, or to a surface or bulk nitride in nitrogen chemistry. Thus, the volcano plots actually have inherently assumed that materials which “teeter” on a phase transition between two stoichiometric phases would be optimal catalysts. Similarly, reducible oxides that easily form oxygen vacancies, which then serve as active sites, are also an example of a local stoichiometric instability at the site of the vacancy formation. Such vacancies can activate small molecules, such as CO₂, and also operate in tandem with supported metal particles creating active sites at the interface.^{10,11} These can be seen as specific cases of a much broader paradigm.

We posit here that stoichiometric changes in a material that are part of the reaction mechanism is best enabled when the conditions of the reaction put the material at the corresponding phase boundary, such as between (partially) oxidized and reduced phases in oxidation or reduction catalysis.¹² The implication for catalysis design is that the search should aim at the boundary between the two (or more) relevant phases that can co-exist in the reaction conditions that we try to tune.

4.1. CO₂ hydrogenation on Cu/ZnO catalyst

ZnO on copper is an industrially used catalyst for CO₂ hydrogenation to methanol. Many theoretical and experimental studies have been dedicated to finding the active site, and arguments have been made for it to be the Cu-ZnO interface, or the CuZn surface alloy.¹³ A variety of experimental and theoretical techniques have been employed, yet no consensus has been reached. There are also empirical findings such as that the optimal coverage of the Cu surface with ZnO is 0.2 ML, and that islands of ZnO are needed for catalysis, i.e. very small clusters are not active and ZnO itself is not a catalyst.

With the goal of finding the actual active phase of the catalyst, we studied in detail a model where the coverage of 0.2 ML and lower (0.14 ML) were achieved in a small enough unit cell manageable for DFT.¹⁴ We performed grand canonical global optimization of these clusters to

find the chemical composition of the interface under the CO_2 reduction conditions, simultaneously sampling the structure of surface Cu (allowing for partial oxidation, reduction, and alloying), Zn, and placement and content of O and H. We found that reaction conditions place material structure, composition and interactions in a very narrow phase on the phase diagram, and right near the boundaries of multiple phases. The structure is an extended hydroxide, i.e. neither the fully oxidized ZnO, nor a completely reduced metal cluster or alloy. However, the O and H content changes upon the slightest (local) perturbations to the conditions, or in the course of the reaction steps. This ease clearly is instrumental for the CO_2 hydrogenation catalysis (e.g. the O and H are labile and participate in the catalytic reaction). What is also exciting is that at decreased coverage of 0.14 ML, the system immediately collapsed into a CuZn alloy and surface hydride of Cu. This tells us that the optimal coverage of 0.2 ML is essential for the Zn to keep a critical volume to sustain its partially oxidized form. Having more Zn will probably start reducing the number of the active sites, by developing large volumes of ZnO. Thus, the composition/structure of the material and reaction environment place the system in a particularly reactive phase space.

Here, we would like to note that more precision in locating phase boundaries on phase diagrams can be achieved if entropic contributions and anharmonic effects are taken into account, with techniques that go beyond global optimization.¹⁵⁻¹⁷

