Playing with Structures at the Nanoscale: Designing Catalysts by Manipulation of Clusters and Nanocrystals as Building Blocks

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Dedicated to Professor Maurizio Prato on the occasion of his 60th birthday.

The purpose of this Concept is to highlight some of the most recent and promising methods for the preparation of tailored catalysts by designing and preparing the component building blocks and by assembling them in a controlled fashion. We want to emphasize how rational design and synthesis of catalysts must be coupled to precise catalytic and structural characterization of the systems in an ideal feedback loop. New catalyst design and preparation techniques, dictated by information about the active sites that the specific application requires, are frequently available. The building blocks for developing these novel catalysts include colloidal methods for the preparation of uniform nanostructures, physical methods for rational assembly of the building blocks (Langmuir–Blodgett, liquid–air self-assembly), and development of rational interactions between the building blocks for enhanced activity of the assemblies. These methods, which apply techniques normally used in other fields of nanotechnology to catalysis, offer exciting opportunities to help improve currently available catalytic systems in terms of activity, stability and selectivity.

1. Introduction

Catalysis has been an essential part of many industrial and technological developments that have occurred in the past century, and it still plays a central role in the progress of our society. Key examples include the catalytic conversion of oil-derived compounds into a variety of useful chemicals and plastics; the catalytic production of ammonia from hydrogen and nitrogen that revolutionized the preparation of fertilizers and increased food production; the advent of three-way catalysts as a prototypical example of catalysis for environmental remediation. Clearly, catalysis remains central for the development of our society in extremely important areas that affect all of us.

Traditionally, a major part of catalytic science has been empirical. The discovery and optimization of catalytic systems have often been performed by preparing and testing a large number of samples with different compositions, supports, and synthetic methods. Indeed, high-throughput screening of catalysts is still widely used, especially in industry. Although empirical methods can allow the rapid screening of samples, this approach does not make optimal use of our catalytic knowledge.

The development of computational methods to study chemical reactions and materials[1] and the advent of surface science to understand the mechanisms by which active catalysts work[2] has clearly helped guide the screening and targeting of materials with specific catalytic function and improved activity, selectivity, and stability compared to what had been done before.

In parallel to the development of computational and surface science tools, progress in the field of nanotechnology allows structures to be prepared with a very high degree of control at the nanoscale level. Techniques to synthesize nanoparticles and nanocrystals in wide classes of compounds, including metals, semiconductors, metal oxides, with controlled size, shape, and composition are now available.[3] These nanocrystals are becoming the starting components for the rational assembly of nanoarchitectures and functional structures with high complexity for advanced applications in electronics, biomedicine, and catalysis.

Precisely formed nanocrystals can be viewed as analogues of atoms. They can show quantized energy states that depend on their size and shape (quantum-size effects). Furthermore, because of their uniformity (nanocrystals can be prepared with precision of more or less one atomic layer), they self-assemble into superlattices to give supracrystals as atoms in a crystal do.[4,5] These characteristics prompted some to call these new building blocks “artificial atoms” or “atom equivalents”.[6,7]

One can also view these precisely formed nanocrystals as building blocks similar to toy construction bricks. Just as toy construction bricks can have different sizes/lengths, shapes, colors, nanocrystals can be prepared in different sizes, shapes and compositions (Figure 1). Similarly to how complex struc-

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tures can be built by connecting the various toy construction bricks, nanocrystals can be manipulated by exploiting chemical interactions (from weak van der Waals forces to strong covalent or ionic bonds) to precisely place components onto surfaces in a desired fashion. By functionalizing the protective organic monolayer, doors are opened for further manipulation of these tiny building blocks. Self-assembly can also be exploited to organize the pieces into ordered superstructures. In this way, large structures prepared from individual building blocks can show properties that cannot be found in the individual components alone due to the special interactions between the parts.

