Title
Designing clusters for heterogeneous catalysis

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A catalyst is a substance that is not consumed in the reaction, but it provides a reaction pathway with lower activation energy, allowing the synthesis of the desired products at commercially viable rates. Today, catalysis is involved at some point in over 90% of all chemical manufacturing processes, with a huge impact in the world's economy. Being that important, research on catalysis is a continuing developing area, which involves different sciences, such as chemistry and surface science. Catalysis is essential for the production of chemicals, food and medical applications, but it is also pivotal in reducing pollution, and the development of sustainable energy production. Catalysis can be divided into two groups: homogeneous and heterogeneous. In the former the catalyst and reactants are in the same phase, whereas in the latter, the catalysts are solids and the reactants are in liquid or gas phase. The heterogeneous catalysis has the advantage of providing access to environmentally benign chemical synthesis due to the ease of product separation and contaminant waste decrease. Traditionally, this type of catalysis was carried out with a limited knowledge of the nature and morphology of the catalysts. This might lead to undesirable side reactions, low selectivity and small control over the performance of the catalysts. Because of the demanding needs of more complex and higher selective reactions to be catalyzed, the field has undergone great development. Currently, the ultimate goal of research in heterogeneous catalysis is to provide a fundamental understanding of the processes involved in a catalytic reaction. In this way, it would be possible to design catalysts with optimized properties, that are high activity and selectivity, and long-term stability for recovery and reuse.

Industrial heterogeneous catalysts typically consist of small nanoparticles dispersed on high surface area supports, such as oxides or zeolites. Very often, the most effective catalysts are precious metals, which are naturally scarce and very expensive. In this vein, metallic nanoparticles made of just few atoms, the so-called nanoclusters, offer great advantages. The obvious one is that all, or almost all the atoms, are at the surface, so all of them can act as active sites, because they are in direct contact with the reactants coming from the gas or liquid phase. This is illustrated in figure 1, where a metal surface, a metal nanoparticle deposited on an oxide, and a metal nanocluster deposited on the same oxide are shown. In the metal surface, most of the atoms are underneath the first layer, so they do not interact with the reactants and therefore, do not catalyze the reaction. In the case of nanoparticles many atoms are at the surface acting as active sites for the catalysis. Still, a portion of atoms are inside the nanoparticle and cannot act as binding sites for the reaction to be catalyzed. But in the case of nanoclusters, the metal use is optimized, since all of the atoms are exposed to reactants and can take part in the catalysis.

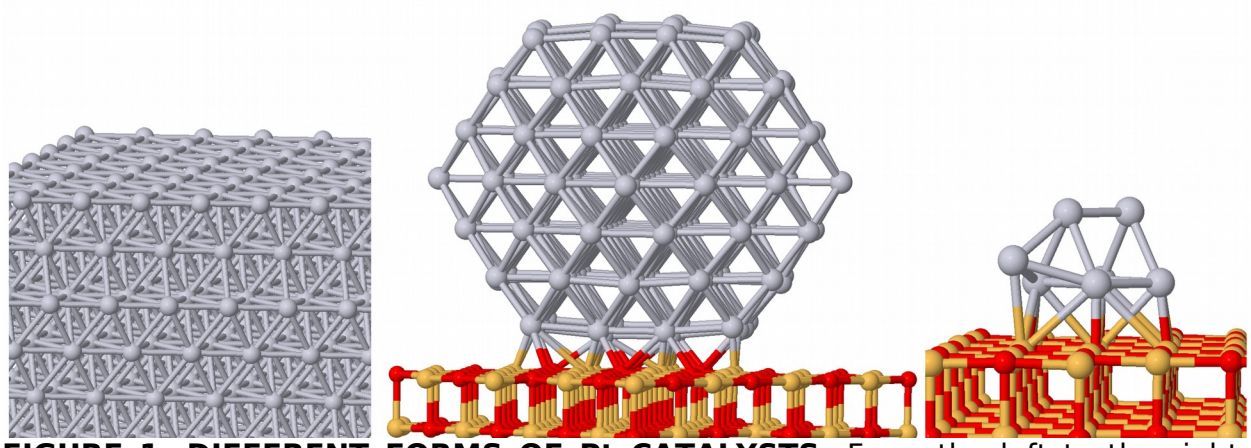

FIGURE 1. DIFFERENT FORMS OF Pt CATALYSTS. From the left to the right: Pt(111) surface, Pt nanoparticle of 146 atoms supported on MgO(100), and a 7 atom Pt nanocluster on MgO(100). In the latter the Pt amount is fully optimized, since all the atoms are exposed and will therefore interact with the reactants.

