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Non-equilibrium restructurings in catalysis: A chemical space odyssey

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Abstract

Understanding the working state of the surface structure is essential for practical rational design of catalysts. Yet, recent studies reveal that under reactive conditions, catalysts can undergo substantial restructuring—often dynamic, geometrically and compositionally complex—that escapes the reach of the conventional static view of catalysis. These phenomena often involve an ensemble of transient, irregular, and heterogeneous surface structures and require sampling a broader set of accessible configurations. Still, even this expanded view can fall short when the system is far from the thermodynamic equilibrium picture. This perspective reviews the growing body of experimental and computational evidence for such non-equilibrium restructuring phenomena. We categorize the scenarios where the system can be stranded, kinetically trapped in metastable regimes and never thermalize, as well as their physical origins. The restructuring arises not only from the intrinsic dynamics of the catalyst but also from the complex interplay with interfacial species, spawning a zoo of restructuring pathways of various chemical nature, sizes, and time scales. To meet the growing complexity, we outline promising directions in computational chemistry, machine learning, and integration with experiments. We call for a shift in perspective: to embrace complexity as a defining feature of catalysis, to not shy away from its inherent messiness, and to revisit deactivated or failed catalysts not as dead ends, but as rich, underexplored gold mines of mechanistic insight.

Introduction

Catalysis is the cornerstone of modern society, underpinning nearly every sector: from plastics to pharmaceuticals, and from fossil fuels to sustainable energy. By lowering activation barriers, it accelerates—or even enables—critical chemical transformations that advance our lives. Given the scale of the industry, even small gains in efficiency can have a massive impact.

Modeling is the prerequisite for rational design. Past approaches in engineering have relied heavily on trial-and-error and empirical rules, and they has been useful for tuning known systems and improving upon old recipes. However, the empirics are often blind to the underlying physics and chemistry and lack the resolution to guide discovery in unfamiliar regimes or to understand the outliers. The advances in electronic structure methods in the past few decades, especially in density functional theory (DFT), have enabled first-principles investigation of surface science problems. Rooted in quantum mechanics, this approach offers insight into the geometry, thermochemistry, and electronic structure of the reaction intermediates on the surface.

Originating from the surface science community, these computational studies are typically done using slab models cut from bulk crystals, which represent the state of a single crystalline sample under ultra-high vacuum conditions or in ideal weakly interacting solutions.[1] For the consideration of cost and that most of the surface science systems being relatively clean, several key assumptions underlie most of the computational catalysis studies: (i) the system can access the thermodynamically most favorable facet or surface phase under synthetic and/or reaction conditions; (ii) the surface structure remains near-stationary and is largely insensitive to adsorbate coverage; (iii) surface sites are well-defined, uniform, and equivalent across the surface; (iv) adsorbates are uniformly distributed, well-mixed, and do not interact laterally; and (v) all reaction intermediates adsorb onto the same set of surface sites.

These assumptions and the derived design principles are largely valid for model catalysts that are more structurally well-defined and rigid. Hence, many computational frameworks based on these assumptions have been successful in understanding reactivity trends in a wide range of heterogeneous thermal and electrocatalytic systems, and have produced many straightforward design principles to guide the experimental discovery.[2]

However, it is becoming increasingly clear in recent years that these assumptions are far from universal. With the development of *in-situ*/*operando* characterization techniques with high spatial and temporal resolution, as well as advances in high-performance computing which enable large-scale configurational sampling, the restructuring phenomena have been observed and investigated both experimentally and theoretically in various seemingly ordinary catalytic systems.[3] In Fig. 1, we roughly map the restructuring phenomena into a space spanned by the extents of deformation of the surface atoms and the incorporation of adsorbates into the catalyst surface. In the lower left region, the catalyst surface stays rigid throughout the catalysis, and all chemistries are confined to the

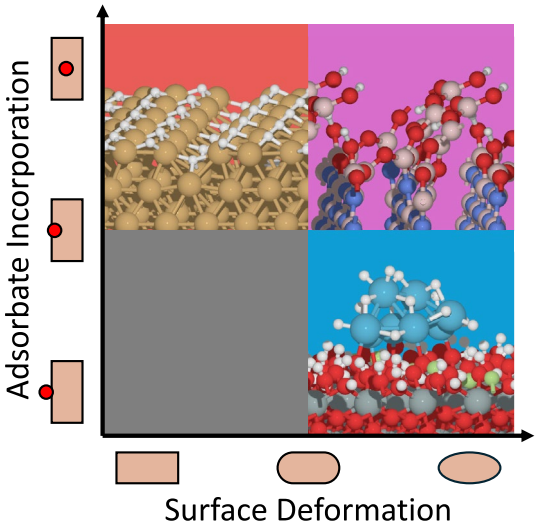

Figure 1. Categorization of restructuring patterns by extents of surface deformation and adsorbate incorporation. The top left, lower right, and top right inplots represent the systems in Refs., 6, 9, and 10 respectively.

top surface. This is where the conventional simplistic models have the most success,[4] which we will not elaborate on in this prospective. In the lower right region, the catalyst structure can significantly rearrange under reaction conditions. A representative system is the sub-nanometer metal cluster: they exhibit high fluxionality, reshaping in response to different reaction conditions and adsorbate coverages.[5] In the upper left, the system undergoes significant incorporation of adsorbates into the catalyst. A prime example is the copper surface in acidic electro-reduction conditions: at high H coverage, the surface forms an ordered partial hydride phase, featuring periodic surface corrugation and formation of subsurface H.[6,7] At the extrema of both factors is the boride surface in oxidative conditions: the surface B content reacts with oxidant to form a partial boron oxyhydroxide over-layer which is non-stoichiometric and amorphous.[8,9]

A complex and dynamic picture is unfolding before us: the structure of the catalyst can evolve beyond recognition in both geometry and composition; structures of active sites may deviate significantly from those found in ideal crystalline surfaces and obey no lattice; adsorbates are often non-uniformly distributed due to local surface deformation, lateral interactions, and fluctuations; and the system can be trapped in a metastable regime on catalytic timescales; the catalytic activity may come primarily, or even entirely, from the transient minority species that can only form under reaction conditions.[11,12]

This prospective article aims to provide a timely account of the recent findings in the space of complex catalyst restructuring, followed by forward-looking discussions on the challenges and potential pathways for reforming the *status quo*. We specifically focus on the system that exhibit drastic dynamics, compositional changes, and/or highly non-equilibrium behaviors. We will discuss why conventional methods are inadequate for treating these systems, how we may be able to address them, and the grand technical challenges along the way. We believe that including more complexity is crucial for not only understanding the outlier but also for designing next-generation dynamic catalysts or other functional materials.

