Ensembles of Metastable States Govern Heterogeneous Catalysis on Dynamic Interfaces

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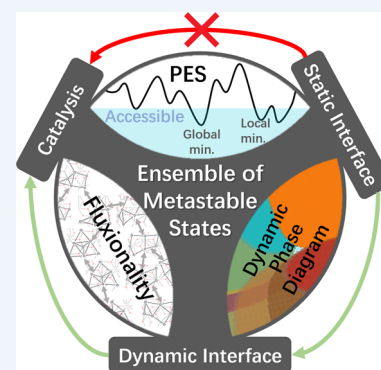
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CONSPECTUS: Heterogeneous catalysis is at the heart of the chemical industry. Being able to tune and design efficient catalysts for processes of interest is of the utmost importance, and for this, a molecular-level understanding of heterogeneous catalysts is the first step and indeed a prime focus of modern catalysis research. For a long time, the single most thermodynamically stable structure of the catalytic interface attained under the reaction conditions had been envisioned as the reactive phase. However, some catalytic interfaces continue to undergo structural dynamics in the steady state, triggered by high temperatures and pressures and binding and changing reagents. Among particularly dynamic interfaces are such widely used catalysts as crystalline and amorphous surfaced supporting (sub)-nanometallic clusters. Recently, it became clear that this dynamic fluxionality causes the supported clusters to populate many distinct structural and stoichiometric states under catalytic conditions. Hence, the catalytic interface should be viewed as an evolving statistical ensemble of many structures (rather than one structure). Every member in the ensemble contributes to the properties of the catalyst differently, in proportion to its probability of being populated. This new notion flips the established paradigm and calls for a new theory, new modeling approaches, *operando* measurements, and updated design strategies.

The statistical ensemble nature of surface-supported subnanocluster catalysts can be exemplified by oxide-supported and adsorbate-covered Pt, Pd, Cu, and CuPd clusters, which are catalytic toward oxidative and nonoxidative dehydrogenation. They have access to a variety of 3D and quasi-2D shapes. The compositions of their thermal ensembles are dependent on the cluster size, leading to size-specific catalytic activities and the famous "every atom counts" phenomenon. The support and adsorbates affect catalyst structures, and the state of the reacting species causes the ensemble to change in every reaction intermediate. The most stable member of the ensemble dominates the thermodynamic properties of the corresponding intermediate, whereas the kinetics can be determined by more active but less populated metastable catalyst states, and that suggests that many earlier studies might have overlooked the actual active sites. Both effects depend on the relative time scales of catalyst restructuring and reaction dynamics. The catalyst may routinely operate off-equilibrium. Ensemble phenomena lead to surprising exceptions from established rules of catalysis, such as scaling relations and Arrhenius behavior. Catalyst deactivation is also an ensemble property, and its extent of mitigation can be predicted through the new paradigm. These findings were enabled by advances in theory, such as global optimization and subsequent utilization of multiple local minima and pathways sampling as well as *operando* catalyst characterization. The fact that the per-site and per-species resolution is needed for the description and prediction of catalyst properties gives theory the central role in catalysis research, as most experiments provide ensemble-average information and cannot detect the crucial minority species that may be responsible for the catalytic activity.

Heterogeneous catalysis is the pivot of the modern chemical industry, enabling the efficient production of over 90% of all commercial chemicals.[1] Central to catalysis research has been the molecular-level insight into the catalytic processes, the state of the catalyst under the reaction conditions, and the nature of the active site. This insight has been enabled by the development of experimental and theoretical characterization techniques. Surface science methods such as XPS, XAFS, XANES, STM, and neutron diffraction, operating at low pressures, are used to characterize model catalysts and inform us about the elementary events possible at the interface. A subset of these techniques advanced to the *operando* regime, probing the state of the system under the reaction conditions. On the theory side, electronic structure, kinetic modeling, and computational spectroscopy give highly specific mechanistic details. The challenge for theory has been to have a realistic-enough model and accurate-enough electronic structure methods for the results to be
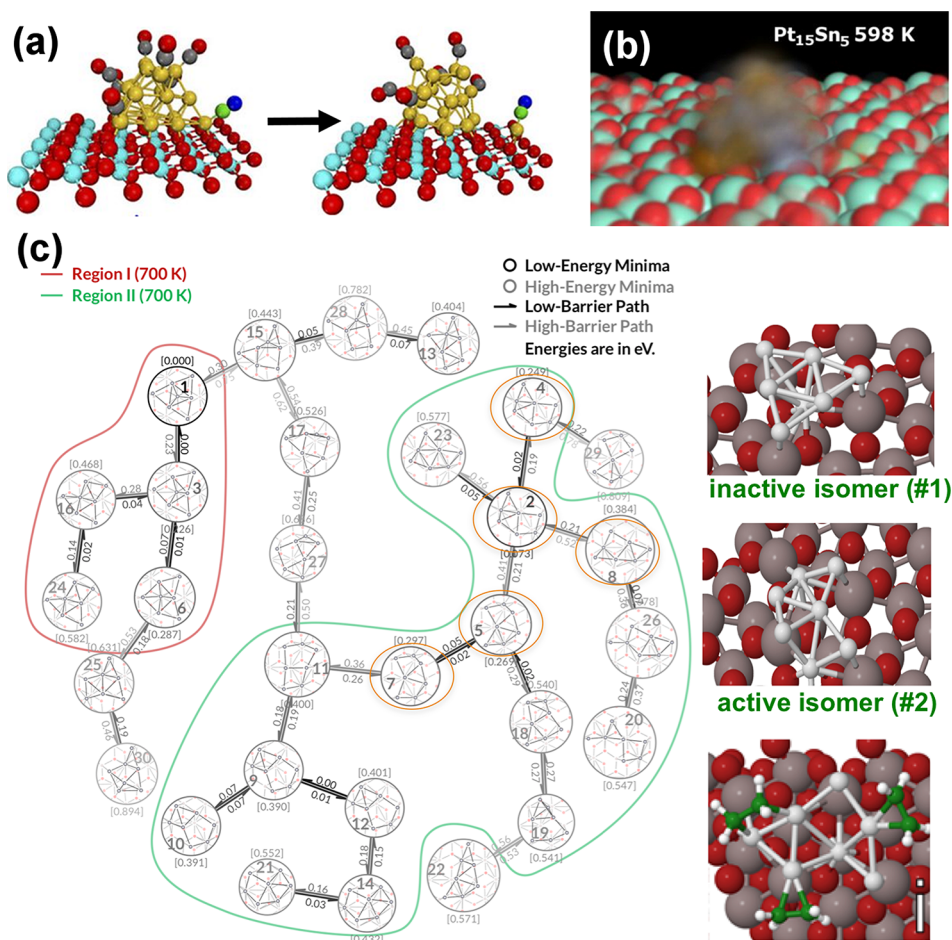
Figure 1. (a) Initial and final configurations from the MD trajectory of $Au_{20}/CeO_2(111)$ showing edge Au dissociating with the CO adsorbate. (b) Time-elapsed rendering of the DFT-MD trajectory of $Pt_{15}Sn_5/\gamma$-Al_2O_3 at 598 K showing the dynamic behavior of the cluster. (c) Thirty isomers of Pt_7 on α-Al_2O_3 accessible at 700 K, with minimal-energy paths forming the isomerization graph. The two lowest-energy isomers are shown in the inset, with the ethylene adsorption further favoring isomer #2. Reprinted with permission from refs 14, 10, and 16. Copyright 2015 Nature Publishing Group. Copyright 2018 American Chemical Society. Copyright 2003 Wiley Online Library.