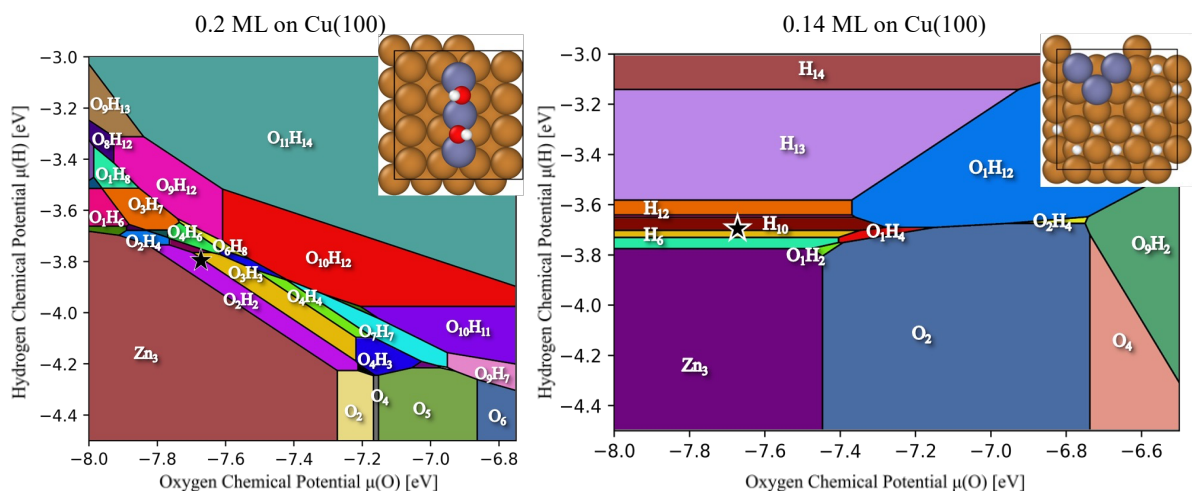


Figure 1. Zoom onto phase diagrams for Zn on Cu(100) at 2 different coverages: the stars indicate reaction conditions, the insets - global minima at the star, showing hydroxylation of Zn at 0.2 ML and a metallic form at 0.14 ML coverage.¹⁴

4.2 Oxidative dehydrogenation of propane on hexagonal boron nitride. In 2018, Hermans et. al discovered a series of borides that catalyze dehydrogenation of propane with remarkable selectivity toward propylene, only featuring different activity as a function of the element alloyed with boron.^{18,19} Interestingly, main-group element-based h-BN was found to be among the most successful catalysts. The unifying factor between all these materials being boron, it clearly appeared to be the active site. Soon, it was recognized that majority of the reaction is the gas phase radical process, and the surface plays the role of radical initiation.²⁰

Extensive characterization indicated that the surface becomes boron-rich, and covered in an amorphous layers of $\text{BO}_x(\text{OH})_y$ under reaction conditions.²¹ Importantly, B_2O_3 is not a catalyst, so the oxidation has to be incomplete for the catalyst to work. We first studied the phase diagram of h-BN, both the basal plane and the edges of a BN-stack, under reaction conditions, via grand canonical sampling with respect to B, O, and H (**Figure 2a**). The effect of temperature is included by expanding the ensembles of structures to have all thermally-accessible structures to each stoichiometry, which shifts the phase boundaries in the reaction-

relevant regime.²² The experimental conditions of catalysis, tuned by the Hermans' group through trial-and-error, roughly correspond to the outlined areas in **Figure 2a**, where multiple phases of the oxidized boron layer meet. The exchange of phases and sensitivity to the slight variations of $\mu(\text{O})$ (which can be local, due to the course of the reaction) can easily lead to stoichiometric changes at a very small energetic cost.

Based on these findings, we proposed several scenarios for the radical-induced propane ODH mechanism (**Figure 2b**). First, the B-B bonds at the interface between $\text{B}(\text{O})_x(\text{OH})_y$ and the boride, being the least oxidized and the closest to the elemental boron in the electronic structure, splits O_2 (a reactant), producing the $\text{BO}\cdot$ radical site that can turn propane into propyl, and launch the gas phase reaction. Itself, the site then becomes BOH , which can release H_2O and regenerate B-B bonds. Alternatively, the B-B site can split H_2O (a product), producing BOH and BH , the latter reacting with O_2 to create $\text{HCOO}\cdot$ in the gas phase. Notice how these types of sites exploit the ease of oxidation and reduction – a hallmark of a near-phase-boundary behavior, and the phase boundary is reached by the reaction conditions, again, found by trial-and-error.