Where ab initio thermodynamics fail

Identifying the surface structure of the catalyst is the very first step in a computational catalysis study. To estimate the relative stability of different surface facets and terminations, the catalysis and material science community has mostly relied on models based on thermodynamic metrics, i.e., ab initio thermodynamics.[1]

For nano-crystals, Wulff construction predicts the thermodynamic equilibrium shape and the area distribution of various facets according to the surface free energy. For surfaces of polycrystalline nanoparticles in reaction conditions, surface phase diagrams provide a map of the most stable surface phases as a function of temperature and partial pressures of gas-phase species. This involves not only the different facets of the original crystal structure but also different phases and stoichiometries.[13] This has been particularly successful in metals and oxides exposed to reactive gases at elevated temperatures, such as in thermal catalysis or catalytic combustion. Under electrochemical conditions, ab initio Pourbaix diagrams extend this analysis to include the effects of electrode potential and pH.[14] These diagrams further include surface states in aqueous environments, and even dissolved species of different oxidation states. They allow researchers to evaluate the stability of the surface, or to pinpoint or correlate likely surface composition and adsorbate coverage to given electrochemical conditions.

These thermodynamic-based models serve as conceptual maps that relate thermodynamic surface stability to chemical potentials, offering a starting point for modeling realistic catalytic interfaces. Construction of these diagrams often rely on a relatively small number of surfaces and adsorption configurations constructed from a set of known crystalline phases (taken from databases) and/or systematic permutations. This practice, guided by domain knowledge and intuitions, prescribes configurational constraints to cost-effectively capture the presumably relevant regions of the chemical space.

The crystal structure databases such as Materials Project[15] provide access to a large library of experimentally confirmed and theoretically predicted crystal structures, stable and metastable, across the periodic table. However, the restructured surface, often with low symmetry and non-stoichiometry, may not have any bulk counterpart, and the convenient constraints aforementioned would routinely break down. For those cases, we have no choice but to explore the relevant structures systematically. For relatively simple systems, a combinatorial study would be affordable. But for larger and more complex systems, we need highly efficient minima search algorithms to locate the relevant global and/or local minima on the high-dimensional and non-convex

potential energy surface (PES). If the system also significantly varies in composition, the chemical space of study will be a set of intersecting PES's of all possible compositions. The thermodynamic metric then becomes the grand potential Ω, i.e., grand canonical free energy, which is a function of composition of the catalyst and chemical potentials of chemical species involved in the catalysts. Ω spans a grand canonical free energy surface (FES) and allows for comparing thermodynamic stability of structures of different compositions.

The recent decade has seen a rise of global optimization algorithms for minima search of fluxional clusters and restructuring surfaces, many of them supporting varying compositions such as Grand Canonical Monte Carlo (GCMC),[16] Grand Canonical Basin Hopping,[17] and Grand Canonical Genetic Algorithm (GCGA).[18] They enable highly efficient autonomic exploration of the off-stoichiometric chemical space, suffering little human priori or bias. The samples from an extensive GC global optimization search, including global minimum and accessible local minima of each composition, naturally constituting a statistical ensemble of stable and metastable catalyst states.[11]

The grand canonical ensemble representation has provided valuable insights into various restructuring catalysts. By applying statistical models such as Boltzmann statistics, the population of every state in the ensemble can be calculated based on the Ω. Ensemble-based models naturally allow coexisting phases of similar energetics at the same set of chemical potential, revealing minority species which turned out to play a major role in reactivity.[8,19]

However, even if we are able to find every minima on the FES, the ensemble representation is still rooted in a thermodynamic picture. The population distribution of catalyst states is evaluated from thermodynamic metrics and can only reflect the scenario of global thermodynamic equilibrium. When the systems goes off-equilibrium, which can cover more systems than expected as we will elaborate on later, there can be qualitative deviation from the equilibrium distribution with chemical consequences (Fig. 2).

The fight between kinetics and thermodynamics has been studied extensively in nanocrystal shape prediction under different synthetic conditions.[20] In most cases, experimental efforts are made to bias the system into specific kinetic shape which is richer in high-index facets than thermodynamic equilibrium shape.[21]

The formation of a partial oxide over-layer on catalysts such as boride[19] and Ag[22] also has kinetic origin: if the catalyst were to follow the thermodynamics completely, it should fully combust in oxygen into a bulk oxide phase. However, these catalysts only undergo oxyfunctionalization in a few top layers, and O is unable to go deeper into the bulk region. This can be attributed to the strong O-surface bonds, leading to high barrier of inward diffusion and the tendency to form a protective oxide film over the surface.[23] Hence, the effective chemical potential of O, screened by the over-layer, suffers this kinetic penalty and becomes lower as we go deeper into the bulk.

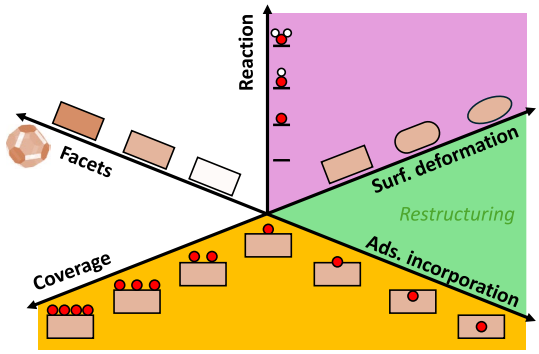

Figure 2. The degrees of freedom of a restructuring catalyst in operation. The boxes represent the catalyst surface and the spheres represent adsorbates and reaction intermediates.