reliable. Despite the known limitations, theory provided useful and complementary insights, trends, and suggestions to experiments in catalyst discovery.[2] Still, in some cases, the discrepancy between theory and experiment has been inconsolable and not always easily blamed on the error in density functional theory (DFT) prevalently used in catalysis research. Clearly our models are often insufficient.

The molecular view of the catalytic interface has been largely inspired by what surface science could probe and theory could affordably model: a largely stationary surface, a nanoparticle, or the global minimum (GM) of a supported cluster. This well-defined and stable structure of the interface has been presumed to be the active phase whose geometry would be largely maintained during the catalytic process. However, the real catalytic interface is subject to heat, illumination, electrochemical potential, and the pressure of reactants, products, and solvent.[3−5] Such conditions can bring a dynamic interface into motion, as was seen by *operando* measurements. Nanoparticles and nanostructured surfaces have been observed to undergo restructuring.[6,7] The interfaces supporting subnano clusters, or amorphous and understoichiometric surfaces, are even more dynamic because they have more unsaturated bonds.[4,8,9] Clearly, this motion should thermally populate new local minima on the free-energy surface of the catalyst, which could play a nontrivial role in catalysis. However, in most theoretical

studies, the PES is not thoroughly sampled, and only the GM or a few putative minima were desired and used in mechanistic calculation. Our contribution consists of the extension of the paradigm in catalysis modeling toward including those metastable catalyst states present under the reaction conditions and describing the interface as a statistical ensemble of many states, not just one. On this basis, we arrived at a number of surprising findings that now change our thinking about catalysis when the interface is highly dynamic. We largely focus on surface-supported clusters but venture into extended amorphous surfaces, and we describe how the paradigm also applies to more stationary interfaces.

■ DYNAMIC CATALYSTS ARE ENSEMBLES OF MANY DISTINCT STATES

Metallic clusters are held together by delocalized, nondirectional chemical bonds, causing structural flexibility and relatively flat and anharmonic potential energy surfaces (PESs). Geometries of clusters are easily influenced by atomic substitution, change in the charge or the support, and the adsorption of molecules. Most obviously, the structure can just relax upon adsorbate binding. We showed that clusters may also thermally cross small barriers separating the local minima, and the available minima and the barriers may change as a
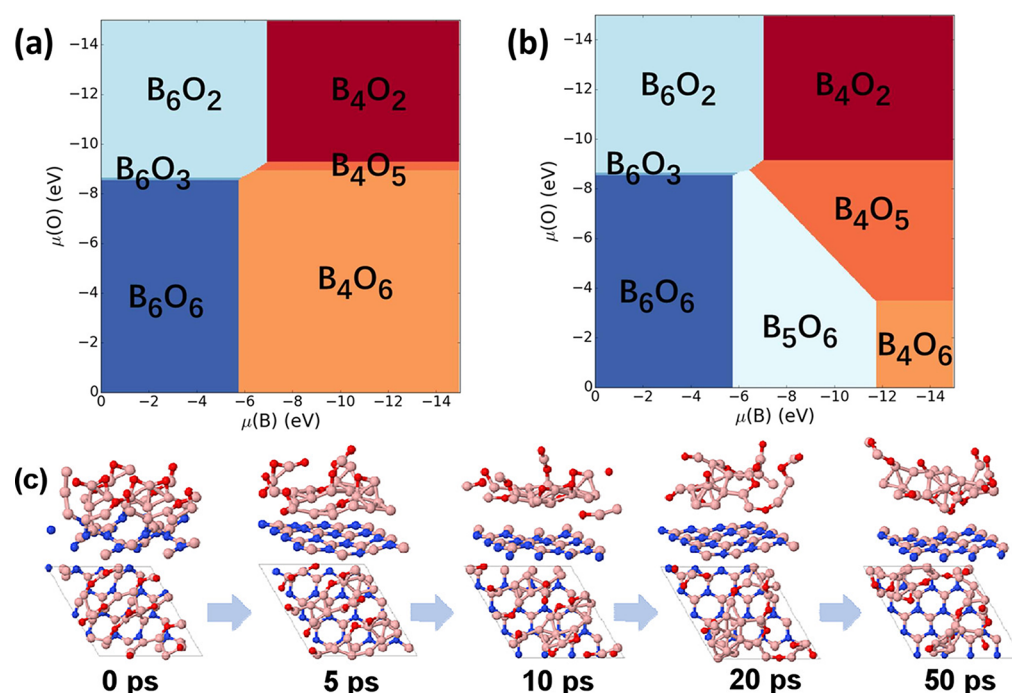
Figure 2. Phase diagram of the BO layer on h-BN at temperatures of ODHP as a function of $\mu(B)$ and $\mu(O)$, based on (a) GMs and (b) thermal ensembles of states of each stoichiometry. (c) Snapshot from a supporting MD simulation showing high fluxionality of the BO layer. Reprinted with permission from ref 21. Copyright 2019 American Chemical Society.

function of the bound adsorbates.[10,11] In fact, dozens if not hundreds of minima can be populated at catalytic temperatures (e.g., 300−700 K), which is a strikingly large number. The resulting ensembles of states may dynamically evolve during the reaction.[12]

Evidence for this kind of fluxionality exists in experiment and simulations. The in situ time-resolved structural characterization by energy-dispersive X-ray absorption fine structure (DXAFS) was used to demonstrate the CO-induced disintegration of Rh clusters on Al_2O_3 under 26.7 kPa CO at 298 K, occurring on the time scale of 0.8−3 s.[13] For supported Au clusters, the PES is apparently flatter and rearrangement time scales are shorter,[9] so ab initio molecular dynamics (MD) was able to show significant restructuring involving CO adsorption-induced dissociation of Au-CO entities to the support (Figure 1a).[14] Isomerization without disintegration was also filmed: Pd_4 clusters on graphene isomerize on time scales of seconds, leading to all accessible geometries coexisting at finite temperature.[15] The fluxional behavior of supported Pt and PtSn nanoclusters was demonstrated,[10] using a combination of DFT, MD, and XAS (Figure 1b). Note that the relatively long time scales involved in the fluxionality with barrier crossing generally limit the insight that MD can provide. The exhaustive sampling of the PES is necessary, and it gives a very rich picture of the states accessible to the catalytic interface. For example, Pt clusters on $\alpha\text{-}Al_2O_3$ access ∼30 distinct minima in under 1 ns (Figure 1c).[10] If this same $Pt_7/\alpha\text{-}Al_2O_3$ cluster is covered with adsorbates (e.g., ethylene[16] or hydrogen and alkyls[16]), as in reactions of dehydrogenation, then cluster shapes again change beyond recognition.

