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Abstract

It has recently been shown that the dynamic behaviour of surface-supported nanocluster catalysts in realistic reaction conditions defies conventional models used in catalysis. This opens new doors in catalysis by giving more leverage in catalyst design, but also requires a major revision of the understanding of how dynamic heterogeneous catalytic interfaces operate, as well as of the computational approaches of catalyst modelling, and experimental methods of catalyst characterization. Major aspects of the new paradigm include the collective action of many catalyst states that form a statistical ensemble in reacting conditions, the catalytic activity and selectivity being driven by rare and metastable catalyst states, reaction thermodynamics and kinetics being controlled by different states of the catalyst, broken scaling relationships, non-Arrhenius behaviours, and catalyst dynamic restructuring being an essential part of the reaction mechanism. For computation, this complexity means the departure from the standard DFT calculations of reaction mechanisms on a single catalyst structure. For experiment, it calls for the development of *operando* characterization tools with the per-site resolution and the ability

to find the minority sites that govern the catalytic activity. For catalyst design, the goal becomes the creation of the catalyst state (geometric and electronic) that might not be present in the as-prepared catalyst, but would develop in the reaction conditions and would have the desired activity then. While cluster catalysts are the most dramatic in their dynamic fluxionality, other amorphous interfaces also exhibit some of it, and thus are also subject to similar paradigm revision.

Graphical/Visual Abstract and Caption

INTRODUCTION

NO ATOM IN THE CLUSTER CAN BE IGNORED

Although the term "nano-technology" was coined by Norio Taniguchi[1] in 1974, the brilliant idea behind it was first introduced at the American Physical Society meeting at California Institute of Technology in 1959 by Richard Feynman almost six years before he won the Nobel Prize in physics. However, it took scientists more than 20 years to put the idea into practice when the Scanning Tunneling Microscope (STM) was invented by Gerd Binnig and Heinrich Rohrer at IBM's Zurich research labs in 1981.

Since then scientists in various fields have been trying to explore the nano-regime in order to find state-of-the-art applications in their field, and catalysis is no exception. One of the most important studies which showed how particles in the nano-regime would behave significantly different from their bulk counterparts was done by Haruta et al.[2] in 1987. They showed that gold nanoparticles, in spite of bulk gold being quite inert,[3,4] are not noble at all and have the ability to catalyse reactions. Unexpectedly, these nanoparticles can catalyse CO oxidation at temperatures as low as -70 $^{\circ}$C. Nano- and especially subnano clusters, in which there are only up to 30 atoms per cluster, have unique and extraordinary properties. In this size-regime every single atom is important and should not be ignored.[5] Moreover, extrapolating properties from larger clusters does not work in this regime, which is, thus, called non-scalable. This nonscalability feature also means that the cluster of each size has unique properties. For example, Pt_7 and Pt_8 when deposited on α-alumina, though similar in size, exhibit distinct catalytic activities toward ethylene dehydrogenation.[6] In

this case, one additional Pt atom is a game-changer, and significantly decreases the activity of the Pt cluster toward dehydrogenation reaction. Furthermore, it has been shown that each of MgO-supported Pt_n clusters (n = 8–15) has their own unique properties for ethylene hydrogenation which cannot be extrapolated from the larger scale region.[7] This is, in fact, in stark contrast to what has been observed for bulk platinum. Different crystal planes of platinum show the same turnover frequency for hydrogenation reactions, which makes the reaction insensitive to the structure of bulk platinum.[7,8] Moreover, it has been shown that Pt clusters dispersed on SnO/Al_2O_3 can be up to 100 times more active than the conventional Pt or V catalysts used for oxidative dehydrogenation of propane.[9] Size-selected Pt clusters deposited on rutile TiO_2(110) can also catalyse CO oxidation.[10] Interestingly, there is an increase in catalytic activity for Pt_n at n = 8 which is exactly where a structural transition from 2D to 3D happens, as has been confirmed by scanning tunneling microscopy (STM). Again, every single atom appears to play an important role at this size regime.

Of course, this unprecedented property is not unique to Pt clusters, and has been observed for clusters of other elements as well. For instance, Hutchings et al.[11] investigated the activity of different size gold clusters dispersed on iron oxide using aberration-corrected scanning transmission electron microscopy (STEM). They found that gold clusters with only ~10 Au atoms are the most active toward CO oxidation. The difference in activity between the clusters of different sizes has been again attributed to their morphology (monolayer or bilayer on the support), which depends on the number of Au atoms present in the cluster. In another study, Vajda et al.[12] explored the ability of Au_{6-10} clusters to catalyse propylene epoxidation, and attributed their high activity to the large fraction of Au atoms being undercoordinated. Pd clusters deposited on reduced graphene oxide also show interesting behaviour in the subnano-regime, and can be used for selective oxidation of alcohols.[13]

We should again emphasize that the number of atoms in each subnano cluster is important to determine its electronic structure and properties. On the one hand, the size-sensitivity of the catalytic properties is a lever of catalyst fine-tuning, which is exciting. On the other hand, this presents a challenge for experimentalists in the catalyst preparation: an atomically precise size-control is required for certain activity or selectivity of the catalyst. Additionally, keeping the small clusters at the desired size rather than sinter on the support (i.e. catalyst stability) is also a challenge. Finally, and that is the central topic of the present review, cluster catalysts challenged the computational characterization, and really took the field of computational catalysis to its hitherto unknown frontier, due to

the special dynamic behaviour of nanoclusters. This behaviour also made apparent the need for advances in experimental *operando* characterisation. The story unfolds from the attempts to identify the shape of cluster catalysts in the reaction conditions.

THE GLOBAL MINIMUM STRUCTURE OF THE CLUSTER CATALYST: NOT TRIVIAL, NOT STAYING PUT, AND NOT ALONE.