The kinetics of reaction steps can also play a role in biasing the system out of its thermodynamic equilibrium distribution. For example, sub-nanometer Pt cluster forms a partial hydride in conditions of electrocatalytic hydrogen evolution reaction.[10] At higher overpotentials, thermodynamics predicts that the cluster should get further hydrogenated and eventually disintegrate into molecular Pt hydride, because the chemical potential of H is supposed to almost linearly increase at more negative potentials. However, this prediction overlooks the role of HER kinetics—at very high H coverage, the electrochemical and thermochemical formation of hydrogen gas from adsorbed H would increase significantly. This would not only directly deplete the H coverage, but also release hydrogen gas to increase its interfacial concentration and modify the effective chemical potential of H at the interface.

Copper in acidic electro-reduction condition is another system where the Pourbaix diagram fails to quantify the conditions corresponding to the surface phase transitions, although the surface phases can be identified. This is largely due to the complexity of the free energy landscape where the system need to travel a long path in the compositional space. To be specific, in acidic media, Cu surface can restructure into striped patterns[24] whose atomic structures have been identified from *ab initio* grand canonical minima search.[6] However, the Pourbaix diagram based on the sampled ensemble would fail to predict the onset potential of initial restructuring. This discrepancy is attributed to the non-ergodicity of the system in that it can only move locally in the coverage space (gaining or losing *H one-by-one) which limits its evolution and leads to kinetic and entropic (configurational) trapping in a metastable regime that is rich in local minima. These factors cause a "lagging" effect with respect to the thermodynamic phase boundaries in the Pourbaix diagram. In acidic CO_2RR conditions, thermodynamics predict that the Cu surface should be under either CO-only or H-only coverage at oxidizing or reducing potentials, respectively. At an intermediate potential, the GM of the system would switch from CO-only to H-only state. If the system were to be ergodic and fully equilibrate, then we would expect it to replace all surface adsorbates at

once, skipping all mixed coverage states in between, in a "teleporting" fashion. However, with multiple local barriers involved along the diagonal path in the coverage space, the whole progression is quite kinetically sluggish, which has been confirmed by ensemble-based kinetic Monte Carlo simulations.[25] The picture is similar in neutral and alkaline media where the system would be trapped in a metastable regime of mixed OH and CO coverage, which has been confirmed by in-situ Raman spectroscopy.[26] Within catalytic time scales, Cu surface would always be trapped within a metastable regime of surface roughening. Hence, systems alike (characterized by a discrete switching of the global minimum instead of a continuous shift) would respond to varying condition too slowly to reach the global thermodynamic equilibrium in time, rendering the thermodynamic phase boundary inadequate to predict the conditions corresponding to the reconstruction.

Some surface phase transitions are further dependent on nucleation motifs which can only form in surface regions with high enough local adsorbate coverage. The locality arises from fluctuation of adsorbate coverage distribution via a convolution of various adsorbate-related events:[6] Intra-surface diffusion of adsorbates tends to homogenize the coverage by smoothing out local fluctuations, effectively opposing the formation of high-density regions that could serve as nucleation sites. In contrast, exchange between the surface and the electrolyte–such as adsorption or desorption events—can introduce abrupt, localized changes in coverage even on a clean crystalline surface. These stochastic exchange processes can give rise to transient spikes in local adsorbate density, which are necessary for the system to access configurations of initial nucleation, even if the thermodynamic criteria have been met.

Sintering is another case governed by kinetics. The thermodynamic fate of any supported single atoms, clusters, and nanoparticles are all a sintered monolith, which is like the argument of "in the long run we are all dead." The tendency and rate of sintering are what really matters and they are dependent on the kinetic and entropic factors of particle fragmentation, diffusion of adatoms/clusters, and their coalescence over the support.[27,28] These elementary processes are highly diverse in size and time scales, and they are dependent on the combined effect of intra-metal and metal-support interactions.[29]

The ensemble representation is based on the assumption that the catalyst remains in a minimum-energy configuration throughout the catalytic cycle, i.e., structural restructuring occurs much faster than the catalytic events themselves. However, if the timescales of restructuring and reaction become comparable, significant coupling between the restructuring coordinate and the reaction coordinate can arise, leading to dramatic changes in both reaction thermodynamics and kinetics.[30,31] If, conversely, restructuring is much slower than the reaction steps, the catalyst structure can be treated as effectively stationary; yet, catalysis would proceed vertically from any point on the configurational landscape of surface structures. In this regime, non-equilibrium configurations, though transient, may exhibit substantially higher reactivity.

Stranding! in the metastable regime

In the following, we illustrate four different cases where the catalyst system is stranded in a metastable regime and unable to thermalize.

It is typical for fluxional systems to have multiple restructuring pathways, and then the evolution would be determined by combined kinetic and thermodynamic control. In Fig. 3(a), let us consider a system with three representative pathways: the first one (orange colored) is a minor elastic structural change with very low barrier, and the end state is near-degenerate with the initial state; the second one (blue colored) is a mild restructuring step with low barrier and being slightly downhill; the third one is a major surface phase transition involving a very higher barrier but with a highly stable end state. Under typical reaction temperatures, the major restructuring would be kinetically inaccessible, and the thermodynamic driving force for the minor restructuring would be too weak. As a result, the system would tend to mildly restructure and remain in that state, although it is neither the most downhill process or the one with the lowest barrier.