Although this Account extensively discusses catalytic clusters, structural fluxionality is characteristic of many amorphous interfaces and some typical amorphous supports.[17] In addition, perfect crystalline surfaces can become amorphous through heat or electrochemical treatment,[18] suggesting the

key role of surface dynamics under the reaction conditions. For example, hexagonal boron nitride (h-BN) came as a surprise as an earth-abundant catalyst in the oxidative dehydrogenation of propane (ODHP).[19] h-BN itself is inert, but under conditions of ODHP, its surface layer becomes partially oxidized amorphous BO_x.[20] Global optimization found many low-lying local minima of varying stoichiometries of BO_x on h-BN. On the basis of Boltzmann statistics, we constructed a "hot" phase diagram with respect to the chemical potential of O and B, where every phase is an ensemble of many states populated at ODH temperature (Figure 2a,b).[21] With the temperature and partial pressure of reactants changing, the distribution of states changes accordingly, and the phase diagram becomes dynamic. Specifically, stoichiometries with more thermally accessible metastable states get effectively destabilized at higher T, and phase boundaries thus shift. We further found that some specific electronic states of B (involved in B−B bonds and having atomic charge between those in boron oxide and elemental boron) appear on the interface only at high T.[21] We now have preliminary indications that those rare sites are catalytic.

Another relevant example is that organometallic complexes grafted on amorphous surfaces exist in diverse coordination microenvironments, each with slightly different activity. The Scott and Peters team developed elaborate approaches to identify the most active sites in this context and also realized that catalysis is likely governed by minority species in the ensemble.[22]

ENSEMBLES OF METASTABLE CATALYST STATES REDEFINE PROPERTIES OF THE INTERFACE

It is essential to capture the full vastness of the configurational space of fluxional interfaces because each populated local minimum can contribute uniquely to the activity and selectivity, and the effect of some metastable members of the
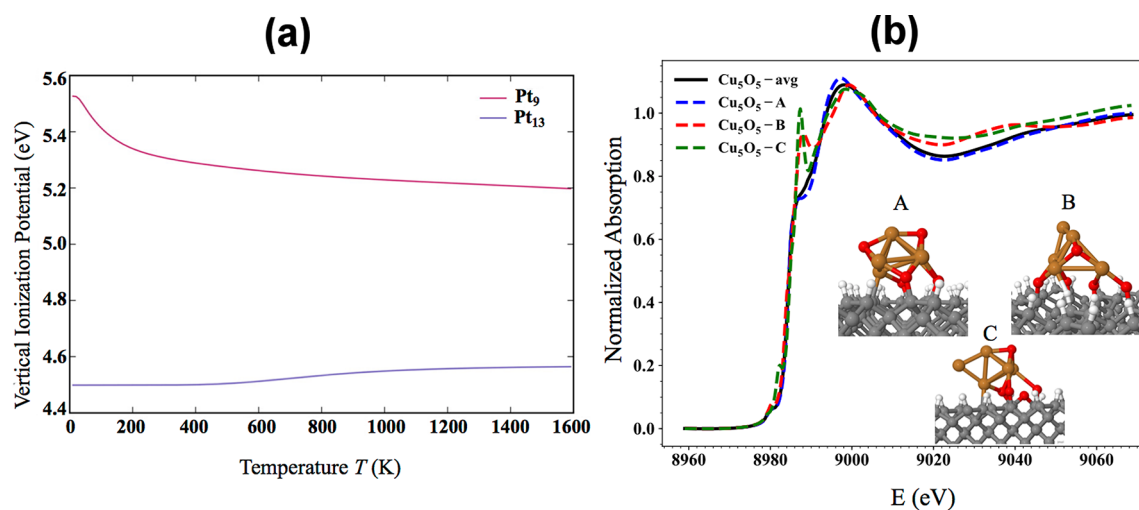
Figure 3. (a) Ensemble-average VDE for gas-phase Pt_9 and Pt_{13} as a function of temperature. (b) XANES of all thermally accessible Cu_5O_5/UNCD isomers (A–C) obtained from global optimization. The ensemble-average spectrum was calculated at 535 K. Reprinted with permission from ref 8. Copyright 2016 American Chemical Society.
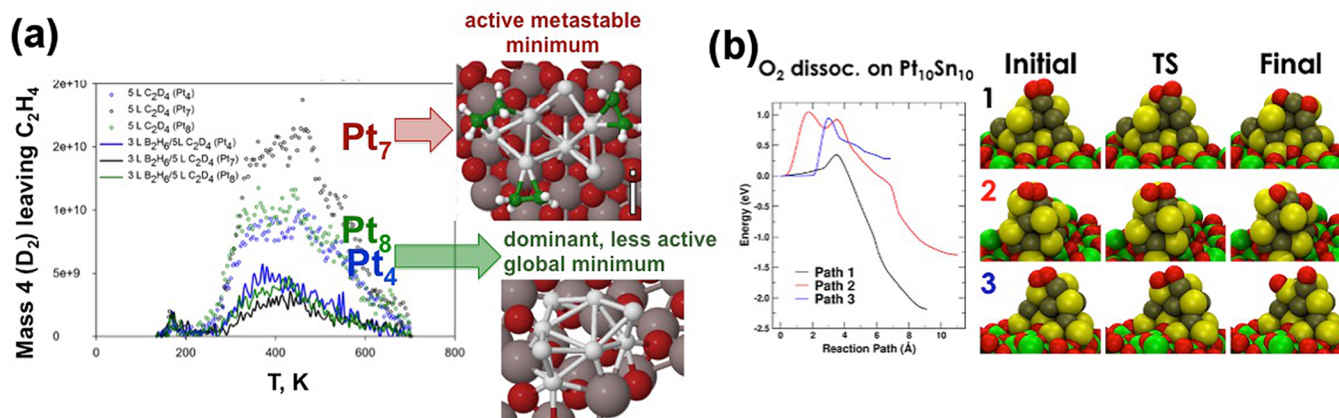