The key question in modelling catalytic reactions is the structure of the catalyst and the nature of the active site, in realistic conditions. Always being a nontrivial task, it is truly complicated for surface-supported cluster catalysts. High temperatures (~300 ˚C in thermal catalysis), coverage with adsorbates, or the presence of electrolyte and electrochemical potential (in electrocatalysis) significantly affect the structure of both the nanocluster (due to its dynamic nature), and the support (by causing defects).[14-17] Given that, it is crucial to develop an accurate, yet computationally practical model to describe the system.[18] For a long time, the prevalent approach in modelling cluster catalysis was finding the isolated cluster structure in the gas phase, and then putting it on the support and relaxing the geometry. However, it is known since 1970s[19,20] that clusters majorly change shapes in the presence of the support – a concept of strong metal–support interaction (SMSI), and also the adsorbates.[21] For instance, it has been shown that Pt_{13} cluster shape will significantly change when deposited on CeO_2.[22] Even different surface cuts could lead to different stable cluster structures: AIMD simulations revealed that the $CeO_2(110)$ surface provides the most stability for the Pt_{13} nanocluster (Figure 1). The Authors also analysed the effect of solvent on the electronic structure of the supported Pt_{13} cluster, and found that the cluster is further oxidized in the aqueous phase compared to the gas phase, since more electrons are transferred from the cluster to the support.
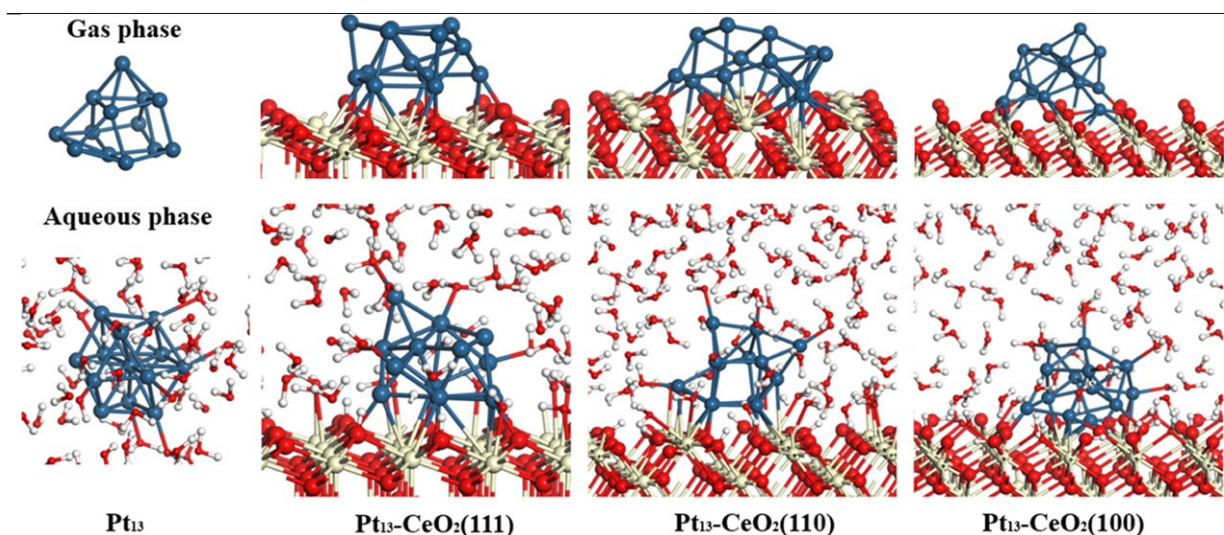
Figure 1. Optimized geometries of isolated and CeO$_2$-supported Pt$_{13}$ cluster in vacuum, aqueous phase, and deposited on CeO$_2$ after 10 ps AIMD simulations. Ce (light yellow), O (red), Pt (cyan), and H (white). Figure adapted from reference 22 with permission. Copyright 2018 American Chemical Society.

As another example, Keller et al.[23] investigated the effect of three different supports on the interfacial geometry of VO$_4$ cluster. They found that the tetrahedral VO$_4$ deposited on SiO$_2$ catalyst shares only one of its oxygens with the support despite the classical model that assumes three O atoms are shared with the support. This is also true when VO$_4$ deposited on Nb$_2$O$_5$ and ZrO$_2$ supports; however, the cluster shape has a more distorted geometry rather than the ideal tetrahedral, especially when deposited on ZrO$_2$. They also showed that the V-O$_b$ and the V$\cdots$M$_{support}$ distances depend on the geometry of each support surface. On the other hand, sometimes the support does not have a significant influence on the geometry of clusters. For example, it has been shown that Pt$_{13}$ has very similar shape in the gas phase and when dispersed on graphene.[24] Thus whether or not the support can significantly affect the cluster geometry and electronic structure depends on the nature of cluster and the support. Sasahara et al.[25] have shown that among three different anchoring sites that rutile (110) can provide to a single Pt atom, O-vacancy site is the only one that can stabilize Pt atoms. There is also an electron transfer from Pt atoms to TiO$_2$ at these sites. Moreover, by introducing heteroatoms such as N, B, P, and S in the carbon-based supports one can tune the properties of the deposited cluster through strong metal–support interaction including electronic, geometric, and dispersion effects.[26] In general, it is hard to predict whether or not and to what degree the cluster will change shape upon adsorption, but it is definitely unsafe to assume that it would not.

Hence, the next hot focus of the computational works on cluster catalysis became the finding of the most stable structure (the global minimum) of the nanocluster, on different surfaces and eventually in the presence of adsorbates. The central assumption in these works was that the global minimum would contain the active site. Generally, the global minimum structure cannot be guessed, because chemical bonding in clusters is generally not well-understood. Hence, the structures need to be found using stochastic global optimization and smart sampling techniques, many of which have been developed for this purpose, including Particle Swarm Optimization,[27,28] random search,[29,30] Genetic Algorithm,[31-35] Basin Hopping,[36-38] and Simulated Annealing,[39] in combination with ab initio electronic structure calculations. These simulations are intensely expensive, particularly for surface-deposited clusters, and so empirical potentials[40,41] and potential energy surface fitting techniques[42-44] have been utilized to accelerate the optimization process, and to enable modelling larger clusters.[45] Through global optimization it was unambiguously shown that clusters on surfaces and clusters in the gas phase can look completely different, have different charge and spin state, chemical bonding, and hence, reactivity.[6,12,41,46] In fact, whether the cluster has unpaired electrons (open shell) or not (closed shell) can affect cluster selectivity and the mechanism of the reaction. The interaction between the cluster and the adsorbate can sometimes change the binding mode of adsorbate from the weakly π-bound to the strongly di-σ bound adsorbate.[7,47-49]