As reaction condition changes, the free energy landscape of the system would also evolve correspondingly, leading to altered relative thermodynamic stability of the minima and causing morphological changes. By including the condition dependence in the ab initio thermodynamics,

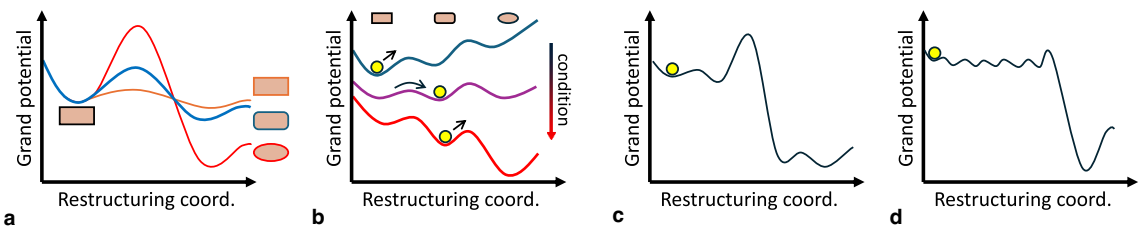

Figure 3. Scenarios where the catalytic system can be stranded in a metastable regime: (a) kinetic origin of mild but neither full nor no reconstruction; (b) local trapping in metastable regime causing lagged response to varying condition; (c) trapping in a metastable sub-ensemble due to high barrier separating two local fluxional regions; (d) entropic trapping in a vast and flat free energy landscape. Boxes represent the catalyst surface, and the yellow sphere represent the state of the system on the free energy surface.

condition-dependent phase diagrams can be constructed to identify which surface phases would be stabilized for any given condition. However, this approach usually assumes that the system can always access the global thermodynamic equilibrium as the reaction condition varies, which may not always be the case. Inherently, the effect of changing condition is rather local—the system at a minimum on the FES can only feel the changes in its local curvature, unaware of the changes elsewhere [Fig. 3(b)]. The response to changing conditions is hence more dependent on kinetics. In systems where restructuring involves significant local barriers along the way, the starting configuration may be kinetically limited, causing a significant lagging effect where the system requires a much longer time scale, or a stronger bias, to equilibrate to the new global minimum configuration.[6] In some cases, the system would equilibrate so slowly that it can be viewed as "stranded" in a metastable local free energy well in the catalytic time scale.[25] This effect can be highly relevant in catalyst with strong condition-dependent restructuring behaviors and in oscillating/pulsing conditions.

There are also fluxional systems that intrinsically have kinetically separated regions in the configurational space [Fig. 3(c)]. They usually feature multiple flat sub-regions that are separated from each other by high free energy "ridges" which are unsurpassable within catalytic timescales. As a result, the system would depend strongly on the initial distribution of configurations, as each state can only access its local sub-region. The system would then behave not as a globally equilibrated ensemble but a collection of locally equilibrated sub-ensembles. This effect is quite common for sub-nanometer clusters supported on strongly interacting substrates, where the cluster-support interaction imposes high barriers to the isomerization processes involving specific geometric changes.[32] As a result, initial configuration and the anchoring site dictates the sub-ensemble that it can populate and access. The division of sub-ensembles is also highly dependent on the coverage of adsorbate as they modify local bonds. Binding of merely one adsorbate can further change the effective barriers to reach thermal equilibration by up to 0.3 eV.[33]

The adsorbate-induced restructuring of extended surfaces typically involves not a single elementary step with a high barrier but a long sequence of many low-barrier events [Fig. 3(d)]. The barriers may be so low that one can be prompted to consider that they are negligible and the system can fully equilibrate. However, the whole process can span a very long path across the configurational space, whereas the system (behaving classically) can only access and move within its local region in the configurational space. Moreover, the evolution of the system is likely not a single path but a collection of many branching interconversion steps,[33] effectively creating an entropic labyrinth. In this case, the system would tend to spread out within the flat and expanse metastable regime, instead of forming one ordered global minimum phase. This phenomenon has been observed for various roughened[25] and/or amorphized[8,34] surface systems, which should form a single crystalline surface phase according to thermodynamics, but would instead form a messy mixture of metastable surface motifs.

Even if the system exhibit certain non-equilibrium characters as discussed afore, it is far from straightforward to identify the relevant regions in the configurational space which is too large for a strictly ab initio exploration.

In some fortunate cases, operando characterizations can inform key surface species or motifs,[6,7,19,35] based on which one can "prescribe" sub-ensembles ad hoc. Although a single collective variable to cover the whole restructuring event is usually lacking, the sampling of such prescribed regions can be achieved by biasing the minima search with some geometry- or property-based constraints.[31]

Otherwise, one can only rely on the ex situ characterization of the fresh and/or the spent catalyst for understanding of the starting and/or ending state of the restructuring. With no hint on the potential structural evolution pathways, an explicit kinetic simulation is needed. In addition, the restructured patterns and their early-stage motifs usually involve highly undercoordinated atoms, non-directional bonding, amorphousness, irregular sites, and local environments that are not well captured by common graph or lattice representations or homogeneous/mean-field treatments. Therefore, the low-cost cluster expansion or lattice kinetic Monte Carlo (kMC) methods would be less useful for these scenarios, and one would need an approach with minimal assumptions such as temperature-accelerated molecular dyanmics (MD) or off-lattice (or object) kMC which grow exponentially more expensive in the grand canonical ensemble.[25] Hence, a deep iterative integration between experiment and theory is especially crucial in making investigations on restructurings both effective and affordable.

No innocent species at the interface

Surface restructuring is not limited to the intrinsic dynamics of the catalyst itself, but is often strongly influenced or even driven by interfacial species and external stimuli. In realistic reaction environments, catalyst surfaces are rarely isolated—they constantly and dynamically interact with adsorbates, solvents, ions, and/or fields that can alter the free energy landscape, promote specific atomic rearrangements, and kicking the system into configurations that are otherwise inaccessible in cleaner conditions (Fig. 4). In the following, we will highlight the necessity of considering the full reaction environment, and

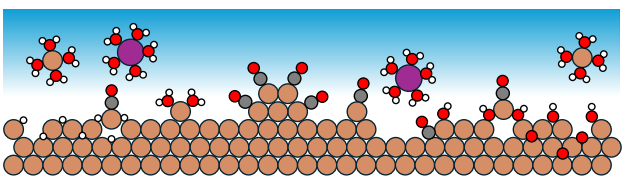

Figure 4. Schematic of a catalyst surface interacting with various species at an electrochemical interface.

its interdependence with the catalyst structure and dynamics, in capturing the full picture of restructuring phenomena.