Moreover, these sub-nanometer particles usually posses special reactivity and selectivity, and size-dependent properties, due to the low coordination of the atoms and the quantum confinement. Because of these particularities, exciting and unexpected catalytic properties arise. This can be translated into lower reaction temperatures, and thus, energetic savings. With dwindling supplies of precious metals and increasing demand, metallic nanoclusters are thus key to reach cheaper and greener industrial processes. Probably the most surprising case is gold. Bulk gold is chemically inert, for example it does not chemisorb oxygen. This is why jewelry made of gold does not get oxidized, unlike other metals such as iron. This is good for jewelry, but not for catalysis. On the contrary, gold nanoclusters have been found to be extremely good catalysts for a number of reactions, and they do chemisorb O_2 dissociatively. For example, in gold catalysts deposited on iron oxide, nanoclusters composed of about 10 Au atoms were identified as the true actors in the catalytic oxidation of CO.[1]

Surface deposited metallic nanocatalysts are, however, extremely complex systems and they present important challenges in order to achieve a routine use in industry.[2] One of this difficulties arises from the fact that they are thermally unstable. Small bare nanoclusters are unstable toward further growth, and they tend to coalesce forming bigger nanoparticles to increase the coordination number of the metal atoms and minimize their surface energy. As a consequence, they lose the reactivity and catalytic activity. This problem is even more pronounced considering that catalysis is usually carried out at very high temperatures. A key aspect to make catalysis that involve clusters of specific sizes is to prevent clusters from sintering. Stability of the catalyst in general (against sintering, or poisoning) and catalytic activity are opposing trends: systems that are too stable are not catalytic (e.g. bulk Au), whereas systems that are very catalytic are also reactive in general, i.e. unstable (like Fe^{2+} cations). Hence, designing catalysts is a matter of striking the right balance.

1 SIZE DOES MATTER

Usually size selected clusters are produced using a gas phase cluster ion source, then they are size selected with a mass selector and, afterwards, deposited on a substrate. It is so impressive the development of such experimental techniques, that nowadays surface-deposited metallic clusters of a specific size and composition can be synthesized and characterized (mostly with spectroscopic and microscopic techniques) with outstanding precision. Where experimental techniques are not yet at hand, however, computational theory has become an essential tool as a predictive basis for guiding experiment. Indeed, the improvement of computational methods and capabilities allow the prediction and also the understanding and realization of new materials at the atomic level, avoiding, in some cases, the high cost of experimental random trial-and-error search. Small nanoclusters are treatable with state-of-the-art computational methods. By means of computational modeling we can obtain a rather full picture of the properties of a polyatomic system and help elucidating the structure-activity relationship. Indeed, experiments rely on computational investigations and the synergy between theory and experiment has enabled the fast development of this field. Nevertheless, as we will see later, there are still important avenues that need to be addressed.

As we have explained, metallic nanoclusters exhibit different properties from those of the metal bulk, and they offer the possibility of using a reduced amount of precious metals. The size, as well the shape, of these nanoclusters is an extremely sensitive factor influencing the catalytic properties. The addition or removal of just one atom can greatly impact the activity and selectivity of the catalyst. For example, quasi-2D Pt_7 particles deposited on aluminum oxide (Al_2O_3) are significantly more active than Pt_8 particles, that have 3D shape, deposited on the same surface, for dehydrogenation of alkanes.[3] In contrast, Pt_8 supported on rutile (TiO_2), which has a 3D morphology, is a better catalyst for CO oxidation than smaller Pt clusters.[4] These examples evidence that through minor changes in size and composition, the catalytic properties can be potentially tuned. A new horizon full of possibilities emerges in the field.