Figure 4. Effect of evolving ensembles of catalyst states on the catalytic mechanism: (a) Ethylene dehydrogenation on size-selected $Pt_{4,7,8}$/Al_2O_3 monitored via D_2-TPD shows Pt_7 having the highest activity; the effect was linked to the access of Pt_7 to higher-energy active isomers, in contrast to Pt_8. (b) Reaction paths for the dissociation of O_2 on $Pt_{10}Sn_{10}$ as a function of nanoparticle disorder show different behaviors, from exothermic to endothermic. Reprinted with permission from refs 16 and 28. Copyright 2017 American Chemical Society. Copyright 2014 American Institute of Physics.

ensemble may override the effect of the GM. These minima also affect other properties such as the binding configurations and IR spectra of the bound reactants, intermediates, or poisons.[8,16,23] Hence, it is essential that reactivity is also studied on the ensemble level. The contributions of coexisting structures to properties can be assessed statistically, and every property can then be described as ensemble averages. At elevated temperatures, the contribution of GM becomes less significant, while the local minima gain influence. The denser the manifold of accessible states, the more the properties of ensembles are temperature-dependent. If we assume no kinetic hindrance to minima population and that the system can sufficiently equilibrate, then we can apply simple Boltzmann statistics to calculate the probability of a minimum to be populated, P_i, as

$$P_i = \frac{Z_{elec,i} Z_{trans,i} Z_{vib,i} Z_{rot,i}}{\sum_i Z_i} \approx \frac{g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}}$$

where $Z_{elec,i}$, $Z_{trans,i}$, $Z_{vib,i}$, and $Z_{rot,i}$ are electronic, translational, vibrational, and rotational partition functions, respectively. Then, every minimum contributes to every property in proportion to P_i. Hence, any observable property of a dynamic cluster-decorated interface would form a broadened distribution, and the maximum would shift as a function of T.

A very simple example is the vertical electron detachment energy (VDE) calculated for the ensembles of Pt clusters in the gas phase.[8] The global and local minima for these clusters were found using a basin hoping (BH) algorithm operating on a neural network (NN) trained to represent the DFT PES. Every obtained minimum was refined with DFT, and duplicates were removed. The Boltzmann population probabilities were assigned to the minima. Entropy in the calculations was based on harmonic vibrational analysis and symmetry/degeneracy of the cluster forms, and the electronic entropy was ignored as the electronic excitations were beyond the thermal reach. The ensemble-average VDEs as a function of T are shown in Figure 3a for Pt_9 and Pt_{13}. It is apparent that the average signal shifts strongly with T, and the trend is different

for the two cluster sizes. Clearly, the VDE measured by *operando* photoelectron spectroscopy at higher T should not correspond to the VDE of the GM, and the computed spectrum would not reproduce the experiment unless it was based on the appropriate ensemble of states.

Ensemble effects can be electronic in origin. For example, recently it has been shown that the conventional representation of the static charge of a supported metal atom can be misleading.[24] Instead, several well-defined charge states of Pt can coexist and dynamically interconvert in CO oxidation on Pt/CeO$_2$(100).[24]

XANES is often employed to characterize cluster catalysts. We studied how thermally accessible non-GM isomers may contribute to the *operando* XANES spectra. Figure 3b shows calculated XANES spectra for UNCD-supported CuO clusters.[25] The shown isomers are populated at 535 K. A specific selectivity in cyclohexane dehydrogenation was observed. We found that the XANES spectrum is distinct for every isomer due to differences in the geometry and binding with the support. The average XANES is then an ensemble property (Figure 3b), but it closely resembles the spectrum of GM isomer A. We see that the *operando* signal can be heavily dominated by the most abundant species, which may not be the most catalytically relevant, as we show next.

■ EVOLVING ENSEMBLES AFFECT MECHANISMS OF CATALYZED REACTIONS

When a multitude of catalyst isomers coexist under catalytic conditions, any one or a few of them can be most effective in catalyzing the reaction, despite the potentially lower population in the ensemble. For example, we showed this in a joint theory−experiment study on ethylene dehydrogenation on size-selected Pt clusters on α-Al$_2$O$_3$ (Figure 4a). Pt$_7$ and Pt$_8$ exhibited markedly different activities (measured by TPD/R), despite similar sizes, as well as the computed shapes and electronic structures of the GMs. The size-dependent activity could be explained only when thermally accessible ensembles of states were considered. Pt$_7$/Al$_2$O$_3$ easily accesses isomers that are flatter on the support and draw more electrons from it. At 700 K, we predict the isomers of that flatter type to constitute more than 30% of the population. These more negatively charged isomers more efficiently activate ethylene toward dehydrogenation and are responsible for the avalanche of dehydrogenation events at higher temperature and ethylene coverage. At the same time, for Pt$_8$, GM is much more prevalent at all temperatures, while its higher-energy isomers are less negatively charged and thus less efficient in ethylene activation. Hence, as a function of temperature, the behaviors of the Pt$_7$ and Pt$_8$ ensembles diverge, and Pt$_7$ becomes more active due to the recruitment of more active isomers into the population. Note that while the "every atom counts" phenomenon in cluster catalysis has been known for a while,[26] theory did not provide an explanation for it. We showed that (at least for dehydrogenation on Pt clusters) the number and nature of the metastable states in the catalyst ensemble recruited under the reaction conditions can explain it. As another example, for the dehydrogenation of methane on gas-phase Pt$_{13}$, it was theoretically shown that the second-lowest-energy isomer has a significantly smaller barrier than the global minimum.[27] Rehr and Vila showed that, depending on the isomer of supported PtSn, the barrier to O$_2$ binding is markedly different (Figure 4b).[28]

The message is quite disheartening for surface science characterization, which measures an ensemble-average signal and thus mostly reports on the most abundant sites and may miss the weak signal from the important minority sites. New *operando* techniques with below-angstrom resolution for observing the atomic structures and improved time resolution used to capture the dynamics are required to investigate the true nature of the active site. At the same time, theory begins to play an ever more significant role in catalyst characterization since it has access to the per-site and per-state information about the system.