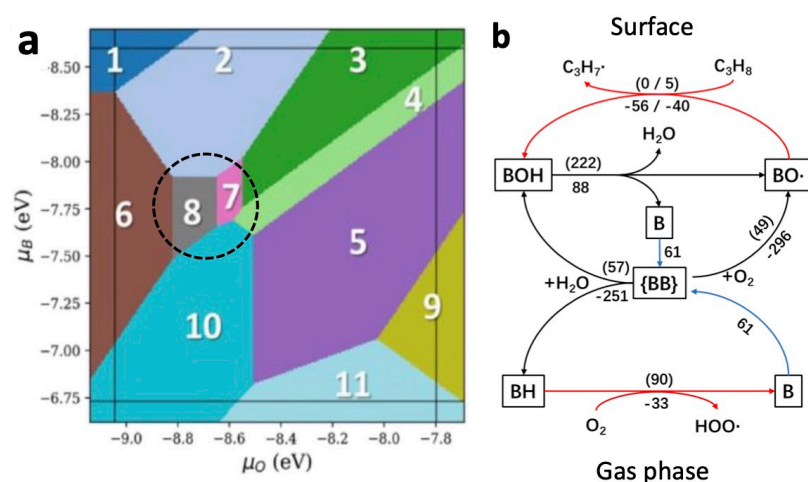


Figure 2. h-BN in propane ODH: (a) simulated phase diagram with the reaction conditions outlined, showing many different phases meet; (b) Proposed radical mechanism where “hot” surface sites are best at radical initiation. Adapted with permission from Refs. 18 and 20.

5. Structural transitions as a class of a boundary

5.1. Supported cluster catalysts – exploiting shape transition enabled by fluxionality

Supported metal and alloy particle catalysts are widely used. While such catalysts in practice are polydisperse, research of model catalysts that are prepared by size-selection or size-control offers great insight into what the most active particle sizes are. Indeed, size-selected model catalysts have been studied in surface science and *operando* experiments, and showed strong and non-monotonic size-dependence of activity.^{23,24}

Sub-nano cluster catalysts are also fluxional, featuring multitude of structures and stoichiometries in reaction conditions.^{25,26} Cluster catalysts operate as statistical ensembles of many states, each with a variety of exposed sites, which can dynamically interconvert on the timescales similar to that of the catalyzed reaction. Hence, this discussion embraces the ensemble paradigm.

One illustrative example is alumina-supported Pt clusters. They have been studied for the catalysis of several reactions, and particularly alkane dehydrogenation. Intriguingly, the cluster sizes of 7 or 8 Pt atoms have repeatedly been cited as the most active.²⁷⁻²⁹ He^+ ion scattering,

and CO TPD were both used to determine how many Pt atoms (and CO binding sites) are exposed at the surface of the cluster, and showed that right at the 7-8 Pt atoms-size threshold, there is a change of the cluster morphology from single layer to bi-layer (**Figure 3a**).²⁸ In other words, the Pt₇₋₈ cluster size puts the system at the boundary of a structural change. Indeed, thermally-accessible isomers of these clusters are of both dimensionalities. Cluster tendency to dynamically change shape across this shape-change boundary is relevant to the observed reactivity.

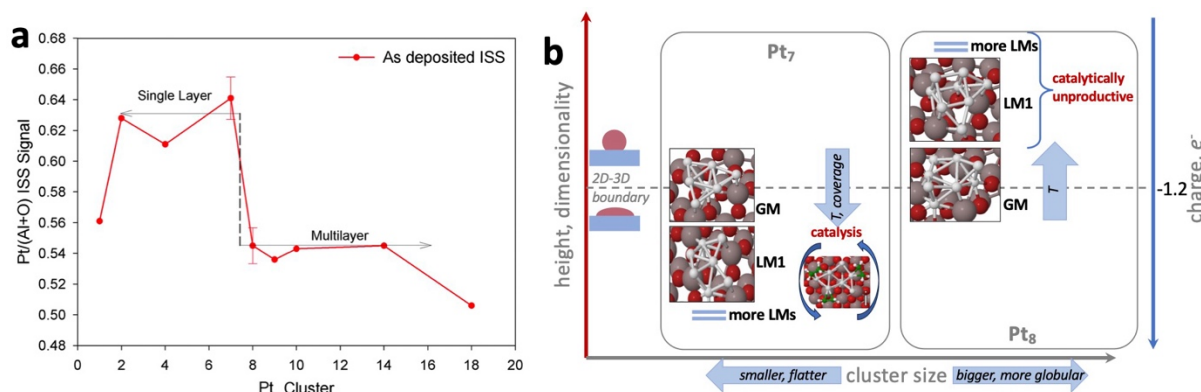


Figure 3. (a) He⁺ ISS showing dimensionality change for supported Pt clusters at the Pt₇₋₈ cluster size. (b) Pt_{7,8}/α-Al₂O₃ show different behavior upon exposure to high temperatures and coverages during ethylene dehydrogenation. Cold clusters in vacuum (the two GMs) both sit at the 2-D-3D boundary of structural transition. When exposed to reaction conditions, Pt₇ populates flatter and more reactive LMs, whereas Pt₈ accesses more globular and less reactive LMs.