Although there have been relatively few connections between the fields of catalysis and nanocrystal synthesis in the past, these two disciplines are clearly related (catalysis always relied on the use of nanoparticles/nanostructures as active phases due to the increased surface area for reactivity). Traditional methods for the preparation of catalysts generally involve either impregnation procedures, ion exchange, or thermal decomposition of organic, inorganic, or organometallic precursors. Although these methods have been successfully applied to many important industrial processes that have allowed the technological advances of the past and present century, the materials that are prepared are generally heterogeneous in terms of active phases/sites, making it difficult to relate the activity of such systems to the structure of their active sites. For example, the heterogeneous reactivity of Au was independently and simultaneously discovered during the ‘80 s by Masatake Haruta (CO oxidation) and Graham Hutchings (alkyne hydrochlorination), but most aspects of its reactivity are still far from being completely understood. Understanding the nature of active sites or phases for a particular reaction is important for allowing the preparation of tailored catalysts that outperform those currently in use, with beneficial consequences for sustainability and for process economics. One of the most elegant examples of this is the understanding of the reactivity of Fe-based systems for ammonia synthesis using surface science techniques, which led to more active and stable catalysts that improved the production of fertilizers (see for example Noble lecture by Gerhard Ertl). These aspects clearly reveal that a strong interplay between the synthesis of precise nanostructures and their use in catalysis can be the key for improving both the understanding and the implementation of catalytic systems.

The conceptual differences between conventional and nanoscience-based methods for preparing catalysts are shown schematically in Figure 2. Conventional techniques provide samples that are typically heterogeneous. After materials are tested for a particular reaction, the samples that are found to be more active and/or selective are studied more in detail. Because the materials undergo unknown structural changes during synthesis, significant effort must be expended to understand what makes the catalyst efficient. With nanoscience-based techniques of preparation, the information flow is reversed: by starting with uniform systems where any particular sites are tuned to a fine extent, each specific sample can be studied for the particular application and the results can be correlated to the particular sites present in the different systems. Once the active sites for that particular application are known, one can go back to the synthesis and fabrication procedure to prepare samples featuring those particular sites with exclusive selectivity to provide systems with the characteristics that are desired.

This Concept aims to highlight some of the most recent advances in the preparation of tailored structures and architectures as catalysts to fundamentally understand catalytic reactions and prepare more active, stable and/or selective catalysts. A selection of the most successful examples that coupled precise fabrication with catalytic reactions will be presented in order to highlight how the successful implementation of techniques from nanotechnology can lead to the preparation of catalytic systems with unprecedented properties.

2. Use of Uniform Nanocrystals in Catalysis

The use of uniform nanocrystals in catalysis was proposed long ago, but new methods are only now available for the precise
engineering of the active sites. Synthetic techniques have been developed that can now produce nanocrystals with size distributions below 5% (corresponding to a precision of roughly one atomic layer) and with tailored shapes. The use of these nanocrystals can bridge the material-pressure gap in catalysis, providing systems that possess structures as precise as those of model single crystal surfaces but having high-surface areas that can be studied under realistic reaction conditions (atmospheric or higher pressures).

2.1 Exploring the Reactivity of Different Exposed Facets

The preparation of metal nanocrystals with different shapes in high yields allows the reactivity of particular facets or sites for catalytic reactions to be studied. For example, Somorjai’s group demonstrated that Pt cubes which expose exclusively {100} facets to the fluid phase can show catalytic properties very close to Pt {100} single crystal surfaces in the hydrogenation of benzene to cyclohexene. Because the materials can be tested...
in conventional catalytic reactors, they hold promise for the application to industrial processes. The authors observed that the planar sites (irrespective of their crystallographic orientation) were active for the semi-hydrogenation reaction of 2-methyl-3-butyln-2-ol in water to the corresponding alkane, whereas edge sites were responsible for the full hydrogenation to the alkane. This led the authors to conclude that cubes of 3–5 nm edge length should be the most active for the reaction in terms of productivity and selectivity. Unfortunately, reconstruction of catalytic surfaces under the action of adsorbates can occur even at room temperature and care must be taken when assessing structure–activity relations of the type shown in these two examples. Nevertheless, these are elegant examples of how nanotechnology can help provide information about facets with the desired activity and selectivity in a reaction.

2.2. Catalysis with Size-Selected Clusters

Very small clusters can exhibit peculiar catalytic properties due to their high surface-to-volume ratio and their distinctly different electronic structure compared to that of corresponding bulk materials or larger particles. Indeed, small clusters have electronic configurations that are between those of molecules (distinct, localized electronic orbitals with specific HOMO–LUMO gaps) and that of bulk metals (conduction bands with an appropriate Fermi level at a given temperature). As such, the transition between aggregates of tens and hundreds of atoms to that of thousands atoms can result in sharp differences in the catalytic properties due to the different electronic interactions that can occur between metal clusters and the support and/or reactants. In this sense, Au clusters have demonstrated very interesting catalytic properties that vary much depend on the cluster size.