Clusters may change not just the shape but also the number and types of adsorbates and effective chemical compositions under catalytic conditions. For example, partially oxidized clusters of Cu and Pd deposited on various supports appear to undergo partial reduction at elevated temperatures, as judged by in situ XANES.[12] In collaboration with experiment, we showed that supported PdO clusters produce mainly benzene in ODH of cyclohexane, whereas CuO clusters produce cyclohexene at unprecedented rates.[12] For the selectivity on CuO/UNCD clusters to emerge in calculations, it is essential to capture their significant restructuring upon adsorbate binding and partial reduction at reaction temperatures. The Cu$_5$O$_3$/UNCD ensemble appears to be more prone to yielding cyclohexene than the fully oxidized Cu$_5$O$_5$.[12]

Even when the catalyst itself is more stationary and not prone to extreme dynamism, arrangements of adsorbed reactants, intermediates, and products can create diverse local environments. Lateral interaction among different adsorbates can change the system state and lattice configuration. The same chemical reaction becomes subject to a wide range of microscopic events, leading to significant differences in activity, selectivity, and even reaction pathways, which makes surface catalysis a complex multiadsorbate and multi-time-scale reaction network. To address this, Xu and co-workers proposed a method combining explicit diffusion-only kinetic Monte Carlo (KMC) with implicit KMC in the phenomenological kinetics (PK) form to account for lateral interactions among adsorbates in catalysis.[29] For the model system of ammonia decomposition, lateral interactions between adsorbed N are found to significantly affect the shape of the volcano plot and its maximum position, suggesting the need to include lateral interactions in the catalyst description and design. The number of adsorbates is another factor contributing to the state diversity. The cluster expansion (CE) is a theoretical framework used to treat multiadsorbate systems, and Schneider and co-workers approximate ternary CE as a linear combination of three binary CEs by fitting to the DFT database.[30] The three-binary-to-single-ternary (TBST) approach shows good agreement with results by full ternary CE, with the number of needed DFT data points greatly reduced.

Because the ensemble of the catalyst states changes as a function of the adsorbate(s), in the limit of full thermodynamic equilibration the free energy of every point along the reaction profile of a catalyzed reaction can be governed by a different catalyst state (with the state being a dynamic collection of many structures). The free energy and all ensemble-average properties of every intermediate would be defined mainly by the most stable and hence dominant species in the current equilibrium ensemble. On the other hand, every TS would be dominated by the most active and possibly less populated
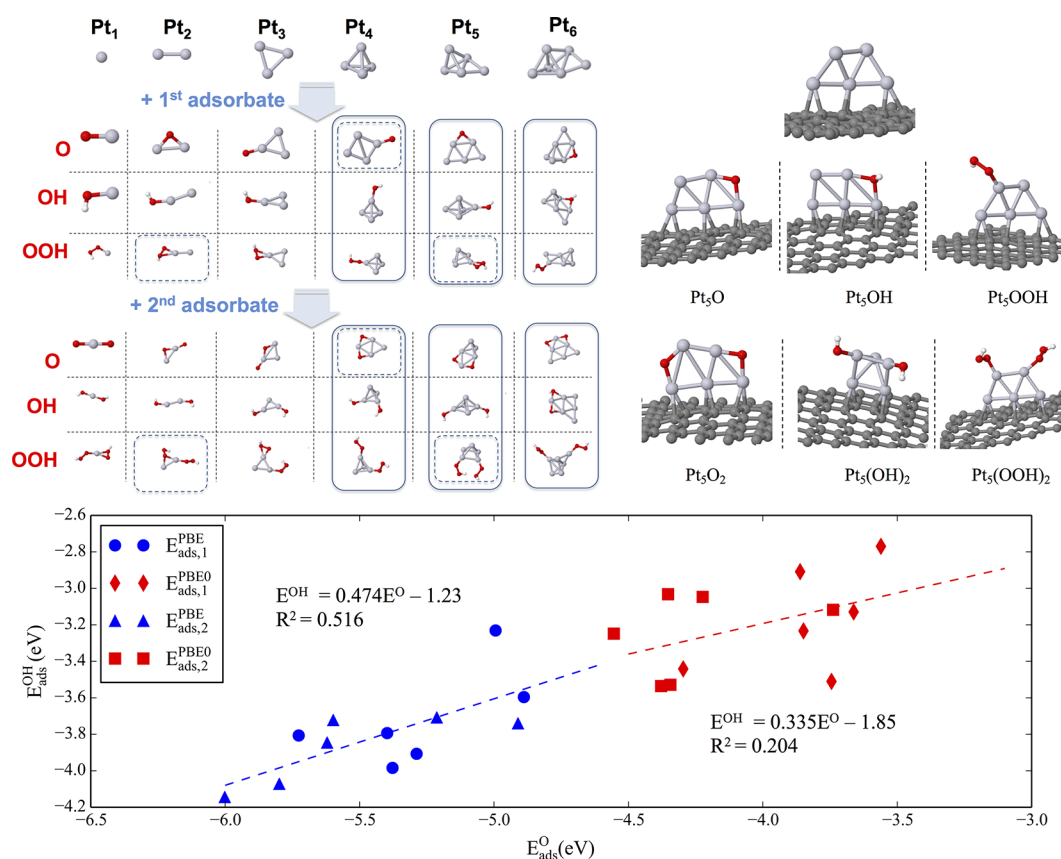
Figure 5. GM structures of gas-phase and graphene-supported Pt clusters with and without O, OH, and OOH adsorbates (TOP), and the poor correlation between OH and O adsorption energies using PBE and PBE0 functionals, illustrating the breakdown of scaling relations for fluxional clusters. Adapted with permission from ref 32. Copyright 2019 American Chemical Society.

catalyst states, whose contribution to the rate would be prorated by the probability of the species' existence.

One straightforward consequence of the different stationary points on the reaction profile being controlled by different catalyst states is the breaking down of scaling relations. The scaling relationships are linear correlations between the thermodynamic properties of chemically related species (including TSs) across different extended surfaces used in catalysis. These relations result in volcano plots, wherein the most active catalyst binds the adsorbate neither too strongly to not react nor too weakly to not bind, and then it shows up at the top of the volcano. These powerful relations allow the description of catalytic systems by simple descriptors such as the coordination number, the position of the d-band center, and partial charge. However, they also impose fundamental limitations on the catalyst maximal performance. Therefore, there has been some effort to find a way to overcome these constraints.[31] We showed that metal clusters, because of fluxionality[4] and shape sensitivity to even chemically related adsorbates or their different numbers, do not follow the scaling relationships, almost as a rule.[32] In our considered example of the oxygen reduction reaction (ORR) catalyzed by gaseous and graphene-supported Pt clusters, which is illustrated in Figure 5, the binding energies of molecular fragments O, OH, and OOH break the scaling relations because of the ever-changing cluster shapes.[32] Similar breakdowns of scaling relations through different mechanisms have been reported in other catalytic reactions.[31,33]