For example, Pt₇/α-Al₂O₃ is much more active than Pt_{4,8}/α-Al₂O₃ for ethylene dehydrogenation.²⁹ Global optimization showed that supported Pt₇ and Pt₈ have very similar global minimum structures. However, higher temperature accesses 2-D minima of Pt₇/α-Al₂O₃, which extract more electrons from the surface, and feature stronger ethylene binding and dehydrogenation. In contrast, Pt₈/α-Al₂O₃ accesses only less active 3-D structures of lower reactivity. Hence, Pt₇/α-Al₂O₃ crosses the 2D-3D boundary to increase the catalytic activity, whereas Pt₈/α-Al₂O₃ is just on the 3D side of the 2D-3D boundary and cannot exploit the same 2D-3D instability to drive the dehydrogenation catalysis (**Figure 3b**).

Other structure-sensitive reactions may go better on Pt₈ instead, benefitting from the higher Pt-Pt coordination number of available sites that the system easily accesses amass, at elevated temperatures. For example, for CO oxidation Pt clusters with more well-defined facets are more active, likely due to decreased binding energy of CO and lesser poisoning.^{29,31}

5.2. CO₂ reduction on Cu and surface restructuring

Cu is the most effective catalyst for electrochemical CO₂ reduction reaction (CO₂RR), because it is the only metal that can reduce CO₂ beyond CO and to C₂⁺ products, albeit with poor selectivity. Interestingly, perfectly polished surfaces of Cu do not produce any CO₂ reduction products, and instead catalyze only the parasitic hydrogen evolution reaction (HER). However, after some time in electroreduction conditions, the Cu electrodes undergo morphological changes. First, Cu adatoms appear (**Figure 4a,b**), and eventually surfaces develop steps, vacancies, and small islands.³² Once roughened, the surface catalyzes CO-CO coupling and C₂⁺ production. In other words, the CO₂RR makes its own active sites.

Among the factors that promote surface roughening, adsorption of CO, H⁺, and O-containing species, under voltage and electrolyte, have been proposed.³²⁻³⁴ We sampled the geometry of the Cu (100) surface simultaneously with the CO and H coverage.³⁴ As a function

of the reducing potential, the preferred coverage changes sharply from CO-only to H-only. The surface does not exhibit reconstruction under either of these uniform coverages. However, in the metastable space of co-existing CO+H coverage, accessed only when we pushed the system over the kinetic barrier of coverage change, the Cu adatoms appear (**Figure 4c,d**). Interestingly, the potential at which thus roughened Cu can be accessed coincides with the CO₂RR onset potential – approximately -0.5 V. Again, the reaction utilizes roughened surfaces, accessed in conditions of structure-coverage instability.