The frontier of these kinds of efforts includes not only sampling the cluster shape, but also allowing the cluster compositional change during the global optimization. For example, in the oxidizing atmosphere, the metallic cluster can uptake oxygen, but the amount that it would uptake is in question, and depends on the partial pressure of oxygen, temperature, and likely also the cluster geometry. In this case, the global optimization has a grand canonical flavor. For instance, Hensen and co-workers[50] employed a basin hopping approach in the Gibbs ensemble (GCMC-DFT) in order to optimize the structure of the CeO_2–supported Pd_8 clusters in contact with gaseous O_2. This approach helped them to find stable Pd_8 cluster oxides on $CeO_2(111)$ without knowing the stoichiometry of the oxide *a priori*.
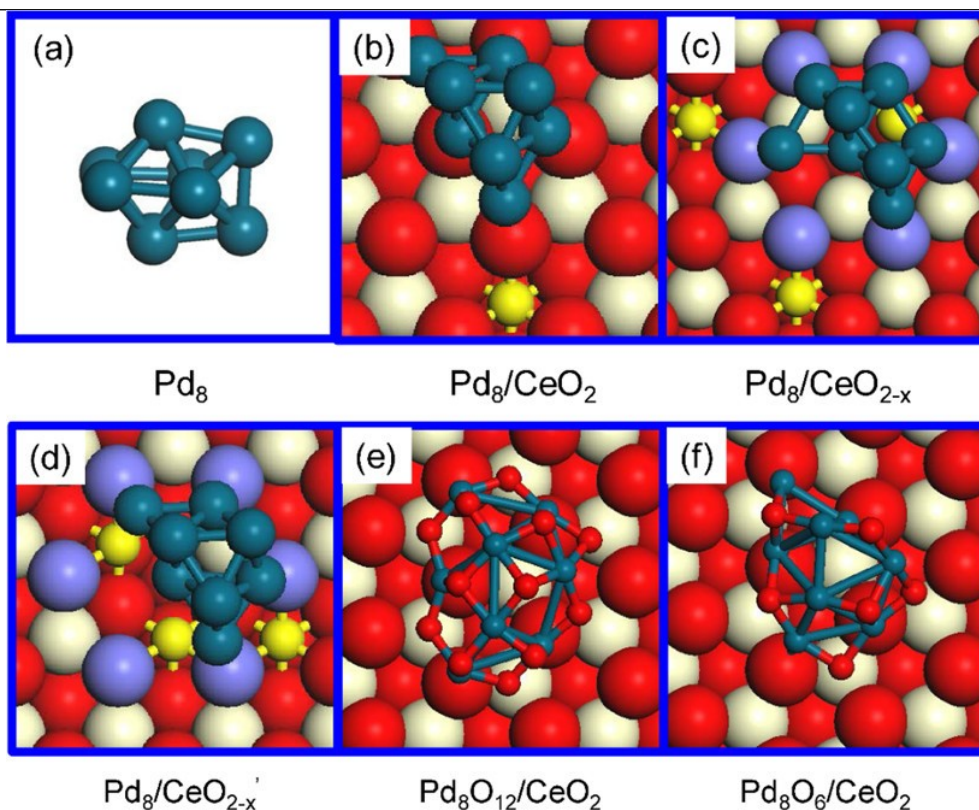
Figure 2. (a–c) Optimized structures of gas phase Pd_8 and Pd_8 deposited on the stoichiometric and defective ceria surfaces. (d) Metastable structure of Pd_8 on the defective ceria. (e,f) Structures of Pd_8O_x/CeO_2 (x = 12 and 6) obtained by GCMC-DFT at 300 K with oxygen atmospheres of 1 atm and 10^{-20} atm, respectively. Color coding: cyan, red, white, and small yellow spheres represent Pd, O, Ce^{4+}, and Ce^{3+} atoms, respectively; the purple spheres in defective ceria represent O atoms adjacent to O vacancy sites. Figure adapted from reference 50 with permission. Copyright 2018 American Chemical Society.

Figure 2 shows the global minimum structure of gas phase and surface-supported pure and oxidized Pd_8 cluster. As can be seen, the bicapped octahedral structure of gas phase Pd_8 undergoes a significant change when deposited on ceria. Note that the shape and composition of the support are assumed to not change in conditions of this catalysis, which is a necessary and typical approximation helping the feasibility of the calculations. Three different palladium clusters, Pd_8, Pd_8O_6, and Pd_8O_{12} were used to show that the activity toward CO oxidation would increase upon oxidation of CeO_2–supported Pd clusters. Additionally, this works suggested, for the first time, that linear scaling relations may apply to cluster catalysis; specifically, in CO oxidation reaction on ceria–supported Pd clusters there is a linear scaling relation between the activation energy and the CO + O binding energies. Janik et al.[51] used a related approach to get insight into the stable geometries and stoichiometries of Pd clusters

on ceria in conditions of methane activation. In their study, to take into account the change in the chemical composition of Pd clusters in contact with gaseous oxygen, Grand Canonical Monte Carlo combined with ReaxFF[52] was used.
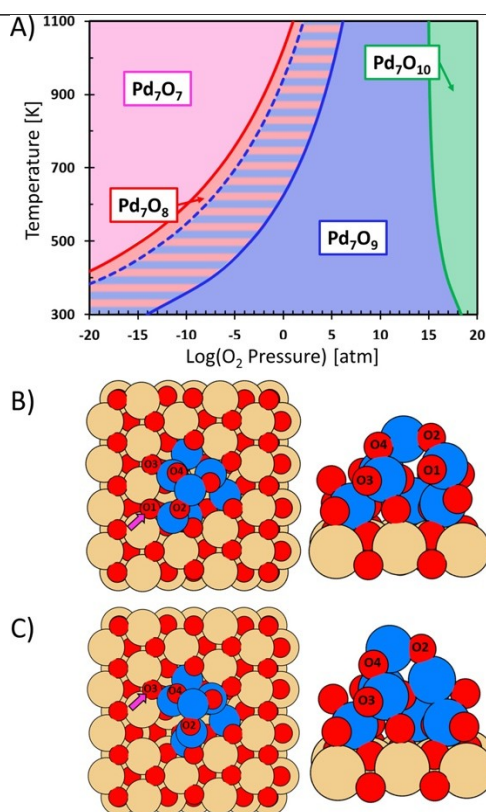

Figure 3. (a) Phase diagram of Pd oxidation states in the $Pd_7O_x/Ce_{33}O_{66}$(111) model obtained from ab initio calculations. The solid shaded regions separated by solid lines indicate stable regions in (T,P) space. The striped region and dashed line indicate the region where the supported Pd_7O_8 cluster is thermodynamically stable, yet methane activation is kinetically preferred over the Pd_7O_9 cluster. (b, c) DFT optimized structure of the embedded $Pd_7O_9/Ce_{33}O_{66}$(111) cluster model (panel (b)) and the $Pd_7O_8/Ce_{33}O_{66}$(111) cluster model (panel (c)). Hydrogen abstraction sites during methane activation are indicated by arrows. Figure adapted from reference 51 with permission. Copyright 2016 American Chemical Society.