Another consequence of the ensemble representation has to do with the whole notion of the reaction mechanism. The mechanism may involve catalyst isomerization as part of the reaction coordinate. There could be several states of the catalyst with competing levels of activity, which would produce a swarm of different reaction mechanisms that collectively yield experimental observables, such as rates and product distributions. Hence, a single reaction profile on a dynamic interface is likely to be completely misleading, as we began demonstrating.[12]

The ensemble representation leads to a different view of reaction kinetics. First, the conventional Arrhenius picture needs to be reconsidered. As T increases, chemically distinct states of the catalyst get recruited, so the Arrhenius plot should be nonlinear. A proposed simple modification to the Arrhenius equation using an ensemble-average representation is to write the apparent activation free energy in terms of activation energies of every state weighted by Boltzmann populations:

$$\Delta G_{ens}^{\ddagger} = \sum_{i=1}^{n} P_i \Delta G_i^{\ddagger}$$

Hence, the modified formula for the rate corresponding to the ensemble, r_{ens}, can be written as

$$r_{ens} \propto e^{-\Delta G_{ens}^{\ddagger}/RT} = e^{-\sum_{i=1}^{n} P_i \Delta G_i^{\ddagger}/RT}$$
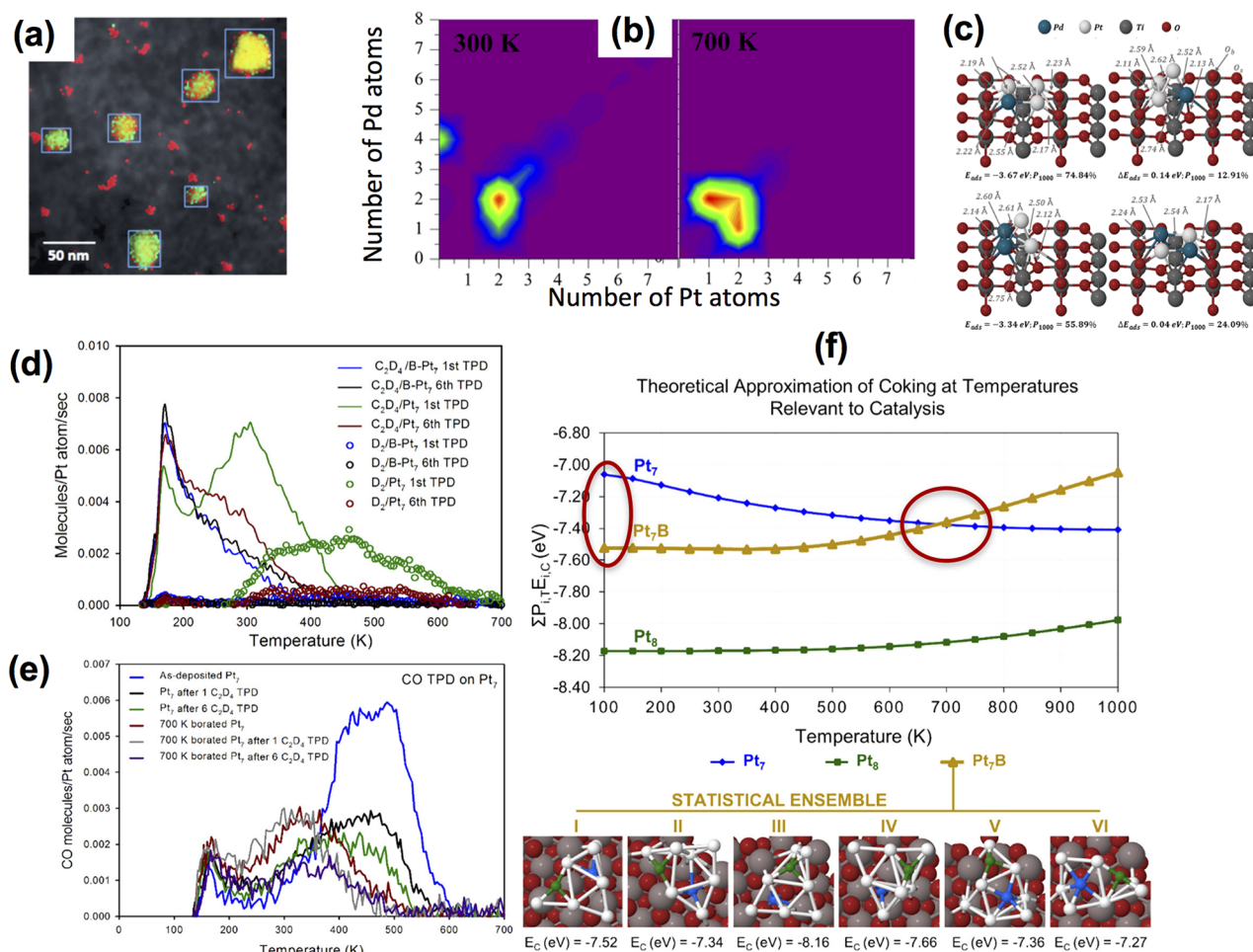
which can be further simplified as

Figure 6. (a) Experimental STEM shows that mixed PtPd particles resist sintering more than pure Pt or Pd particles. (b) Monte Carlo simulations of Ostwald ripening based on ensembles of cluster isomers for every size and stoichiometry show the highest survival of mixed PtPd clusters at 300 and 700 K, in agreement with experiment. (c) The two lowest-energy isomers for tetraatomic PtPd clusters, showing no apparent differences. The stability against sintering was explained by increased configurational entropy. (d) Experimental C_2H_4 TPD on Pt_7/α-Al_2O_3 and Pt_7B/α-Al_2O_3: after the first through fifth ethylene dehydrogenation, ethylene binding sites go away on pure Pt_7 but remain intact on Pt_7B, as seen from the sixth TPD. Lowering of the ethylene binding energy upon cluster boration is also seen from the position of the TPD peak. (e) CO TPD on Pt_7/Al_2O_3 and Pt_7B/α-Al_2O_3 after the same first through sixth ethylene TPD, showing the disappearance of the Pt sites (due to coking and sintering) for pure Pt_7, and the preservation of the Pt sites for Pt_7B. (f) Theoretical assessment of coking on Pt_7/Al_2O_3 and Pt_7B/α-Al_2O_3: the low-T ensembles suggest a higher coking propensity for Pt_7, but for rising T, the ensembles show opposing trends, with Pt_7 coking more and Pt_7B coking less, in agreement with the experiment, due to the enrichment of the ensemble with the isomers having a lower affinity for C. Adapted or reprinted with permission from refs 35, 37, and 23. Copyright 2013 Wiley Online Library. Copyright 2014 and 2017 American Chemical Society.

$$r_{ens} \propto \prod_{i=1}^{n} \left(e^{-P_i \Delta G_i^{\ddagger}/RT} \right) = \prod_{i=1}^{n} \left(e^{-\Delta G_i^{\ddagger}/RT} \right)^{P_i} = \prod_{i=1}^{n} r_i^{P_i}$$

The latter equation shows that the final rate of the reaction catalyzed by an ensemble of clusters is proportional to the product of rates of each individual cluster corrected by a Boltzmann factor.