We are still learning the reasons behind the behavior of these nanocatalysts. To start with, it is fundamental to consider how the nanoclusters are affected by the surface underneath, since most of the metal atoms are at the interface with the support. This support alters the morphology of the cluster and it has an enormous influence in both, the catalytic performance and the stability against sintering. Some supports, such as reducible oxides (TiO_2, CeO_2, ...) tend to withdraw electrons from the metal, whereas non-reducible oxides (MgO, Al_2O_3, ...) donate electrons to the cluster. Although the charge transfer between the surface and the metals is usually small, surface defects (such as oxygen vacancies, which are very frequent in oxides) can make this charge transfer more pronounced. Sometimes, this charge transfer has even the power to activate or deactivate the catalysts.

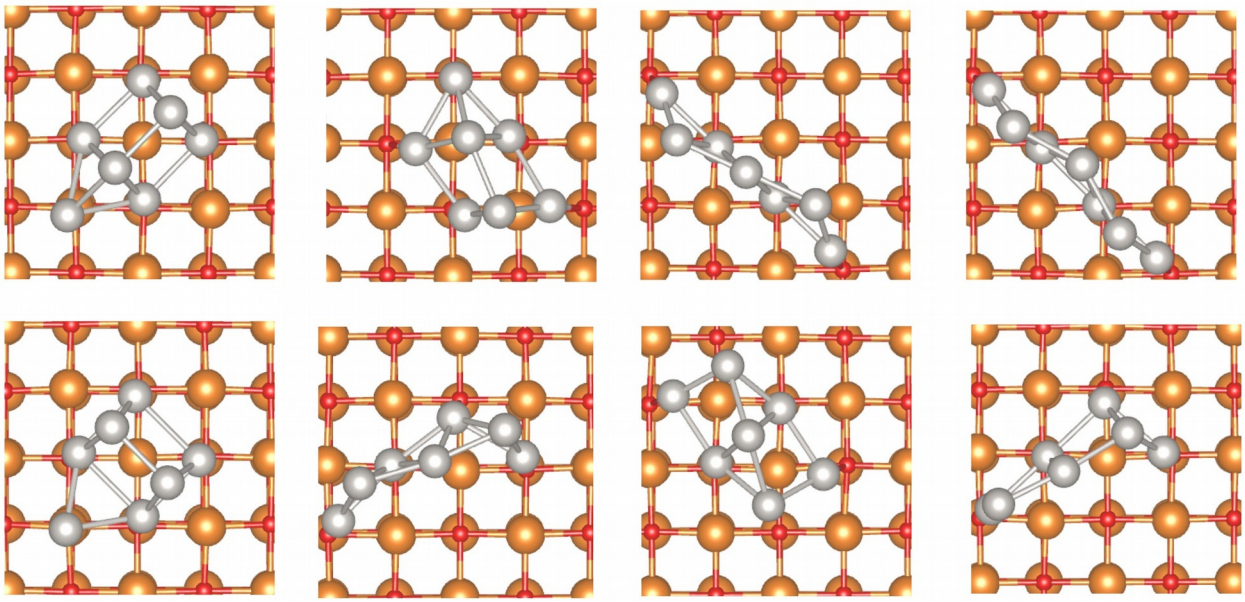

FIGURE 2. Pt_7 ISOMERS ON MgO. Top view of all the Pt_7 isomers supported on a perfect MgO(100) surface that are theoretically predicted to be populated at 700 K.

2 CLUSTERS ARE FLUXIONAL AND POLYMORPHOUS

Until very recently, size specific clusters were considered as a single entity, adjusting its shape only slightly upon reagent binding. We are now starting to realize that this is a rather simplistic view of the true nature of nanocatalysts, which is far more complex than that. And theory has proven to be invaluable in this breakthrough. In fact, a cluster with a given size and composition has many isomers with similar energies. This means that several isomers with different structure, and thus, different catalytic properties, will be present in conditions of catalysis. Moreover, the most stable isomer might not be the most catalytically active! This realization is a game changer for the field. In order to reproduce the experimentally observable size-specific catalytic performance of clusters, their properties must be ensemble-averaged. Evidently, this adds a level of complexity when studying such systems.

Let us take Pt_7 supported on a perfect MgO(100) surface as example. In Figure 2 we show all the isomers that are theoretically predicted to be populated at 700 K. The presence of many structural forms could be called polymorphism. Some of these structures have more spherical and compact shape, while others are more planar-like. As a result each of them exhibits different binding sites, with different coordination and different affinity towards different reagents. From a computational standpoint, it is complicated to determine the most stable geometries of a specific nanocluster, because clusters shape is not just a cut from the bulk. A variety of algorithms have been developed and are currently being developed for this task, the bottle neck being the computational time to compute all the possible geometries at the electronic structure level.