Thermodynamically stable Pd_7O_x at different temperature, T, and pressure, p, are shown in Figure 3. Using a quantum/classical approach they demonstrated that Pd(IV) oxide would be stabilized on ceria due to its interaction with the support, yielding low methane activation barriers. The enhancement in oxide formation of Pd clusters due to the effect of CeO_2 is in agreement with the work of Farrauto et al.[53] and Nilsson et al.[54]

Although sophisticated sampling and advanced optimization methods may correctly identify the global minimum structure of the cluster catalyst, it is not the ultimate, complete representation of the active site. First of all, unlike extended surfaces, catalytic clusters do not stay put in their starting global minimum during the reaction. Cluster compositions can change. For example, Vajda et al. showed that the oxygen content in oxidized clusters of Cu and Pd changes as the operational temperatures of the catalysed reaction are reached.[55] Naturally, clusters may also undergo partial poisoning.[6,56-61] In such a context, a relevant question for modelling is: which particular cluster composition or compositions represents the active site(s)? Clusters may also sinter on the support, i.e. grow in size, losing size-specific catalytic properties.[62-65] But even more subtly, clusters of fixed stoichiometries may change shapes. Landman et al.[66] introduced the concept of dynamic structural fluxionality in cluster catalysts. They investigated the binding and activation of O_2 on the MgO-supported gold nanoclusters, as a crucial event in the process of catalysed CO oxidation, and stated that the adjustment of shape during the reaction increases the catalytic performance of the cluster.[67,68] Fabris et al.[17] investigated the importance of cluster fluxionality, viewed similarly, as a structural adjustment to the nature of the adsorbates or stage of the catalysed reaction, during CO oxidation on gold clusters deposited on both stoichiometric and defective $CeO_2(111)$. They additionally found that cluster mobility about the O vacancies significantly helps the CO oxidation corroborating the significance of cluster dynamics in describing the reaction mechanism.

However, the global minimum of the surface-deposited cluster, and its changing geometry during the reaction still do not produce an adequate representation of the catalytic system. Recent advances led us to a striking realization that this single structure is not alone in conditions of catalysis, and instead, many structural forms of the cluster are thermally accessible, jointly constituting the nature of the catalyst.[6,15,46,69] We showed that all practically interesting properties of cluster-decorated interfaces at typical temperatures of catalysis, such as ionization potential,[43] heat capacity,[44] poisoning propensity,[46] sintering tendencies and mechanisms,[57,63] catalytic activity and selectivity[6,46,48] are very different if a statistical ensemble of many states is considered, rather than just the global minimum. It is in fact intuitive that higher-energy metastable structures should be more reactive and thus can play a major role in catalysis.[48] This gives rise to a heretic idea that the global minimum might be catalytically dead, and it is those rare, transient, thermally-populated structures that do all the turnovers. Substantiating this hypothesis is the finding that nanoclusters have nearly flat (low-barrier)

potential energy surfaces, allowing them to easily isomerise, visiting dozens of isomers on the timescales on the order of nanoseconds at catalytic temperatures.[69] Hence, the nature of the catalyst is dynamic, and the active site (and potentially catalytic mechanism) might not be just one, but a swarm of many. This has major implications for how we think about cluster catalysis, and how we model it. Indeed, a paradigm shift is needed, toward statistical mechanical ensembles of many catalyst states. We began developing this paradigm.

ENSEMBLE REPRESENTATION OF CLUSTER CATALYSTS

The need for the ensemble representation of cluster catalysts became apparent in our joint theory-experiment studies of dehydrogenation on Al_2O_3-supported Pt clusters.[6,46] The goal was the selective dehydrogenation of alkanes to alkenes, and thus ethylene was considered as the substrate, in fact representing the intermediate of interest, which would either desorb or dehydrogenate further. Alumina-deposited Pt_7 and Pt_8, despite remarkable similarity in size, the globular shapes of the global minima, as well as charge transfer from the support in the global minima, were shown experimentally to have very different activities. Namely, Pt_7 dehydrogenates ethylene much more efficiently (Figure 4).[6] Theory revealed the reason for this to be an easy access of Pt_7 to a family of higher-energy isomers that are single-layer on the support and acquire 0.2 e$^-$ more from the support, allowing them to activate ethylene more strongly. At $T = 300$ K, when dehydrogenation begins, ca. 15% of the population goes into those single-layer minima, and the population grows at higher T. They perform the reaction. Pt_8 has a very stable and less active global minimum, such that 99 % of the population occupies this minimum at 300 K. Other more active isomers of Pt_8 do not get thermally-populated, and the catalyst remains weaker. Thus, the global minimum picture of catalysis is completely misleading, as it would not differentiate between Pt_7 and Pt_8. In fact, none of the previous theoretical studies were able to reproduce and explain the remarkable size-dependence of the catalytic activity of clusters, so widely documented in the experiment.
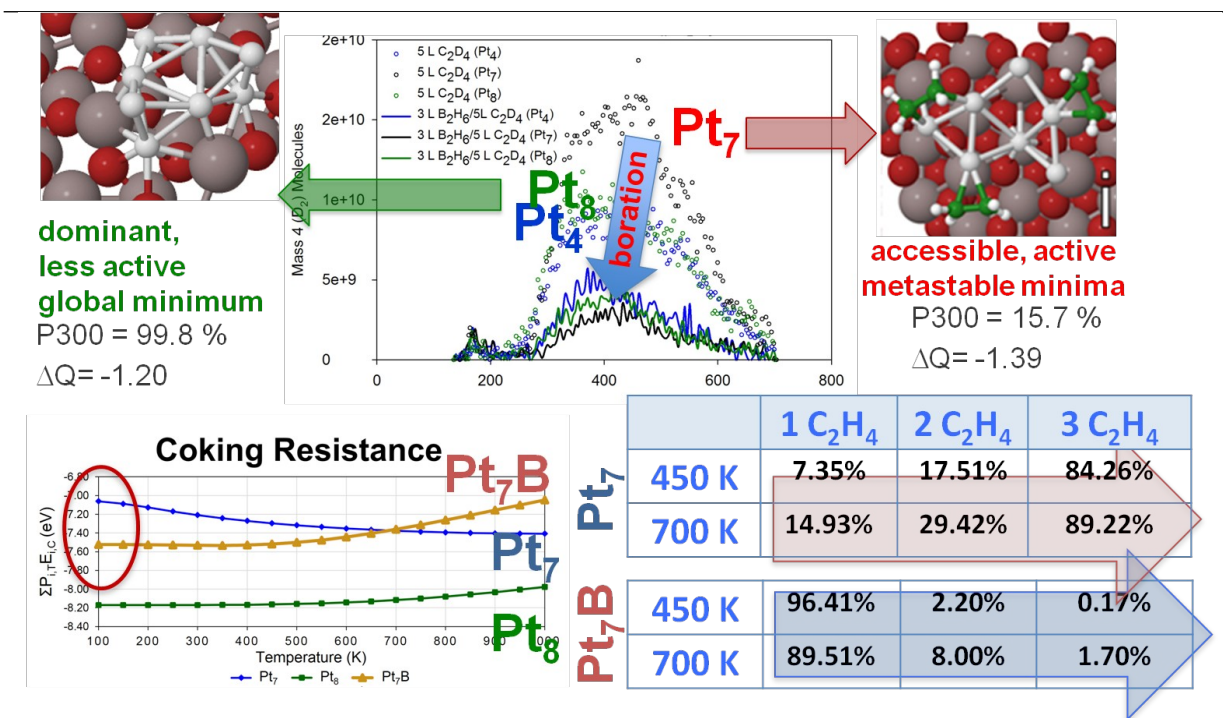
Figure 4. (TOP) Experimental temperature programmed desorption spectra for dehydrogenation of deuterated ethylene on size-selected Pt_n clusters on Al_2O_3: the difference in activity is explained on the basis of accessibility of highly-active metastable states of Pt_7, not characteristic of Pt_8 that has a highly dominant global minimum. P300 – population of the given isomer at 300 K. ΔQ – charge transferred from the support to the cluster (Bader charge scheme). The blue arrow represents the effect of cluster boration on the catalytic activity (smaller activity means less coking), measured experimentally. (BOTTOM) Theoretical modelling of coking reproduces the reduction of activity and coking upon boration, but only at high T, when the ensemble of cluster states is expanded toward metastable states. Figure adapted from references 6 and 46 with permissions. Copyright 2018 American Chemical Society.