◼ ENSEMBLES OF CATALYST STATES AND DEACTIVATION

Catalyst deactivation under realistic catalysis conditions also needs a full ensemble-based description. Surface-supported nanoclusters deactivate mainly via sintering (merging to form larger particles with lower surface energies) and poisoning (e.g., coking). Sintering can happen via particle migration and coalescence or Ostwald ripening that involves single atoms dissociating from a cluster, migrating on the support, and associating with other clusters while statistically favoring the

larger ones. Ostwald ripening is the more prevalent mechanism for the clusters that we studied. In simulations of Ostwald ripening, we considered Boltzmann ensembles of all cluster isomers of every accessible composition and size up to four to five atoms.[34−36] Beyond that size, cluster energies were extrapolated on the basis of the number and kind of atoms in the cluster. The cluster dissociation energies and the PESs for the monomers on the support (as a grid) were precomputed using DFT. The simulations then followed a Monte Carlo scheme and involved cluster dissociation, association, atom migration, and atom evaporation and redeposition. One illustrating example is supported PtPd clusters. It was seen in the experiment that these clusters as the 50/50 Pt/Pd ratio sinter less than pure Pt or Pd clusters (Figure 5a).[37] We simulated Ostwald ripening on rutile at different temperatures and starting Pt/Pd ratios (Figure 5b). We found that mixed PtPd clusters sinter less quickly.[35] The analysis showed no particular structural or electronic differ-

ences between clusters of different Pt/Pd ratios (Figure 5c). We eventually correlated the sintering inhibition with the configurational entropy and accessible to these clusters, which is the highest for the 50/50 ratio. In other words, within every accessible geometry, these clusters have more ways to arrange the Pt and Pd atoms, thereby lowering the free energy, and that is yet again an ensemble property that cannot be captured at the level of a single structure.

We found a striking impact of the metastable states on the poisoning of cluster catalysts. We predicted that alloying supported Pt clusters with B should help mitigate both coking (by stopping alkane dehydrogenation at the olefin) and sintering.[38] This was experimentally confirmed: size-selected Pt clusters on α-Al_2O_3 were borated postdeposition by adding diborane and heating.[23] These model catalysts showed significantly tempered ethylene dehydrogenation activity and no deactivation after several catalytic cycles, in stark contrast to pure Pt counterparts (Figure 6d,e).[23] Boron does this by forming strong B–O bonds between the cluster and the surface, cutting down the net charge transfer from the support to clusters from 1.2 to 1.4 e to 0.3 to 1.0 e, thus reducing the binding energies of ethylene and products of deeper dehydrogenation including carbon itself (Figure 6f). Furthermore, theory showed that the higher-energy cluster isomers in the PtB ensemble are increasingly worse at activating ethylene and binding carbon, so as T increases, PtB/α-Al_2O_3 cokes less and pure Pt/α-Al_2O_3 clusters coke more. In fact, at low T (in the limit of GM being the only populated species), Pt_7B/alumina should coke more than Pt_7/alumina, in disagreement with the experiment (Figure 5f). We clearly needed an ensemble in order to capture the experimentally observed phenomenon.

All of our subsequent work that involved alloying Pt for selectivity control has involved an ensemble representation. One well-known dopant for Pt in the bulk and in nanoparticles is Sn, which is known to reduce coking. We showed in a joint theory–experiment study that the effect of Sn is also robust in small clusters and that the anticoking mechanism is different from that induced by boration.[39,40] In contrast to PtB, PtSn clusters supported on amorphous silica and α-alumina have an unchanged or even increased affinity for ethylene from that of pure Pt clusters. The selectivity arises from Sn and Pt mixing within the cluster and forming strong covalent bonds, quenching all unpaired spins, and eliminating the adjacent Pt sites, both of which are required for ethylene activation. Hence, ethylene desorbs. The effect is persistent across all thermally accessible isomers in the catalyst ensemble. We also identified Si and Ge as two highly promising dopants, which should surpass the effects of both B and Sn on the selectivity and coking resistance of Pt clusters.[41,42] The mechanism for Si and Ge is electronic spin-based, similar to that of Sn. Again, the entire ensemble of states was simulated and analyzed to confirm that no accessible isomer could break the desired trend.

■ COMPUTATIONAL AND EXPERIMENTAL METHODS OF CHARACTERIZATION OF DYNAMIC CATALYSTS: CURRENT STATUS AND REQUIRED UPDATES

Accessing the ensembles of states on dynamic catalytic interfaces requires computational methods to address the problem at several different levels. To locate the GM and local minima on the PES, global optimization techniques are needed. The most popular ones include the genetic algorithm,[43,44] particle swarm optimization,[45] and basin hopping.[46] Many of these techniques have been developed in our laboratory,[8,47] including the very first genetic algorithm for clusters.[44] One possible advance needed here is to increase the efficiency of these algorithms in finding the local minima because by definition they target the GM discovery and not necessarily the characterization of the full PES. Sampling in trained potentials is also welcome since the computational cost associated with global optimization is very high.

Another complication is finding the lowest-energy pathways for catalyst isomerization, especially in the presence of adsorbates and/or during a reaction step. We need to identify catalyst structures that are likely to be connected by a direct isomerization pathway. Geometric similarity may be used as a criterion.[4] Next, matching the atoms from one structure to another can be highly nontrivial. It is not unique, and the associated computed barriers will be different.[4] The multitude of adsorbate configurations drastically increases the number of possible pathways. Certainly, such studies are possible but extremely costly. One way forward could be fitting a simplified potential for the entire system (surface, cluster, and adsorbates), including the regions of TSs, to enable quick qualitative estimates of the barriers and the kinetic accessibility of all isomers in the network. We are working on this development.