Reactants can actively induce surface restructuring, sometimes far beyond simple coverage effects. In many cases, adsorption of reactant molecules would not merely occupy existing sites but initiate significant distortion in the surface structure, leading to reconstruction, faceting, or even formation of entirely new surface phases. This has been seen in cases only involving the simplest adsorbate of all, H, and even for extended surfaces.[36] These transformations are accompanied by major changes in both geometry, stoichiometry, and electronic structures, and these in-situ formed phases in many cases convert the catalyst into a different active species.[10] Such restructuring may be reversible by restoring the chemical potential of the reactants with a dynamic equilibrium between the bare-pristine and bound-restructured phases, or it can be irreversible if the formed phases are too thermodynamically or kinetically trapped or have propagated into surface structures of larger scales.[37]

During catalysis, reaction intermediates present at low coverage can act as potent drivers of surface restructuring. Certain intermediates, especially those that are polar and in high coverages, can strongly interact with undercoordinated surface atoms, displacing them and initiating cascade effects that propagate reconstruction.[25] Even if the intermediate is transient and in the minority, it can become enriched at induced structural irregularities in a self-reinforcing manner. In general, its restructuring influence can be highly site-specific, giving rise to spatial heterogeneity that evolves throughout the catalytic cycle.

Solvent molecules, particularly water, can play a significant role in driving surface phase transitions. In aqueous (electro-) catalysis, water dissociation products, especially hydroxyl, can interact strongly with surface metal atoms, stabilizing new surface terminations or transforming into hydroxide layers.[38] These solvent-induced surface phases typically have substantially different properties from the original catalyst surface, including altered oxidation states, coordination environments, or electronic structures. The interfacial solvation effects, which favors protruding and polar motifs, can also stabilize reconstructed surface phases, or promote local metastable surface species.[39]

Electrolyte ions are also not always spectators. In electrochemical environments, both anions and cations can interact with the surface via electrostatics to influence adsorption energetics and solvent organizations.[40,41] The change in adsorbate coverage and arrangement on surface can also alter the surface properties greatly.[37,42] The electrolyte ions can also directly bond to the surface with specific adsorption, which can In some cases, the ions, from electrolyte or as impurities, can incorporate or intercalate into the catalyst surface and cause major surface reconstructions.[43]

Different surface phases often exhibit markedly different responses to applied external fields. For example, supported metal clusters can undergo potential-dependent isomerization, driven by differences in the potentials of zero free charge (PZFC) and effective interfacial capacitance among isomeric states, leading to state-specific potential dependence of electronic-free energies.[5] Electric and magnetic fields can induce similar effects[44] by exploiting variations in polarizability and spin states between surface phases, enabling preferential formation or even operando switching of specific surface configurations.

In thermal catalysis, vibrationally excited reactant molecules can transfer substantial energy to the catalyst surface upon collision, facilitating enhanced surface fluxionality.[45] Such non-equilibrium energy transfer can transiently raise the local surface temperature and promote barrier crossing for restructuring events. This mechanism enables high-barrier processes to occur and metastable phases to form even under otherwise insufficient environmental temperatures. In photocatalysis, local surface structures can be brought into electronically excited states, enabling access to configurations that are otherwise unstable in the ground state. From a condensed matter perspective, the migration of hot charge carriers and subsequent recombination events can locally elevate surface temperatures and initiate redox dynamics, which may couple to surface restructuring processes.[46] The most extreme scenario might be plasma catalysis which involves not only vibrationally and electronically excited species of high kinetic energy but also various highly reactive molecular fragments. The top surface of the catalysts would hence undergo higher fluctuations in surface composition and geometries.[47] These effects are still not quite predictable in a generalizable way, as the efficiency of energy transfer depends on various factors such as vibrational mode matching, rigidity of the surface motif, and local binding geometries.

The crossroads of competing pathways

Restructuring is not a single process but rather an umbrella term encompassing a variety of phenomena with fundamentally different physical and chemical origins.[48] While the most stable state (global minimum) of a system is unique, the number of accessible metastable states is vast, especially under reaction conditions. These metastable configurations can interconvert through numerous potential pathways, each with its own energetic and kinetic profile, and the competition among these pathways can collectively influence the catalytic behavior. Rather than following a single dominant transformation, the catalyst may explore a dynamic ensemble of restructuring pathways that fluctuate across timescales of catalysis and contribute in aggregate to the experimentally observed activity and selectivity (Fig. 5).

A binary metallic alloy nanoparticle provides a clear example of such structural diversity, as it can exist in the form of a solid solution, intermetallics, core–shell configuration, or partial or full phase segregation, often kinetically controlled during synthesis. The relative thermodynamic stability of the configurations, as well as the kinetic barriers of their interconversion,

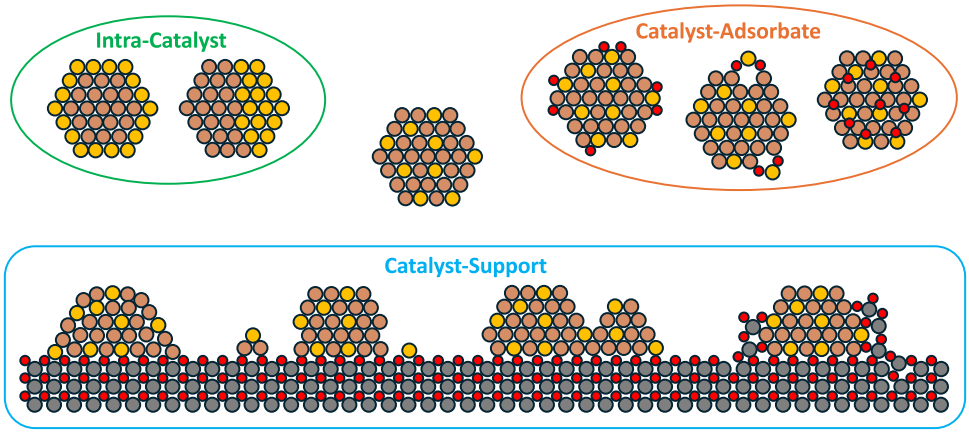

Figure 5. Schematics of various restructuring pathways that a crystalline alloy particle can take.