Next, following our theoretical proposal that dehydrogenation can be made more selective by adding some boron to Pt, experiment was done, and confirmed the effect.[46] In calculations the global minimum of Pt_7B on Al_2O_3 has in fact greater affinity to carbon than does the pure Pt_7 on Al_2O_3. It is only when the temperature is increased and the population is expanded toward multitude of very different metastable states does the coke affinity evolve so that borated clusters coke less than the pure.[45] Borated clusters also dehydrogenate ethylene less than pure clusters, but again, only upon modelling them as ensembles. Just the global minima of alumina-deposited Pt_7 and Pt_7B have similar activities. Another recent purely-theoretical study by Sun and Sautet[70] investigated the hydrogen evolution reaction and methane activation on the Pt_{13} cluster covered by H atoms (gas phase $Pt_{13}H_{26}$). The second lowest-energy structure, rather

than the global minimum, was shown to have the highest activity toward methane activation, and dominate the catalytic performance despite being a minority species in the population.
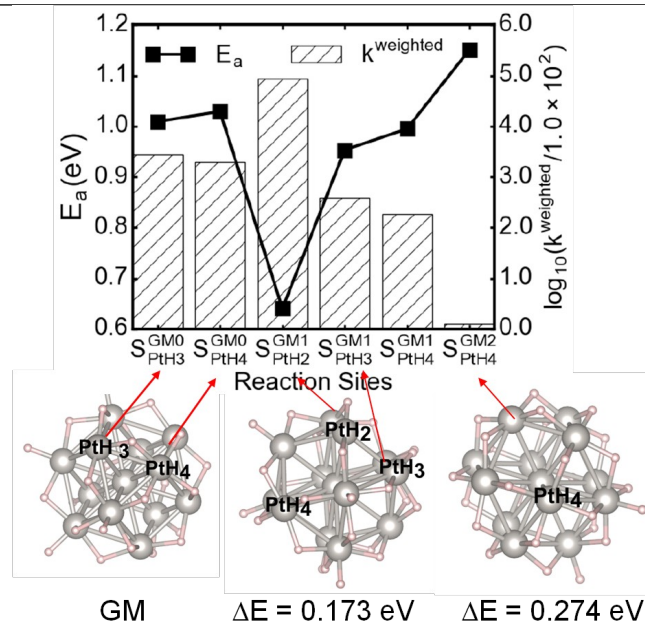

Figure 5. Three local minima structures of $Pt_{13}H_{26}$ which can catalyse methane activation. The activation energies (E_a (eV)) and the relative contribution to the reaction rate (rectangle bars) are shown for these three structures. The weighted reaction rate constant is given with a reference of 1×10^2 at 400°C. Figure adapted from reference 70 with permission. Copyright 2018 American Chemical Society.

The listed observations point to the need of computing the observable properties of cluster-decorated catalytic interfaces as ensemble averages, as was emphasized by Alexandrova et al.[6,15,44,46,48,56,57,63] This means that in addition to the global minimum structure one should take other energetically accessible structures into account. Every structure present in the ensemble will contribute to the observable, and its contribution will be weighted by its population in the ensemble. Every structure present in the ensemble will contribute to the observable, and its contribution will be weighted by its population in the ensemble. The state of the catalyst is no longer a structure, but a collection of many structures that dynamically interconvert. At finite temperature, the ensemble average of any property (like energy) can be computed by taking the weighted average of that property corresponding to each isomer:

$$\text{(1)}$$

In principle, to compute the probabilities (P_i), one should consider the electronic, vibrational, and rotational degrees of freedom of the system to obtain their corresponding partition functions. (The translational part could be neglected since it is basically the same for all isomers.) The Boltzmann factor can play an important role especially when it comes to calculating the kinetic properties of the system, since it adds the effect of other energetically accessible isomers to the kinetics of the system providing a more realistic picture of the reaction. In summary, the state of the catalyst is no longer a single structure, but a collection of many structures that dynamically interconvert. The number of these minima can be dauntingly large (e.g. on the order of 30 easily accessible isomers[69]), and unfortunately we cannot tell *a priori* which structure or structures are going to dominate certain properties. Hence, it is critical to perform thorough sampling of the system, but with the goal of finding all thermally-accessible minima, and not just the global minimum.

IMPLICATIONS OF THE ENSEMBLE NATURE AND DYNAMIC FLUXIONALITY ON REACTION THERMODYNAMICS, KINETICS, MECHANISM, AND SCALING RELATIONSHIPS

Since the cluster shapes adapt to the bound reagents, they may rearrange depending on the bound reaction intermediate, i.e. in the course of the catalysed reaction. In fact, the entire ensemble of cluster states may be undergoing continuous changes, and every well on the reaction profile is then characterized by a unique equilibrium ensemble. This poses two key mechanistic questions: When does this rearrangement take place, concurrently with the reaction step, or sequentially with it? And, does the system have enough time to dynamically equilibrate in every well on the reaction profile, or does it instead keep some structural memory for the catalyst and evolves off of the equilibrium? Each possibility would bring profound and different implications to our understanding of cluster catalysis mechanisms, and the theory needed to describe them. Certainly, cluster dynamics is not to be ignored in order to accurately describe the reaction.

The dynamic coupling of cluster rearrangement to the reaction step should depend on the reaction energy barrier and cluster rearrangement barrier. If the barriers are very different it might be safe to assume that

there is a low probability of the coupling. On the other hand, if the barriers are close to each other, it is not straightforward to say whether or not the coupling is possible.[69,71] Additionally, some of the local minima can be kinetically trapped or inaccessible due to the high-energy barriers to rearrangements. Therefore, ultimately, a robust description of the system should include thermodynamics, kinetics, and then also actual dynamics to address the issue of relative timescales and the possible divergence from equilibrium.