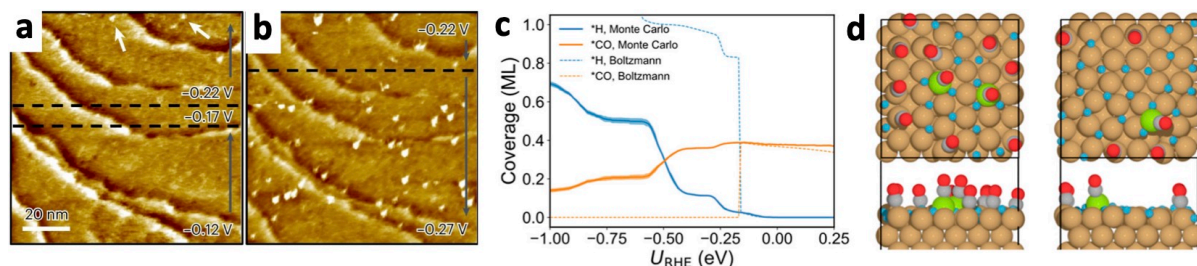


Figure 4. (a) in situ STM images recorded during potential changes from -0.12 to -0.17 and then to -0.22 V (a), further decrease to -0.27 V (b), in CO₂RR conditions, showing nanocluster formation. Quasi-kinetic Monte Carlo simulations of the surface structure and coverage evolution: (c) H and CO coverages as functions of electrochemical potential, from thermodynamics only (dashed lines), and with inclusion of kinetics (solid lines); (d) Notable structures with elevated Cu under a mixed coverage of H and CO. Color code: Cu-brown; H-blue; C-gray; O-red; and elevated Cu-green. Adapted with permission from Ref. 32 and 34.

6. Electronic boundaries

6.1. Spin cross-overs in atomically dispersed metal catalysts

Carbon-embedded Fe atomically dispersed metal catalysts exhibit spin cross-overs and multi-state reactivity, as was recently explicated theoretically.^{34,35} For oxygen reduction reaction (ORR) catalyzed by Fe single-atom supported on C₂N (C₂N-Fe), it is found that ORR is driven by electron transfer from Fe to O₂, and that the amount of electron transfer is affected by the electronic spin moments of the catalyst. The spin was varied computationally, and spin trended nearly linearly with the catalytic activity. Energetic access to spin state change in the process of the reaction is therefore a characteristic of a good ORR catalyst. Hence, a plausible design strategy for atomically dispersed metal catalysts can be geometric deformations achieved via local environment engineering, to bring the site closer to the spin crossover.

While this Article focuses in heterogenous catalysis, we note that in natural metalloenzymes, having an active site at the cross-over point between two or more electronic states is a known catalytic strategy. For example, in [NiFe]-hydrogenases, the protein macrostructure stabilizes a high-energy geometry of the active site where the singlet and triplet spin states are degenerate.³⁷ The spin change is required during the (de)hydrogenation reaction, and thus the constraint lowers the reaction barrier. Electronic state changes are also prominent in FeS clusters in biology, usually responsible for electron transfer.³⁸ In this case, the multitude of magnetic couplings creates many electronic states degeneracies, which the system exploits for electron transport – whatever the perturbative effect of the environment.

Here we note the DFT (whether pure or hybrid) is inherently limited in conditions of strong electronic correlation. Indeed, boundaries in the sense of electronic configuration change can coincide with Born-Oppenheimer surface crossings, which will not be adequately described by DFT.

6.2. Redox switching in atomically dispersed metal catalysts

Catalyzed reactions on supported atomically dispersed metal catalysts, which are used in various industrial applications,³⁹ share many mechanistic attributes with the redox properties of oxide/nitride/carbide/etc. surface described above and with organometallic complexes. For example, catalytic cycles on atomically dispersed metals typically involve oxidation state changes of the active metal center. Taking the classic example of alkene hydroformylation, the metal center (usually Rh or Co) cycles through +1 and +3 oxidation states via oxidative addition and reductive elimination steps.⁴⁰ The redox cycling induces a change in the preferred coordination environment of the metal center (e.g. square planar to octahedral for Rh^{+1} and Rh^{+3} , respectively) and thus enables the adsorption and reaction between multiple reactants at a single active site. Similar redox cycles likely exist for most chemistries on atomically dispersed metals. In this case, the phase boundary for catalyst optimization could be hypothesized as the metal center having equal preference to be in both oxidation states, rather than having a clear preference for one or the other, thus facilitating both the oxidation and reduction reactions in a catalytic cycle. This is also analogous to the boron example above that is easily oxidized and reduced.