Lambert and co-workers reported on selective oxidations employing 55-atom gold clusters. Au catalysts were prepared using SiO₂, carbon and boron nitride as inert supports that are not expected to electronically interact with the supported particles. Samples with 55-atom clusters as well as with larger particle sizes (from 4 to > 30 nm) were tested for the selective oxidation of styrene with O₂ in the absence of initiators. The larger particles were inactive, but catalysts based on 1.4 nm particles (the size of 55-atom clusters) gave good conversion and selectivity. Although the authors did not speculate about the site at which dissociative adsorption of O₂ would take place, this work clearly showed how electronic and geometric properties of supported particles might become fundamentally important in driving catalytic reactions. Being able to quantitatively prepare only the active phase of a catalyst (in this case, 55-atom Au clusters) would become therefore crucial for obtaining highly active and selective systems.

Corma’s group recently reported on the use of very small Au clusters (< 20 atoms) for organic transformations. When conducting alkyne hydration reactions with less than 100 ppm of Au precursor, the authors observed an induction period before products were formed. Spectroscopic evidence indicated the induction period was due to formation of Au clusters containing five to nine atoms. Such clusters were formed at concentrations of Au precursor even in the ppb range, implying turnover numbers (TONs) of ~10⁷ and turnover frequencies (TOFs) of ~10⁶ h⁻¹, thus approaching rates observed with enzymatic catalysis. The authors proved that nanoclusters were important by synthesizing Auₓ and Auᵧ clusters protected by dendrimers and demonstrating the reaction proceeded with no induction period when these were present, corroborating the idea that size-selected clusters were the active species for the reaction.

The ability to tailor nanocrystals and clusters at the atomic level can also change the properties of the clusters. Zhang et al. preferentially deposited Au atoms at the vertices of 1.8 nm Pd particles. In this way, the Au atoms were located at the positions with the lowest coordination number. Furthermore, the presence of Pd next to the Au atoms influenced the electronic properties of Au. It was shown that the appropriate Au-modified Pd particles were the most active catalysts for glucose oxidation reported so far, with TOFs of the order of 200 000 h⁻¹. Pd or Au particles of similar size, or even Au-modified Pd particles with random configurations, were at least 20–30 times less active under the same conditions (Figure 3). The authors explained the observed reactivity by electronic effects resulting in partial negative charges accumulating at the top of the nanoclusters.
Au atoms. These negatively charged atoms likely interact more favorably with molecular O₂ to form hydroperoxo species that are found to be important intermediates in this type of oxidation reactions.

2.3. Extracting Structure–Activity Relations with Uniform Nanocrystals

The oxidation state of metal atoms in a nanocrystal is strongly dependent on size and this can have important implications in catalysis. Wang et al. studied this property in Pt by preparing nanoparticles of 1, 2, 4 and 6 nm diameters. Although a catalyst prepared by the authors with the smallest, 1 nm Pt particles had much less Pt⁰ than all the other samples, and most of the Pt was in oxidized state, this catalyst achieved 80% selectivity to formaldehyde under methanol oxidation conditions, while the other samples achieved only 60%, despite a lower rate for the reaction. The authors hypothesized that shorter residence times of methanol and intermediates on the oxidized 1 nm Pt surfaces were the reasons for the peculiar activity of the catalyst with smaller particles.

Preparing oxide nanocrystals with tailored size and shape is also of interest for exploration in catalytic reactions, both as tailored supports and as active phases. Titania, for example, has recently received significant attention due to its favorable photocatalytic properties and much work is presently being carried out in relation structure to catalytic activity. In particular, theoretical observations suggested that the anatase (001) facets should show better catalytic properties than the low-surface energy (101) facets for several photoreactions, in particular for the photodissociation of water. However, it was not easy to test the theory with high-surface-area materials until the report by Yang et al., showing that TiO₂ crystals with exposed (001) facets could be made thanks to the use of HF as shape-directing agent. These crystals were still large, microns in size, limiting their applications in catalysis. A major improvement in the control over size and shape in the nanoscale regime was recently reported by Gordon et al. Their strategy was based on the in situ release of HF from a TiF₄ precursor during the synthesis to accurately tailor the (101)/(001) ratio (Figure 4). The uniform nanocrystals they produced allowed a unique opportunity for studying the reactivity of the two facets for the photoreforming of methanol, as a model reaction, after photodeposition of Pt. Under the conditions used in their study, the authors were able to demonstrate that (101) facets were more active than (001) facets, both before and after removal of the surface fluorine species. Intriguingly, a sample with an almost 50/50 ratio of the two facets gave a H₂ production rate that was intermediate between the two extremes (Figure 4).