The global optimization can be performed on DFT, ab initio, empirical, and semiempirical PES. Force field and NN fitting of an approximate PES can be incorporated to further reduce the computational cost.[8,47] The accuracy of these methods goes against the efficiency of the sampling, so more efficient electronic structure methods are highly desired. Currently, DFT offers a balance between accuracy and computational cost and has been applied to many systems. However, due to its lack of cancelation of the Coulomb self-interaction and single-reference nature, DFT cannot yield meaningful results when treating strongly correlated systems such as late transition metals and rare earth oxides.[48] DFT+U provides a way to treat such systems with a DFT-level cost through the addition of a Hubbard U term to a set of atomiclike orbitals.[49] However, the U is often fitted to a chosen property, via a linear response approach, or to a solution obtained with another imperfect Hamiltonian and may depend on the chemical composition or the pseudopotentials employed. High-level electronic structure methods including Green's function[50] and the screened Coulomb potential[51] have been developed to treat strongly correlated systems. However, for catalytic interfaces involving a large supercell and coverage, those are unaffordable. Hybrid-DFT with stochastic exchange may offer a practical way to handle large systems with improved accuracy and efficiency compared to those for DFT, but they are still single-reference. Dispersion interactions can significantly contribute to nearly all covalent and noncovalent interactions, including H-bonds, metal coordination, adsorbate configuration, and reaction energetics.[52] Efforts have been made to provide an affordable method for the accurate evaluation of dispersions. Dispersion correction methods developed by Grimme focus on improving the thermodynamic results at little additional computational cost.[53]

On the experimental side, *operando* spectroscopy is very promising for catalyst characterization.[54,55] Measurements of activity and selectivity in situ become possible. In agreement

with the recent theoretical investigations, it has been shown by *operando* studies that the dynamic structural transformations of catalysts under reaction conditions can strongly affect the catalyst performance.[56,57] To address critical mechanistic questions, XAS has become an important tool. XAS has the capability to resolve the electronic structural features of operating catalysts. Furthermore, the combination of small-angle X-ray scattering (SAXS) and XANES spectroscopy in situ studies probes different length scales and can be combined with simulations and machine learning.[58,59] In samples where the signal of the cluster may be overwhelmed by a bulk contribution, more surface-sensitive techniques such as in situ IR and surface-enhanced Raman spectroscopy (SERS) are needed. These *operando* techniques would benefit the field of catalysis if they would gain the ability to detect important minority species at the catalytic interface rather than giving ensemble-average information. Until this is accessible, the role of theory remains singular.

CONCLUSIONS AND OUTLOOK

To summarize, dynamic interfaces are ensembles of many distinct states, not just one. In the limit of the full thermodynamic equilibration of a highly dynamic catalytic interface, along the entire reaction profile, the properties and energies of every intermediate and every TS are dominated by a different state or states of the catalyst. Intermediates would be mainly defined by the most thermodynamically stable and hence dominating species in the ensemble. TSs would be defined by less prevalent but more active states of the catalyst. The ensemble would generally change as a function of the bound intermediate (including changes in structure and adsorbate nature and number). Each well on the reaction profile should be characterized with an ensemble of metastable states independent of the ensemble of the previous well. From this perspective, basing all intermediate geometries on the starting geometry of the interface could make the constructed reaction profile problematic. Catalyst isomerization steps thus should be part of the catalytic process. For the less stable but more active species to be the active sites, the catalyst needs to be able to reach those species through isomerization. In addition, the reaction profile might be not one but many, all with slightly different mechanisms and rates and operating as a swarm. This picture is much more complicated than what can be found in the majority of the catalysis literature, where the catalyst is not undergoing any major changes beyond relaxation and there is only one reaction profile.

We showed that all major properties of supported cluster catalysts, including activity, selectivity, stability against sintering and poisoning, and *operando* spectra, are affected by the presence or even dominance of the metastable states. Some intriguing results of this include the routine breaking of scaling relations and non-Arrhenius behavior. A much-needed development in *operando* spectroscopy is the ability to somehow measure minority states, which might contain the active site(s).

One open question is that of the relative time scales. Do the catalytic systems really have the time to undergo this constant reorganization that would allow them to operate on the minimum free energy reaction path as an equilibrium ensemble? For example, in enzymatic catalysis, the full equilibration all along the free-energy surface is standardly assumed and treated through extensive sampling combined with free energy perturbation (FEP).[60] Or does the reaction

instead proceed along a series of metastable states, keeping some memory of the initial state of the catalyst that it was when the reagent bound to it? This picture would be closer to the modeling approaches that dominate the catalysis literature now, but in our studies, we have seen that such modeling leads to selectivities and cluster size and composition dependencies of activity that do not agree with the experiment. The partial equilibration of the catalyst along the reaction profile, where the current ensembles are neither fully equilibrated nor correspond to the GM of the initial state, would be truly difficult for theory.

It is also interesting to know the degree to which the importance of ensembles changes as we consider larger catalytic particles. While we do not have the full answer to this question, it can be reasonably hypothesized that larger particles would retain their structure in the bulk but undergo dynamic surface reconstruction and exhibit varying coverages around different active sites, forming ensembles in these ways.

Another key question is that of the possible dynamic coupling between the catalyzed reaction and catalyst reorganization. Are there reaction steps that involve not just the movement of light-reacting atoms but also catalyst isomerization? While we do not yet have a complete and general answer, we have made several initial observations. For adsorbate-free supported Pt clusters, the isomerization is quite fast but not faster than the catalyzed reactions of dehydrogenation. The reaction dynamics is then decoupled from the cluster dynamics: facile cluster isomerization can be induced by a reaction step, but it is delayed and occurs as an independent step. The picture might change when the reacting atoms and cluster atoms are closer in mass. Similarly, can the binding of a reagent, which can have a large kinetic energy and be vibrationally excited at high *T*, trigger catalyst isomerization? This coupling could in fact facilitate the catalyst equilibration toward the most stable ensemble with the bound reagents. We began investigating this aspect of cluster catalysis through dynamics simulations, paying particular attention to the kinetic energy exchange between the catalyst and the reagent. So far, the results are again system-dependent. Also, reagent scattering, nonreactive adsorption, and reactive adsorption all affect the catalyst dynamics differently.

We hope to construct a unified theory of dynamics in catalysis and have made our first strides in this direction. We see that some catalysis rules are routinely broken on such dynamic interfaces. We develop tools that we need to access the nature and mechanisms of such interfaces. However, we still have a long way to go to a truly generalized theory, as the emerging picture is breathtakingly complex.

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Notes

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Anastassia N. Alexandrova was born in the USSR in 1978. She obtained a B.S./M.S. diploma with highest honors from Saratov University, Russia, and her Ph.D. in theoretical physical chemistry from Utah State University, and she was then a postdoctoral associate and an American Cancer Society Postdoctoral Fellow at Yale University. Anastassia joined the faculty of UCLA in 2010, where she is now a professor and the Vice Chair for Undergraduate Education. The focus of her laboratory is computational and theoretical design and multiscale descriptions of functional materials: catalytic interfaces, ultrahard alloys, quantum materials, photoactive quantum dots, artificial metalloenzymes, and molecular qubits.

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