It can be important to quantify cluster fluxionality. Structural flexibility has been quantified by Yang et al.,[72] although they call it fluxionality, based on the displacement of atoms. Figure 6 shows the stable CO_2 configuration when it adsorbed on Pt_6 cluster dispersed on $TiO_2(101)$. These small Pt clusters can easily adapt their shape upon CO_2 adsorption. In fact they found that there is a linear relationship between the displacement of the atoms in the cluster and CO_2 adsorption energies on different size of Pt_n (n = 4, 6, and 8) clusters deposited on pristine and partially reduced anatase TiO_2 (101). Upon CO_2 adsorption, the Pt-only sites show similar flexibility for all three types of Pt cluster geometries (3D, intermediate 3D/2D, and 2D). However, at the interface edge sites the 3D geometries tend to have high displacement values on average, followed by the intermediate 3D/2D, and planar 2D structures. In this particular case, there are significantly larger geometry changes in 3D structures compared with the 2D one during CO_2 adsorption. They also found a positive correlation between structural flexibility and binding energy, which implies that the easier the cluster can adapt its structure, the better the orbital overlap with the adsorbed molecule is obtained, resulting in stronger CO_2 binding energy. This is fundamentally not surprising; geometric relaxation always leads to stabilization, i.e. lowers the energies of the electronic states. Nevertheless, one should note that reconstruction of the cluster upon adsorption is not exactly the same as fluxionality in the sense of isomer interconversion, where they indeed cross energy barriers.
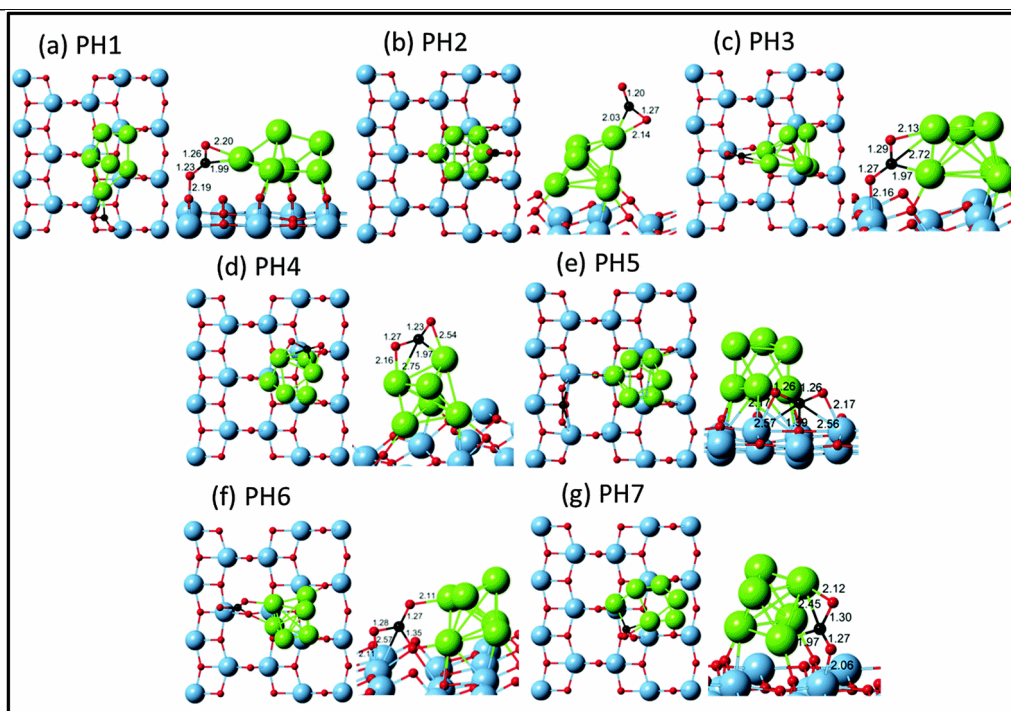
Figure 6. Side and top view of stable CO_2 adsorption configurations on the perfect anatase $TiO_2(101)$ surface in the presence of Pt hexamers (PH) (O in red, C in black, Ti in blue, and Pt in green. The numbers indicate the bond lengths in Å). Figure adapted from reference 72 with permission. Copyright 2015 Royal Society of Chemistry.

A similar study was also done to compare the properties of two isomers of gold clusters in the gas phase and deposited on partially reduced anatase TiO_2 (101).[73] It was also found that the icosahedral isomer binds CO_2 more strongly since it can easily adopt different configurations to have an optimal CO_2 adsorption. This is, in fact, in agreement with the higher displacement of icosahedral isomer predicted by the structural flexibility formula from the study of Yang et al.[72]

If the cluster dynamics happens concurrently with the reaction dynamics, then we need a new definition of the reaction coordinate that includes the rearrangement of the cluster. Simulations of catalysis in this case would become intensely complicated. In all studies so far, the transition states in the reaction were found by moving just the atoms of the reacting system in the presence of the stationary (and merely relaxing) catalyst. The system shown in Figure 5 in fact exemplifies this approach. However, the transition state that does involve cluster rearrangement might never be found because we do not know how the cluster atoms should move to reach it. On the other hand, there are good reasons to hope that cluster isomerization (as opposed to relaxation) and reaction dynamics are

decoupled, which would make modelling easier again. Metal atoms in the cluster are much heavier and so cluster motion, especially major geometric changes, should be too slow as compared to the motion of the light atoms in the reaction. Indeed, in our dynamics studies so far, we see no indication of such coupling. However, MD may still miss the most accessible pathways that include cluster isomerization. We need robust new methods that could discover such pathways. This is a topic of ongoing research in our laboratory.

Regardless of the intensity of dynamic coupling directly to the reaction step, there is still an outstanding question of whether or not cluster ensembles have a chance to fully re-equilibrate during the life-time of a typical reaction intermediate. If at least partial equilibration is possible, then an inescapable conclusion arises that thermodynamics and kinetics of the reaction steps must be controlled by different states of the catalyst: the minima on the reaction profile are dominated by the global minima, whereas the kinetics is governed by the rare and most reactive species. This is not how catalysis has been viewed for decades.

Excitingly, this apparent mechanistic complication could be used to our advantage: The fact that different reaction intermediates and transition states are all bound to different states of the catalyst brings a possibility of breaking scaling relations in catalysis. Scaling relationships provide a simple linear relationship between thermodynamic properties of chemically related species involved in a catalysed reaction, e.g. between NH and NH_2 binding energies in ammonia synthesis, and between O, OH, and OOH in the oxygen reduction reaction (ORR).[74-76] Scaling relationships impose fundamental limitations on the catalyst maximal performance, and so there is a continuous hunt for ways of circumventing them. In our recent study[77] we showed that small Pt clusters do not necessarily follow a highly correlated linear relation and can break the scaling relations, opening opportunities for outstanding catalytic performance. Across small Pt cluster sizes, in the gas phase and when supported on graphene, cluster structure changes dramatically and adsorbate binding site (atop or bridge) also change, when binding O, OH, and OOH (intermediates in ORR), and upon varying coverage. Examples of computed poor correlations are given in Figure 7. This avenue brings a hitherto unexplored powerful catalyst design opportunity, through dynamics as a design parameter, permitting to circumvent scaling relationships in the desired way, e.g. for cheaper ammonia synthesis.