The use of highly uniform, metal nanocrystals to extract structure–activity relationships in ceria-based systems was recently reported by us. Ni, Pd, and Pt nanocrystals with variable size in the range of 1.6–12 nm and size distributions < 6%, were prepared by high-temperature colloidal synthesis. The nanocrystals were then deposited onto both alumina and ceria supports, with the two oxides representing the classes of “inert” and “active” supports, respectively. The alumina samples showed no size dependency for CO oxidation, in agreement with the literature. However, when tested under the same reaction conditions, the ceria-based systems demonstrated a strong size dependency. A physical model built upon accurate TEM structural characterization allowed us to interpret the results in terms of the metal-support interface length: the ratio of perimenter atoms increases going from larger to smaller particles in the same manner that the CO oxidation activity increased, clearly revealing the role of the interface in ceria-supported catalysts for this reaction. The manipulation of the concentration of particular sites a priori was demonstrated to be fundamentally important for correlating structure and activity of these catalysts.

3. Rational Assembly of Nanocrystals

The precise assembly of different types of nanocrystals allows the construction of multifunctional materials with unprecedented control over the interaction between the components. Studying how these interactions affect rates can improve our understanding of the catalytic processes and potentially lead
to the creation of materials with unique properties that outperform currently available catalysts.

3.1. Tandem Catalysts by Langmuir–Blodgett Manipulation

Tandem catalysts are materials that perform two (or more) catalytic reactions in one step. An example of this is given in work by Somorjai, Yang, and co-workers, who prepared a tandem catalyst using a Langmuir–Blodgett technique to assemble monolayers of platinum and ceria cubes on top of a silica substrate. Langmuir–Blodgett is essential for preparing monolayers of nanocrystals and exploring the role of interfaces in catalysis. Their design was inspired by the fact that SiO₂–Pt and Pt–CeO₂ interfaces can catalyze sequential reactions. The authors studied methanol decomposition into H₂ and CO on the SiO₂–Pt interface, and ethylene hydrogenation to propanal using the evolved H₂ and CO at the Pt–CeO₂ interface. The authors demonstrated that the tandem catalyst was indeed selective towards propanal and attributed this result to the proximity of the two sites for the reactions. Although it is not clear how side reactions associated with exposed surfaces of Pt and SiO₂ are avoided, the design and assembly of this system can be an important guide for the preparation of other combinations of monolayered-type, multifunctional structures.

3.2. Controlling Particle Spatial Distribution

The control of particle spatial distributions on a support can have dramatic effects on the catalytic performance of a system. Prieto et al. demonstrated that by using an optimized impregnation method it was possible to precisely locate CuZn particles inside the ordered channels of SBA-15. The distribution of the particles was demonstrated by electron tomography and the catalyst in which the CuZn particles were more spatially isolated showed a much better resistance to deactivation under methanol synthesis conditions compared to traditional systems.

3.3. Binary Nanocrystal Superlattices

Assembling nanocrystals can also be used to understand the effect of interactions between different building blocks on the reaction. By using a recently developed liquid–air self-assembly technique, Kang et al. prepared ordered assemblies, known as binary nanocrystal superlattices (BNSLs), of uniform Au and Fe₃O₄ nanocrystals. In BNSLs, the two nanocrystal types are precisely located inside an ordered structure formed by the two sublattices. The number of contacts between Au and Fe₃O₄ nanocrystals could be tuned by changing the stoichiometry and type of BNSL (Figure 5): each Au nanocrystal experienced different numbers of interfaces with Fe₃O₄ by varying the BNSL type from AB to AB₂ to AB₁₃. The authors were able to show a linear relation between the number of interfaces and the rate of the CO oxidation reaction. Large Au particles (such as the 6 nm ones used by the authors) are usually considered inactive for the reaction. However, this work clearly demonstrated that the atoms at the interface are active sites.

4. Tailored Architectures

Hierarchical structures, where two or more materials are assembled together into a single architecture, are materials that can show properties that the single entities alone cannot. The properties of these structures are based on the tailored interactions that are established between the component parts when assembled into a predetermined geometry.

4.1. Core–Shell Structures

Core–shell structures represent a class of fascinating materials for catalysis. This is due to the fact that the cage provided by an appropriate inorganic barrier placed around the catalytically active core can reduce sintering of the active phase and improve the activity or selectivity by specific core–shell interactions or by sieving effects. Some early reports on encapsulation procedures to improve the thermal resistance of catalysts to sintering made extensive use of silica as the shell material. This was mainly due to the well-known chemistry of the silicon precursors and to our understanding of synthesis techniques involving silicon.