can be highly dependent on the reaction condition.[49,50] In the sub-nanometer cluster regime, the situation becomes even more complex, as the atomic arrangements are often ill-defined and deviate substantially from any bulk lattice order, resulting in unique, fluxional structures with fluctuating coordination environments that defy traditional crystal lattice-based descriptors.[51,52]

Some catalyst systems exhibit highly mobile behavior of the metal content during operation, particularly in the case of single-atom catalysts or metals with low cohesive energy. Depending on the reaction conditions and the reactivity of the catalyst surface, the metal content may undergo simple corrosion and loss,[53,54] or it may dissolve or fragment into smaller interfacial species which can later re-deposit, migrate, re-disperse, or agglomerate into larger-scale particles or surface patterns.[55,56] Sometimes, the dissolved or gas-phase species could be the primarily activity contributor.[19,57] The interaction between supported metal particles and their substrates adds further complexity: strongly interacting supports can distort or even partially "melt" the lattice of the supported metal, leading to highly deformed or liquid-like amorphous structures.[58] In some cases, even larger clusters can "hop" over the support under heavy coverage of adsorbates.[59] Certain reducible oxides can even undergo dramatic redox-induced structural changes, "climbing" onto the particle during redox cycling and encapsulating the metal to varying degrees depending on the operating conditions.[60] These processes may make or break the catalyst, depending on the reactivity distribution of the species that are spawned.

The time and size scales associated with these restructuring phenomena can span many orders of magnitude, from femtosecond-scale bond vibrations to macroscale particle reshaping over seconds or hours. These processes are governed at their core by the extent of geometric change, the strengths of bonds related, and the masses of the atoms involved. Atomic-scale events, such as bond breaking, atom hopping, or vacancy migration, can propagate cooperatively and give rise to larger-scale structural evolution, revealing a multiscale coupling between local chemistry and global morphology that is central to understanding catalyst behavior under realistic operating conditions.

The above discussion focuses primarily on geometric aspects, but it is equally important to recognize that surface atoms can also experience dynamic changes in charge states, which may strongly influence catalytic behavior. For instance, doped reducible oxide supports are known to exhibit dynamics in the charge and oxidation states of surface atoms, even when their geometric structures remain nearly unchanged.[61] These electronic dynamics can play a crucial role in mediating adsorption and activation processes. Similarly, oxide-derived copper surfaces, which retain subsurface oxygen species, show pronounced charge-state variability in surface Cu atoms. Under reaction conditions, these Cu centers can reversibly switch among metallic, +1, and +2 oxidation states at the interface, which contributes to both further morphological changes and catalytic selectivity.[62]

Chemical adsorption and desorption kinetics are highly dependent on the reaction condition, especially the temperature and partial pressure in thermal catalysis and electrode potential in electrocatalysis. Lateral diffusion of adsorbates is typically faster than the adsorption/desorption but can still exhibit a great variation depending on the mass (e.g., *H hopping is 2–3 magnitudes faster than *CO hopping) and the binding site/mode/strength (e.g., $*NH_3 > *NH_2 > *NH$ in diffusion rate).[63]

Regarding catalyst restructuring, the sub-nanoscale clusters are typically fluxional and can rearrange very rapidly within from picoseconds to microseconds, depending on the cluster size. However, on strong-interacting supports, some of the configurations may become inaccessible due to destabilization of rearrangement intermediates, leading to the local fluxionality phenomenon.[32] Extended surfaces typically rearrange much slower in timescales of from seconds to minutes, especially the ones operating at ambient temperature such as aqueous electrocatalysis. However, many common surface restructurings are collective phenomena and involve

atomic-scale species that can generate and diffuse very rapidly, such as the initiation and clustering of adatoms on Cu electrodes.[25] Even for larger-scale step edges of surface oxides, the distribution of restructuring barriers can still be as broad as 2 eV, with several low-barrier concerted modes that propagate the step growth,[23] so one should always be cautious and watch out for potentially low barrier even for seemingly large and rigid systems.

Reaction barriers can also vary greatly on different sites, leading to the possible complication of coupling with catalyst restructuring. However, the catalytically interesting sites typically feature lower barriers and are hence less likely influenced by the coupling. Therefore, it should be safe to assume a decoupled scenario for most of the catalytic systems. But for the coupled scenarios, we should be aware of the barrier reduction effect from the concerted progression along the reaction and restructuring coordinates.[64]

Due to the highly variable and often overlapping time scales of the processes involved, a full kinetic network of all events would be unaffordable even with the advanced sampling workflows and acceleration by machine learning. Hence, a unified and generalized framework to treat these disparate phenomena, and to judge which ones are relevant in catalytic time scale, is still far from realization. Studies of catalyst dynamics will likely remain as system-dependent and case-by-case community efforts in the near future. Nevertheless, deep dives into specific systems can identify the barriers and characteristic time scales of representative processes of different natures, based on which we can make safe assumptions about which species or processes can be treated as quasi-static or mean-field, so that we can focus on sampling into the catalytically relevant chemical subspace.

Turning a foe into a friend

Off-equilibrium restructuring occurs across all stages of catalysis, from the initial synthesis to the activation phase and ultimately to deactivation. During growth of a material, reagents are at a high chemical potential, akin to falling off a cliff, creating conditions that are highly non-equilibrium and dominated by kinetics rather than thermodynamics. In the early stage of nucleation, the seed is typically small and fluxional and can be driven away from its thermodynamic equilibrium by external manipulations. The selective shape or morphology of the resulting catalyst is then determined the kinetics of growth pathways, and the local availability of building units.[21] Understanding the earliest stages of nucleation is especially critical for funneling the system into desirable growth pathways that influence the long-term structure and function of the material.