Cluster dynamics as a catalyst design parameter is also more general. As was already mentioned, geometric flexibility allows for lowering the energy of the molecule-bound cluster state. Hence, reaction profiles for

highly fluxional cluster catalysts would generally have deeper minima for the intermediates, and lower-energy transition states. This can turn non-catalysts into catalysts. Cluster dynamics thus should be viewed as a lever in catalyst design. It should be possible to use it to tune the selectivity of the catalyst, and we have an example of this in a forthcoming publication.
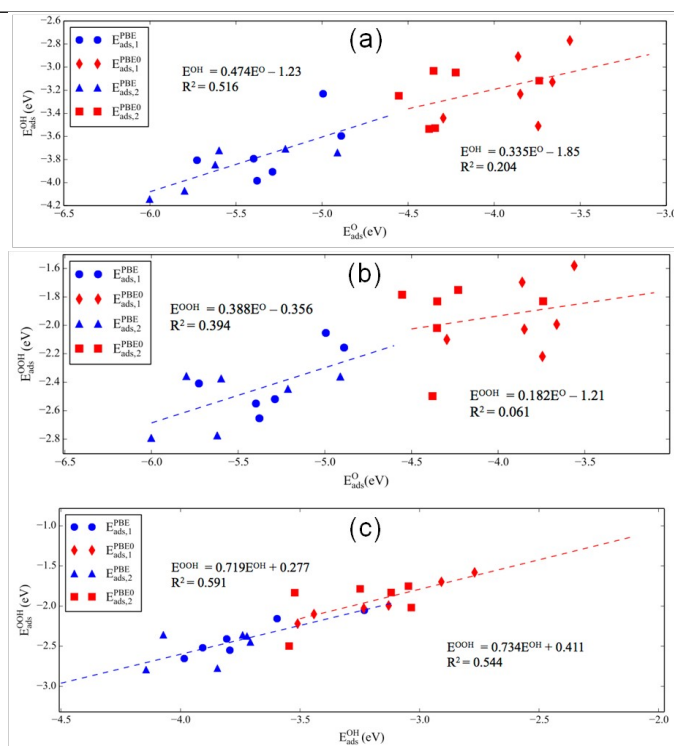

Figure 7. Computed correlations of the binding energies of (A) O and OH, (b) O and OOH, and (c) OH and OOH on Pt_n (n=1–6) clusters in the gas phase, in the presence of one or two adsorbates. Blue – PBE results; red – PBE0 results. Poor correlations are observed due to clusters changing shapes and adsorbate binding sites. Figure adapted from reference 77 with permission. Copyright 2019 American Chemical Society.

Lastly, although clusters with more directional bonds such as metal oxides are more stiff and less fluxional, one should note that these effects are not only characteristic for clusters, but for all highly dynamic interfaces. For example, hexagonal BN in conditions of ODH which is covered in under-stoichiometric and amorphous $BO_x(OH)_y$ layer shows fluxional behavior and the fluxionality and structural diversity emerging under reaction conditions must be taken into account in theoretically descriptions of the catalytic interface.[78] Moreover, for larger clusters, Somorjai et al.[79] showed that the $Rh_{0.5}Pd_{0.5}$ nanoparticles undergo dramatic and reversible changes in composition and chemical state in response to oxidizing or reducing conditions. This behaviour in restructuring and chemical response of $Rh_{0.5}Pd_{0.5}$ under the reaction conditions illustrates the flexibility and

tunability of the structure of bimetallic nanoparticle catalysts during catalytic reactions.

NOTES ON THE COMPUTATIONAL METHODS

Various computational methods have been extensively used to simulate and model different surface-supported cluster catalysts. In this section, we discuss the methods and models that are mainly being used in the nanocluster catalysis community, and emphasize why we need to be careful when using some of these models to describe the catalytic properties when the catalytic interface is so dynamic. It is clear that finding the correlation between catalyst morphology and catalytic performance is essential to designing new catalysts with enhanced efficiency.[14,74,80-87] Hence, a major tool is global optimization, already discussed above, to be used for the finding of both the global and the accessible local minima of cluster catalysts.

Secondly, one should be cautious when choosing the density functional in order to perform DFT calculations on nanoclusters, since the relative energy of the cluster isomers is often dependent on the functional.[44] Additionally, current density functionals often fail to capture the correlation in strongly correlated systems such as late transition metal clusters[88] deposited on rare earth metal oxide supports.[89,90] Cluster oxides of metals such as Mn, Fe, and Co (gas phase or surface deposited) are also common examples of particularly problematic species, exhibiting strong static and dynamic electronic correlations, and thus presenting difficulty for DFT. DFT+U is a common approach to tackle this problem to eliminate the self-interaction error by adding the on-site Hubbard term U to a set of orbitals. This method has been used extensively in the case of ceria to describe its 4f states.[91-93] Although one can choose the on-site Hubbard interaction self-consistently,[94,95] it is usually chosen to fit to a given property, and that makes the method less robust and generalizable. Despite the fact that there are methods that have been developed to improve the robustness of calculation for periodic systems, including Green's function for periodic systems,[96] wave function in DFT embedding scheme for periodic systems,[97,98] hybrid functionals based on screened Coulomb potential,[99-101] and periodic coupled cluster[102-104] there is still a need of reliable and affordable method for surface-deposited nanoclusters. The unit cells required for calculating clusters deposited on surfaces are large, and get only bigger upon incorporation of dislocations, vacancies, and substitutions in the surface. Excitingly, in the last decade, Neuhauser and his colleagues have been developing a set of stochastic

approaches to electronic structure, which are able to describe such large, electronically-heterogeneous systems.[105-111] The key is to replace the summations over occupied (or virtual) orbitals in quantum chemistry methods by sampling over random states, each of which is a stochastic linear combination of all occupied (or virtual) states. In fact, hybrid-DFT with exact exchange,[112-116] especially with 100% long-range-exchange, remove self-repulsion and handle well the different degree of localization required for different orbitals. Note that, in general, hybrid functionals would fail to describe metallic systems; however, for metal clusters with less than a dozen of atoms where the system is far from metallic, or for metal oxides, hybrid-DFT can improve the final results. Nevertheless, such simulations are very expensive due to the exact exchange; this is where the stochastic paradigm comes by using deterministic-type DFT with stochastic exchange.[111] This method uses fundamentally the same techniques needed for local-potential DFT, which handle efficiently cells with up to ten thousand electrons, and scale mildly, as $O(N_e^2)$ where N_e is the number of electrons in the system. Note that in practice even a few hundred samples are sufficient to describe the long-range exact exchange so the combined deterministic-stochastic method is only about two-to-five times more expensive than traditional deterministic local-potential DFT.[111,117]