6.3. Topological phase transitions in topological catalysis

Topological materials have nontrivial topologies of the electronic bands in momentum space within the bulk of the material. Due to symmetry or spin-orbit coupling, bands of different bonding character are allowed to mix, and opening band gaps in the material's bulk. At the materials surface, this band inversion has to get undone, with the band mixing getting forbidden again, the couplings going to zero, the gap between the states closing, and avoided crossings transforming into Dirac cones at the Fermi level. More complicated band structures may arise, such as nodal arcs. This undoing of the band inversion is referred to as the topological phase transition. The thus created topological surface states (TSS) are conducting, and protected by the electronic and geometric structure of the bulk. For this reason, they are expected to be robust to chemical or physical perturbations. An important and intriguing difference between topological catalysts and other types of catalysts is that in the former just one material's phase is enough to make a phase boundary: between a topologically non-trivial phase of the material's bulk and a topologically trivial interface. A wide variety of topological insulators and semimetals have been proposed as catalysts utilizing TSS.⁴¹ While not a traditional type of catalysts, topological materials offer an intriguing example of always being at a phase boundary, due to intrinsic electronic reasons. Thus, they always have potentially useful catalytic electronic states (so long as those do not get physically covered by majorly reconstructed passivating films,⁴² or get rehybridized under the applied electrochemical potential⁴³ in reaction conditions).

Progress and potential

Catalysis has often been understood in terms of balancing competing phenomena: bond breaking vs bond making; adsorption vs desorption; oxidation vs reduction, etc. Here we argue that the competing factors can sometimes be multidimensional and can adopt many different physical "forms", but that the idea of finding optimal catalyst by looking at boundaries in phases or behaviors is quite general. We draw parallels between boundaries in adsorbate coverage, catalyst phase, catalyst physical structure, and electronic structure. It is not surprising that the argument about the active sites of some of the most successful catalysts is ongoing. When several phase boundaries are just a small perturbation away, the result of surface characterization or theoretical exploration will vary drastically, depending on the details of experiments or calculations. We discussed multiple case studies where it seems that optimal

industrial catalysts may exist at particular phase boundaries (e.g. methanol synthesis, Fischer Tropsch), lending credibility to this perspective.

Thus, it seems like the most important initial endeavor in catalyst design is identifying the correct phase boundary. The interchanging phases accessible in conditions of a particular reaction that can take chemical advantage of this boundary is the catalyst design goal. The catalyst can start from a stable phase, but in the steady state it must reach a region of instability that is catalytically useful. Theoretical models should include grand canonical treatment in realistic conditions, and aim to reverse-engineer conditions that would place the system at a boundary desired for catalysis. New active, selective, and stable catalysts are needed in all sectors of chemical industry, and adding rationale to otherwise serendipitous catalyst discovery is a much-desired intervention. We are interested to see how the use of the “phase boundary” perspective may facilitate the design of new catalysts.

Biographies

Anastassia N. Alexandrova is a Charles W. Clifford Jr. Professor in Chemistry and Biochemistry, and Professor of Materials Science and Engineering in UCLA. She obtained a B.S./M.S. Diploma with highest honors, from Saratov University, Russia, her Ph.D. in theoretical physical chemistry from Utah State University, and was then a Postdoctoral Associate and an American Cancer Society Postdoctoral Fellow at Yale University. Anastassia joined the faculty of UCLA and CNSI in 2010. The focus of her laboratory is theory and computation for design and multi-scale modeling of functional materials: dynamic catalytic interfaces, artificial metalloenzymes, molecular qubits and their assemblies, and quantum materials.

Phillip Christopher is a Professor in the Chemical Engineering Department and the Mellichamp Chair in Sustainable Manufacturing at the University of California, Santa Barbara. He earned his B.S. in chemical engineering from UCSB in 2006 and his M.S and Ph.D. in chemical engineering from University of Michigan in 2011. Phil joined the faculty at UC Riverside in 2011 before moving to UCSB in 2018. His labs research interests are in sustainable chemical conversion, heterogeneous catalysis by supported metals, dynamic behavior of catalysts, and photocatalysis by metal nanostructures.

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Author contributions

A.N.A. conceived the idea and drafted the first version of the manuscript. P.S. added more example systems. A.N.A and P.S. collaborated on the finalizing the manuscript.

Declaration of interests

The authors declare no competing interests.

Resource availability

Lead contact: Anastassia N. Alexandrova alexandrova@g.ucla.edu

Materials availability: none

Data and code availability: none

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