Furthermore, structural isomers might interconvert from one to the other, because of the fluxional nature of the metallic clusters, arising from their delocalized and non-directional chemical bonds. This feature is enhanced for real catalytic

processes, where the reactions occur at high temperatures. The fluxionality of clusters' shape is a complication for experimental characterization and computational modeling, but it cannot be ignored, since it is fundamental to the existance of the true active sites. Also, of course, the support will play an important role in the clusters fluxionality, facilitating or hindering certain morphologies. Note that it is also possible that some isomers are kinetically trapped, protected by a large energy barrier.

It can be shown furthermore, that all these minima are generally highly accessible. For Pt_7 supported on α-alumina, interconvert across barriers toward cluster isomerisation has been explored. For this task, a set of algorithms have been created and adapted in a pioneer work,[5] to make the study possible, even if the computational cost for this system of 7 atoms cluster (plus the surface) is still enormous. Here, it has been shown that all the possible P_7/α-alumina isomers can be divided in two sets, see Figure 3. Within each group, the clusters change the shape very frequently (low energies are required for these interconversions), while between the two sets, the structural transitions are less unlikely but still very facile (happen in the time on the order of ns). Interestingly, the most stable Pt_7 isomer is catalytically inactive. The second most stable isomer is catalytically very active. These two clusters furthremore belong to different groups, or basins. Binding ethylene (the explored reactant) to these clusters reverts the prefernce toward making the single-layer, more active isoemr more stable. Pt8, despite being very close in size to Pt7, does not exhibit nearly as much dynamism away from stable and more innert global minimum, and thus has lower catalytic activity. Also, the more reactive Pt7 undergoes coking and ammends to coking supression by doping way more easily than Pt8.[6]

Thus, over the years we have moved from a more traditional single stationary view of the nanocatalyst, to a statistical mechanical ensemble definition of size specific activity of the nanocatalysts. The dynamical and fluxional features further complicate the picture. But the intricacy goes beyond: the relative stability of cluster isomers and the probability for them to be populated might vary significantly with subtle changes in the surrounding environment. A further crucial milestone that needs to be accomplished, is the study of these catalytic systems under realistic conditions.