Finally, treatment of dynamics in cluster catalysis is awaiting some improvement. On the one hand, established rare-event sampling techniques could be adapted or expanded to describe reaction pathways with complications, such as transitions states that involve cluster catalyst isomerization, or escaping the full equilibration in the reaction intermediates. An additional dynamic problem that we did not address in this review is the possible coupling between electronic and nuclear degrees of freedom and the breaking of the Born-Oppenheimer approximation, during such events as, for example, reagent binding. The reagent at high T may arrive with quanta of vibrational energy in various modes of vibration. The catalyst may have electronic states that are closely spaced in energy, and there is a possibility of non-adiabatic coupling in the dynamics, where there is an exchange between electronic and vibrational degrees of freedom. For clusters, this kind of dynamics is less likely than for extended metallic surfaces, and that is the reason this aspect was not addressed in the present review. Molecular orbitals in clusters are separated in energy, unlike for metallic surfaces that have a continuum of electronic states in the conduction band. From our estimations, the electronic entropy of deposited clusters at typical temperatures of thermal catalysis (300–700 K) is negligible. Therefore, it is unlikely that vibrational energy from vibrationally excited molecule

could transfer into the electronic excitations in the cluster through non-adiabatic events.

To summarise, the emerging paradigm of dynamic catalytic interfaces pushes the community toward theoretical methods that are far beyond the common-practice DFT. We need sampling techniques, statistical mechanics, accelerated dynamics, and correlated electronic structure methods that surpass DFT in accuracy and are adapted for extended systems.

EXPERIMENTAL DETECTION OF METASTABLE STATES IN CATALYSIS

The presented theoretical advances put experiment on the spot, presenting it with a challenge of detecting and characterising the minority active species of the catalyst, the true actors in catalysis. One opportunity might arise from the temperature control of the population of metastable states. If a higher-energy metastable state is the performer in catalysis, then gradually turning the temperature down should eventually depopulate that isomer making the catalyst inactive abruptly. The reaction then should exhibit non-Arrhenius behaviour. We are awaiting for an experiment such as this to be done. An invaluable approach is also *operando* spectroscopy. The word *operando*, having its root in Spanish, means working; therefore, an *operando* study implies that the system of interest is being examined while everything is operating. Note that, in practice, in order to study the system of interest, a catalyst in this case, one would usually freeze the catalyst and take a snapshot of what is happening. Although this technique gives great amount of information about the catalyst, it would not depict exactly what is happening in the system. On the other hand, if one investigates the catalyst while it is working is called an *operando* study.[118] In fact, *operando* spectroscopic methodology has been introduced into the catalysis literature not so long ago, in 2002.[119] This technique combines simultaneous *in situ* spectroscopy and kinetic measurements on the same sample and time. Hence, *operando* methodology describes *in situ* spectra under true catalytic operation as determined by simultaneous online activity/selectivity measurements. Determination of intrinsic reaction kinetics of catalysed reactions is of importance in the safe and economical design and control of industrial chemical and environmental processes, and in the development of new and improved catalysts.[120-125] Echoing all the assertions in this review, *operando* studies have shown that catalysts may undergo dynamic structural transformations upon small changes in

the reaction conditions and such transformations have a strong impact on the performance of the catalysts.[126,127] Strictly speaking, the active state of a catalyst only exists during the catalysis. Many crucial mechanistic questions remain poorly understood thanks to the inherent multi-scale complexity of heterogeneous catalytic transformations. In this regard, X-ray absorption spectroscopy (XAS) has become an important technique for studying the mechanisms of catalytic reactions due to its capabilities to elucidate the nature of the atomic and electronic structural features of operating catalysts. For supported size-selected clusters, in order to monitor the formation of complex cluster assemblies through agglomeration, *in situ* studies at different length scales are required. To achieve that objective, Vajda et al.[55] combined small-angle X-ray scattering (SAXS), X-ray absorption near-edge structure (XANES) spectroscopy, ab initio simulations, and machine learning (artificial neural network) techniques. They found that the significant differences between the sizes of particle agglomerates, as probed by SAXS, and the sizes of locally ordered regions, as confirmed by XANES, imply the fractal, grape-cluster-like structure of the agglomerates. As a result, XANES and SAXS provide highly complementary structural information. The findings obtained by their technique can actually have a profound effect on the understanding of particle sintering and assembly processes and of structure−properties relationship in ultradispersed metal catalysts in reaction conditions.

Conclusion

We presented ample evidence that cluster-decorated heterogeneous catalytic interfaces are highly dynamic, fluxional, and present an ensemble of many structural states in the reaction conditions. Considering just one global minimum, and a single reaction profile on this form of the cluster can produce a qualitatively wrong picture of catalysis. This reality is highly demanding of both new theoretical approaches and methods far beyond traditional DFT, and *operando* experimental characterization that would allow pinning down the reaction actors in catalysis. Dynamic fluxionality requires a new paradigm in theory of catalysis, some elements of which began to emerge. Firstly, the flat potential energy surfaces of clusters lead to thermal populations of many structurally distinct catalysts states in conditions of catalysis, and as a result, all properties of such interfaces are ensemble-average. Thus, statistical ensemble representation is required in modelling. Secondly, as has been known for a long time, cluster shapes are critically sensitive to the nature of the bound adsorbates, and so realistic coverage with reagents is very

important to include in modelling. The placement of the reagents is not unique, and that further expands the ensemble of thermally-accessible catalyst states. In the ensemble, the less stable catalyst structures are usually more active and can play an important role in the kinetics of the reaction. Thus the global minimum might not be the structure relevant for the reaction kinetics, i.e. it is catalytically dead. This also implies that kinetics and thermodynamics of the catalysed reaction are controlled by different states of catalyst. In such circumstances, mechanistic studies focusing on the global minimum alone would be misleading. Catalyst dynamics is also an essential part of the reaction coordinate, and the unanswered question is whether or not cluster dynamics can couple to the reaction dynamics directly, majorly changing the nature of transition states. Furthermore, fluxional clusters may exhibit non-Arrhenius behaviour due to their unique dynamics, because as T changes, the ensemble of thermally-accessible catalyst states also changes. Hence, the conventional kinetic models might not hold true for these catalysts. Finally, the fact that, depending on bound intermediate, ensembles of catalyst states change, can potentially break the scaling relations, which are well-established in surface chemistry. This can be used as one of the levers of catalyst design, allowing circumventing the fundamental limitations on the catalyst performance.

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