Within the reactive environment, it is worth exploring how we can deliberately quench or bias the system into amorphous, or partially disordered states, or selected metastable phases with enhanced reactivity. This strategy hinges not only on the initial creation of these active configurations but also on the ability to kinetically stabilize them against structural relaxation during aging, storage, or catalytic cycles. Achieving this requires a detailed understanding of the energy landscape and identifying local minima that are both catalytically competent and sufficiently deep or kinetically isolated to resist transformation into more stable but less active phases over time.[12]

Configurational entropy and structural phase space can be powerful tools to trap a catalyst system within a broad thermodynamically metastable regime. In this context, amorphous and high-entropy catalysts offer a promising direction, as they inherently support a diverse ensemble of local environments that are difficult or impossible to stabilize in ordered bulk phases.[65] These heterogeneous motifs may individually be unstable but are collectively stabilized by entropy and mutual frustration, giving rise to a disordered but persistent structural state. The result is a cocktail of reactive sites with distinct geometric and electronic characteristics, each contributing differently to the catalytic performance and together offering a level of robustness and tunability that is inaccessible in conventional crystalline systems.

Instead of trying to completely suppress destabilization, we could also try to trap the system in a partially destabilized but still active state. For example, ensemble engineering by doping can make Pt clusters coke in a self-limited way so that the active species becomes a partial carbide which is stable upon catalytic cycling.[52] Cu–Pd alloy has also shown self-cleaning phenomenon, rearranging surface and subsurface atoms to refresh the surface of sticking adsorbates.[66]

In dynamic catalysis,[67] periodic modulation of reaction conditions—such as oscillations in temperature, potential, or gas composition—alters reaction energetics to drive otherwise difficult transformations.[68] This approach can also serve as a strategy to prevent deactivation events by continuously steering the system away from equilibrium, enabling reversible restructuring that can be harnessed to sustain or even enhance catalytic performance.[69] Its effectiveness hinges on the system's ability to adapt to external stimuli without settling into a static configuration, thereby broadening and rejuvenating the accessible phase space from early stages of deactivation. The success of such strategies depends critically on identifying and matching the characteristic timescales of reaction steps and restructuring processes, ensuring that restructuring remains responsive to the imposed dynamics without falling out of sync.[70] In this regime, catalysis becomes a matter of managing the temporal coupling between structure and function within a deliberately unsteady state.

Challenges and promises

The challenges in understanding and controlling catalyst restructuring span all major fronts—accuracy, chemical space, and timescale—each presenting fundamental and practical limitations across theory, machine learning, and experiments. These challenges are deeply interconnected and must be tackled in a coordinated manner to unlock predictive and design-level understanding of catalytic behavior under dynamic conditions.

In theory, key difficulties arise from the electronic degrees of freedom intrinsic to complex catalytic materials and interfaces. For transition metal systems in particular, spin states, oxidation states, multicenter bonding, and multi-reference characters complicate the landscape beyond what DFT can reliably capture.[71] Even many seemingly simple systems, such as adsorption of CO reduction reaction intermediates on Cu, have been shown to require many-body or multi-reference treatments.[72] A systematic yet efficient approach is needed to select representative configuration subspaces, especially as the number of metastable structures grows rapidly with system size and complexity. Estimating transition barriers within these intertwined regions also becomes exponentially difficult due to the combinatorial number of interconverting pathways. Moreover, there remains a fundamental gap in the formalism required to address non-equilibrium phenomena in catalysis, where steady-state assumptions no longer apply. Bridging this gap may benefit from borrowing insights and modeling tools from the fields of soft matter, supramolecules, and biophysics where stochasticity, non-linear dynamics, and fluctuation and dissipation are central themes.[73]

There are many analogies between heterogeneous catalysis relevant processes and biological systems, and similar challenges have long been tackled in living systems, where non-equilibrium dynamics and structural fluctuations are fundamental to function. Mechanical and biochemical non-equilibrium processes drive the activities of life across scales, from ATP-powered molecular motors to the evolution of species. Concerted by mechanics and chemistry, living systems exhibit phenomena that defy concepts of inanimate matter systems. Some self-organizing, non-equilibrium dissipative structures also exhibit organism-like behavior, therefore, active matter and bio- physicists have been applying physical analysis tools to describe biological phenomena.[74] For example, by adding a rotational flux component, landscape and flux theory extends potential energy landscapes to non-equilibrium systems to decompose the stochastic dynamics. This theory is used to illustrate the process of development and cell differentiation, to picture the evolution process under environmental constraints.[75] Similar methods may be applied to visualize how catalyst structure evolves in complicated, metastable environments. In many enzymes, folding and catalysis are co-dependent processes. Enzyme activity often requires transition among multiple conformational states that are modulated by binding, catalysis, or energy input. Theoretical models that couple reaction kinetics to conformational transitions, such as multi-state Markov models or energy landscape theory, have been used to describe such systems.[76] These are relevant to restructuring catalysts whose active states may be nonlinearly coupled to local geometry or oxidation state changes. Stochastic thermodynamics provides a framework to extend classical thermodynamics to non-equilibrium systems dominated by thermal noise and molecular fluctuations, such as molecular machines or enzymes. It allows quantification of entropy production, work, and energy dissipation at the level of single molecules. Stochastic simulation algorithms, such as the Gillespie Algorithm, are able to account for heterogeneity and allow exact kinetic simulation of macromolecules. These are also relevant in the modeling of surface catalysts, where individual atom events drive macroscopic change. Simulations of biomolecular processes often rely on coarse-grained models that preserve essential slow variables, compared to atomic models.[77] Enhanced sampling techniques—such as metadynamics, transition path sampling, or umbrella sampling—have been employed to explore protein folding, enzyme catalysis, and structural switching. These methods can offer guidance for sampling metastable configurations in restructuring catalysts. Reaction-diffusion equations are fundamental for describing spatiotemporal organization in reactive media, and were applied to study the filament assembly inside cells.[78] Models like the Turing mechanism and Gray–Scott model explain chemical patterning and instabilities could be applicable to adsorbate restructuring and localized phase separations on catalyst surfaces.