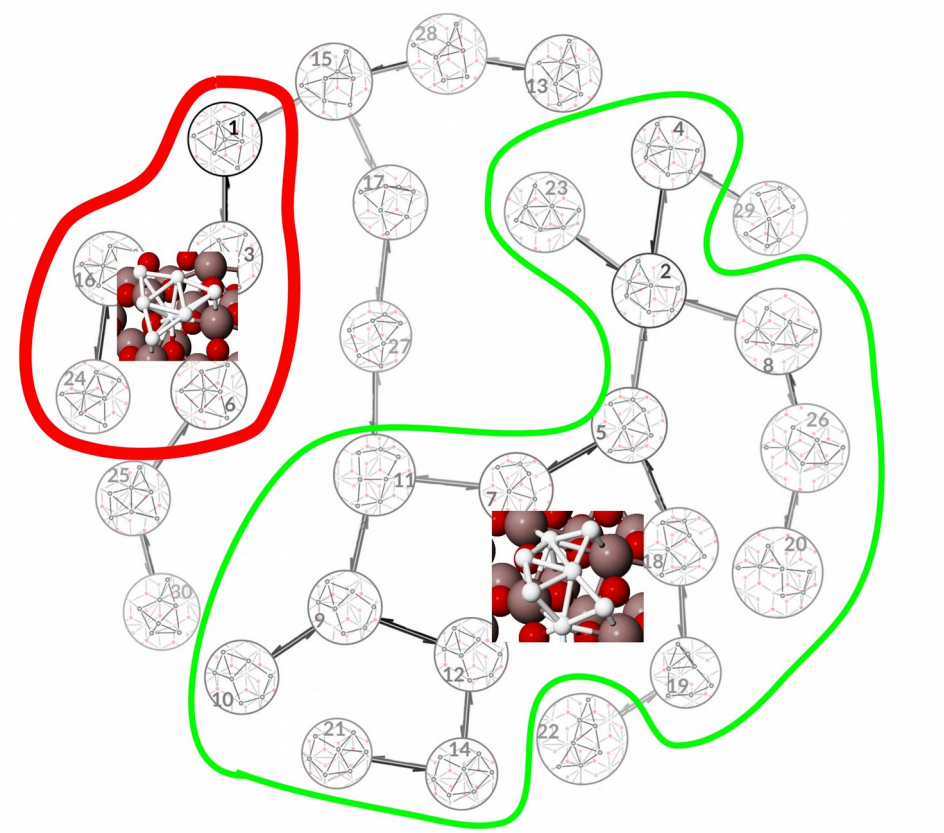

FIGURE 3. PROBABILITY OF INTERCONVERSION BETWEEN Pt_7 ISOMERS. All the Pt_7 isomers deposited on α-alumina and the energy barriers required for the structural transformation between them (numbers on the arrows). It has been seen that the clusters are divided into two groups (circled in red and green). Within each group the probability for the clusters isomerization is high (low energy barriers), but between groups the probability is lower (higher energy barriers). The most stable isomer belongs to the group circled in red, but this isomer is catalytically inactive. The second most stable isomer belongs to the second group (in green) and it is catalytically very active.

3 REALISTIC CONDITIONS

Today, the most important challenges that the experimental characterization and computational modeling need to face are related to the increasing degree of complexity of these systems, along with the need to perform experiments and run simulations under realistic conditions. Many efforts are being done to link model studies with those performed on real catalytic systems, that are inherently more complex. The most relevant factors for realistic reaction conditions are the temperature, coverage of adsorbates (such as the reactants and reaction intermediates) and more realistic substrates (amorphous, defected, hydroxylated, etc.). First, the relative stability of all the isomers and therefore, their population (the probability of them to exist), as well as their tendency or capacity to interconvert from one to the other, will depend heavily on these factors. To recreate the real conditions under which the catalysts operate, it is vital to consider the

presence of the mentioned adsorbates. These compounds can modify radically the population of the isomers, i. e., a given structure can become predominant under certain conditions. This was beautifully shown for Pt_{13} cluster under a pressure of hydrogen (typically in (de)hydrogenation reactions that are catalyzed by platinum).[6] If we model this system without including any kind of adsorbate, we see that there are many isomers energetically accessible at high temperatures, namely, all these clusters will be present in conditions of catalysis. The most stable geometry is shown in figure 4 (left), a tricapped pentagonal prism structure. Adding 18 hydrogen atoms to Pt_{13} leads to a very different picture: the most stable structure has now a different geometry (seashell like geometry, figure 4 (center)), and the number of isomers that would be present in the catalysis is very much reduced (from 49 in the bare Pt_{13}, to 20 in $Pt_{13}H_{18}$). If we keep adding hydrogens (up to 26), about the same number of isomers will be populated, but these isomers will have different shape (figure 4 (right)), and thus, different binding sites. So hydrogen adsorption has a deep influence in the clusters' shape and population. The structural transformation is likely to be driven by the enhanced ability of certain shapes to adsorb hydrogen. This extraordinary capacity of the nanoclusters to adapt upon the exposure of adsorbates might be one of the key characteristics for their outstanding catalytic performance. A more flexible isomer is able to adapt to the environment, increasing the interaction with the substrate as well as facilitating the binding to the reactants, and eventually reducing the activation energy for the catalytic reaction to happen. Indeed, the hydrogen coverage also impacts the catalytic activity, like in the case of methane activation. This activity was studied the mentioned Pt_{13} under different hydrogen pressures and important differences were seen. With no hydrogen, Pt_{13} would deactivate quickly (due to coke formation, a process related to a poor selectivity). In the presence of hydrogen, however, although the catalytic activity is a little lower, the durability of the catalyst is predicted to be significantly longer. So, a more robust catalyst is formed under high pressure of hydrogen. The message of this theoretical work is clear and very helpful for experiments and industry: this type of reactions should be carried out in the presence of hydrogen, to achieve the best performance of this particular catalyst.

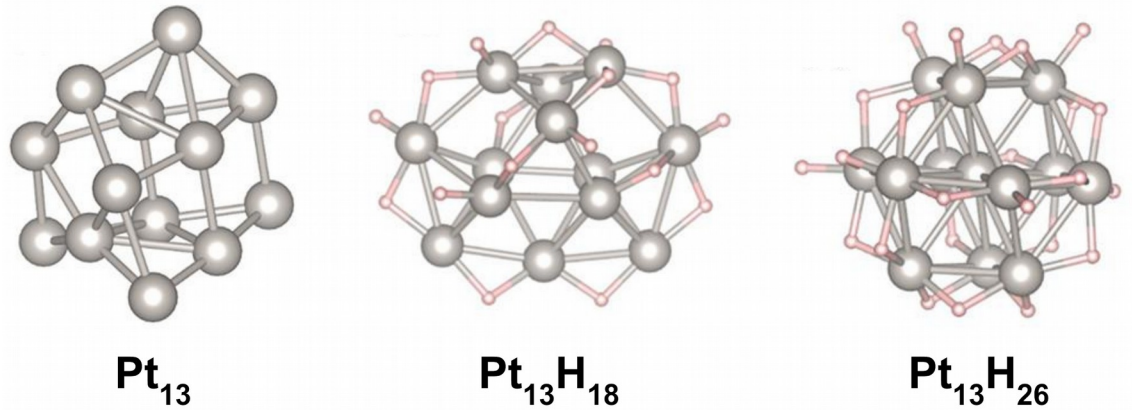

FIGURE 4. CLUSTER ISOMERIZATION DUE TO THE ADSORBATES COVERAGE. The most stable Pt_{13} clusters with (a) no hydrogen, (b) 18 hydrogen atoms, and (c) 26 hydrogens. The clusters' shape is transformed under hydrogen pressures, adapting to enhance the ability of Pt to adsorb hydrogen. It is intuitive to understand that a nanocluster is significantly more flexible than an extended surface or a big nanoparticle, so its flexibility facilitates the binding to the reactants,

and might eventually lead to a reduction in the activation energy for the catalytic reaction to happen.

In addition, the coverage of adsorbates will alter not only the clusters shape and fluxionality, but other properties, like the sintering resistivity (stability). As a result, bridging the pressure gap could lead to a change in the activity, selectivity and stability. Experiments are moving in this direction, from the early investigations under ultrahigh-vacuum conditions to higher gas pressures. Computationally the biggest challenge of modeling a catalyst under a given adsorbate coverage is the fact that it increases heavily the computational cost. Global mimima search techniques to identify the most populated cluster isomers, however, should be extended to include to effect of adsorbates coverage. But bridging the pressure gap also means to take care of its effects on the underlying support, such as the hydroxylation of the oxide surfaces. Finally, in terms of realistic modeling, the transition from ideal crystalline surfaces to amorphous supports, which are relevant in industry, is fundamental. Amorphous supports, as well as defected supports, are irregular and can provide new adsorption sites for the catalysts, affecting their morphology, catalytic activity and selectivity, and the sintering propensity.

4 OUTLOOK

The motivation to advance in the study of nanocatalysts is, as explained in this text, to be able to exploit all their advantages (reduce amount of precious metals, enhance catalytic performance, tunable selectivity), but also to use them as models to expand our knowledge in the catalytic processes. Nanoclusters are appealing materials in the search of more efficient catalysts that will eventually enable industry to work under milder conditions of lower temperatures and pressures. The final goal is to achieve the best performance of the catalysts with a reduced environmental and economic cost. The exchange of information among experimental and computational scientist has been and will be pivotal to continue moving forward in this area.

The electronic structure of clusters and their geometry on a support, including the accompanying cluster–support interaction, are strongly correlated with catalytic activity. At the same time, the population of different isomers will depend on the temperature and the coverage of adsorbates. It is not simple to predict how the structure-activity relation works. Although we have developed useful concepts to generalize how the world works in the nanoscale (high surface-to-volume ratio, quantum confinement), when we go to particular cases (particular size, support, composition, reaction...) we can understand or rationalize the facts a posteriori, but our predictive power is still limited. This is the consequence of highly complex and dynamic systems. The fundamental understanding of catalyst structure and function will open the door to the formulation more generic design strategies, for the expansion of this class of materials.

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