Machine learning (ML) is a highly promising avenue to address many of these theoretical and computational challenges. ML-based classification can help identify and organize the zoo of surface phases and local structural motifs, revealing latent patterns that might otherwise go unnoticed.[79] Another key contribution is in the identification of appropriate collective variables that effectively describe specific restructuring processes, enabling more tractable sampling of complex free energy surfaces.[80] ML interatomic potentials (MILPs) offer scalable acceleration in energy and force evaluations,[81] and recent efforts in training foundation models further reduce the need for training from scratch, opening doors for more generalizable applications or as a starting point for fine-tuning.[82] There has been many successful studies where MLIPS are used to conduct minima search or large-scale dynamics simulation of restructuring catalysts.[83,84] However, a systematic PES softening issue has been recently reported to cause inaccurate barriers, which was attributed to the undersampling of rate events and non-equilibrium structures in conventional MD-based sampling and active learning loops.[85] To sample more metastable, non-equilibrium, and amorphous configurations, temperature-accelerated MD may still fall short. Enhanced sampling such as metadynamics are efficient in sampling the transition state regions, but the performance is highly dependent on the choice of collective variable.[86] Global optimization techniques such as simulated annealing,[87] Monte Carlo,[88] and Genetic Algorithm[89] are more robust in proving consistent distributions of stable and metastable structures across multiple chemical systems, and it can be further boosted by grand canonical techniques to also cover a larger stoichiometric space.[18] On-the-fly active learning workflows with uncertainty quantification can be deployed in closed-loop simulations that adaptively explore the configuration space with minimal supervision. In addition, generative AI has shown strong potential in sampling new structures, outperforming conventional methods

like genetic algorithms and Monte Carlo in global optimization, transition state search, and inverse design tasks.[90,91]

On the experimental side, substantial progress is needed to achieve higher spatial and temporal resolution to capture the transient and localized features associated with restructuring events.[92] Surface sensitivity is critical, particularly for detecting the topmost atomic layers or specific motifs that drive reactivity, so that key signals are not overwhelmed by bulk contributions. Isotope labeling can be needed to identify the origin of species that induce off-stoichiometric restructuring.[93] Multimodal in-situ characterization, combining complementary probes, can provide more accurate structural identification and correlation with catalytic function. In-situ electron microscopy and ptychography provides atomic-level spatial resolution of catalyst structure and its evolution in reactive environment.[94] For electrocatalytic surfaces, electrochemical mass spectrometry (EC-MS) combined with Raman spectroscopy can identify the structure and quantify the coverage of key surface hydride phases.[95] Electrochemical atomic force microscopy (EC-AFM) combined surface-enhanced infrared or Raman spectroscopy can image the morphological changes of the surface while pinpointing the key surface species by spectroscopic fingerprints. Scanning electrochemical cell microscopy (SECCM) is another emerging technique to spatially resolve the reactivity of electrocatalytic surfaces,[96] and it can also be combined with mass spectrometry to yield mechanistic insights into complex electrochemical reactions.[97]

One should also stay wary of the impact of measurement methods on surface structure. For example, many nanocatalysts are highly sensitive to electron dose during operando electron microscopy, which can introduce a convolution of restructuring, damage, or transformations that are not intrinsic to the catalytic process. These beam damages may be mitigated by low-dose techniques or employing liquid helium for cooling, at the cost of resolution or operando functionality.[98] The identification of contaminant species can benefit from an explicit, honest, and detailed report of the environment where the sample is prepared, transferred, and whether/how the sample/holder was cleaned. X-ray spectroscopic methods, although usually considered as non-destructive, may still lead to radiation damage. Electrochemical methods can also suffer accumulation of reaction products or intermediates in the electrolyte, especially the nanopipette set-up in SECCM.

Regarding stability, the time scale of interest to the industry (years) is unaffordable and unpractical for lab-scale testing. This challenge calls for new methods to intentionally accelerate deactivation under well-controlled, harsher conditions, enabling extrapolation and prediction of catalyst stability under realistic operating environments in a rapid fashion. When integrated with computational tools such as forward spectroscopy/microscopy simulation, minima search, and kinetic models, the experiments can efficiently guide and be guided by predictive models.[99,100] This integration enables a synergistic feedback loop between observation and simulation, enhancing the efficiency and accuracy of mechanistic understanding with a higher confidence and in a more timely manner.

Conclusion

The landscape of catalysis, especially under dynamic and non-equilibrium conditions, is increasingly revealed to be a zoo of pathways and processes—formidable in complexity and vast in possibility. As we explore this space, it becomes clear that no single narrative or mechanism can capture the full picture. Instead, the challenge lies in identifying which processes matter under which circumstances. We cannot afford to arrive at the right answer for the wrong reason: overly simplified models or unrepresentative configurations risk misleading conclusions and losing potential design space, especially in systems that are far from equilibrium or structurally dynamic.

In the near term, the field will likely continue to progress through detailed, case-by-case studies, using ad hoc but insightful approaches to dissect individual catalytic systems. However, the long-term goal must be to extract transferable principles and broader trends from this complexity. Achieving this will require a shift in toolkit and mindset, toward community standards and workflows that are both affordable and extensible: algorithms that can customizably bias sampling toward relevant non-equilibrium configurations; low-cost ML models for rapid and accurate prediction of energy, force, and properties across the periodic table; and kinetic simulation architectures that can accommodate large, lattice-free, heterogeneous, irregular, and dynamically evolving systems.

Equally important is a shift in perspective: we need to study not only the catalysts that work, but also those that fail. Unstable, fast-deactivating, and/or morphologically messy samples may hold essential clues about catalytic resilience and transformation pathways. Anomalous and unexpected signals in characterization may in fact reflect important dynamics or minority species rather than noises or malfunctions. By embracing the complexity, rather than filtering it out, we may uncover the very principles that allow us to design better catalysts–not by avoiding the dirtiness, but by learning to work with it.

Author contributions

Z.Z. conceived the prospective and drafted the original manuscript. Z.Z. and X.Z. performed the literature review and edited the manuscript.

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Declarations

Conflict of interest

The authors have no conflict of interest to disclose.

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