The interest in core–shell structures started already in the 90s when the group of Kishida in Japan showed the preparation of metallic particles coated by silica using a microemulsion approach. The strategy was based on the synthesis of metal nanoparticles inside the droplets of the water-in-oil microemulsion and the subsequent hydrolysis of tetraethoxysilicate (TEOS) around the particles. The core–shell-type structure of the catalysts was responsible for their higher selectivity and activity compared to conventional systems for several reactions, including CO and CO₂ hydrogenation and methane dry and steam reforming.

An improvement in this type of synthesis was reported by Yang, Somorjai, and co-workers. They prepared Pt particles encapsulated in mesoporous silica spheres, using a strategy that relies on the use of CTAB as surfactant for the preparation of Pt nanoparticles and as the structure-directing agent for the growth of mesoporous silica around the Pt by a classical Stöber method. The authors demonstrated that the Pt particles did not substantially grow after thermal treatments up to 750°C and the catalysts were active for ethylene hydrogenation due to the porous structure of the silica shell.

The group of Corma employed the organic functionalization of nanoparticles to create gold–organic–inorganic materials as precursors of active heterogeneous catalysts. The idea was to coat Au particles with a mixture of thiols, 1-dodecanethiol and 3-mercaptopropyltrimethoxysilane (MPTS). The latter served as a starting point to grow silica around the particles, while the first served as spacer to avoid complete burial of the particles in the inorganic matrix. After calcination, the samples exhibited very high rates for CO oxidation, comparable to some of the best Au/TiO₂ catalysts.
Fornasiero and co-workers showed the encapsulation of Rh particles inside alumina layers. The simple procedures used in their study were effective in providing catalysts that were active for methane partial oxidation and notably much more thermally resistant, as demonstrated by prolonged exposure under reaction conditions. In an attempt to improve the activity of the system, mixed ceria-zirconia-alumina layers were used with similarly good results in terms of stability for the ethanol steam reforming reaction.

All the previous examples focused on limiting the sintering of the core metal particles and were prepared with “inert” supports, so that the cage effect was primarily a physical method to improve the stability. The development of core–shell structures in which the shell is an oxide that can also act as promoter for a reaction was therefore the next step for exploring this new design for improving activity and stability at the same time. After scattered reports about the preparation of metal@ceria (the symbol @ indicates that the first material is encapsulated inside the second one) that showed promise for the water-gas-shift reaction, we reported the synthesis of Pd@CeO₂ core-shell structures by a self-assembly procedure. CeO₂ is a known “active” support that participates in the catalytic cycle by providing reactive oxygen species. The core–shell structures were prepared by using pre-formed Pd particles, protected by 11-mercaptoundecanoic acid. This thiol kept the Pd nanoparticles dispersed in solution and provided a functional group onto which could be attached Ce(IV) moieties, derived from an alkoxide precursor, followed by hydrolysis of the remaining alkoxide using dodecanoic acid as stabilizer for the ceria shell growth. The core–shell particles prepared in this way were dispersible in low-polarity organic solvents and the same procedure was later demonstrated to be applicable to either Pd or Pt in the core and TiO₂, ZrO₂ or CeO₂ as the shell. The main point here is that a “redox-active” support such as ceria can help improve the catalytic properties of the entire system through tailored metal-support interactions at the extended interface created with the core-shell design. The most interesting demonstration of this effect was indicated in testing of a hierarchical catalyst prepared by depositing Pd@CeO₂ single structures onto a modified, hydrophobic alu-
mina (H-Al₂O₃), Pd@CeO₂/H-Al₂O₃, for CH₄ combustion. The Pd@CeO₂ structures could be deposited in monolayer form on the support and were stable after thermal treatments in air up to 850 °C, demonstrating the stability offered by the ceria cage. Additionally, the role of ceria in providing activated oxygen for the reaction was evidenced by the very high activity observed with this system, with complete combustion of methane occurring under demanding conditions at temperatures near 400 °C.

### 4.2. Hierarchical Nanoarchitectures

The fabrication of core–shell structures can also be used to prepare hollow architectures by using the core material as a template that is then etched away after the deposition of a shell layer. For example, hollow Pd spheres were prepared in this way by the group of Taegwan Hyeon. Large, uniform silica spheres were synthesized by the Stöber method, and then Pd was deposited onto the surface using mercaptopropyltrimethoxysilane to anchor the growing palladium layer onto the silica surface. Etching the silica core away produced hollow Pd spheres formed by small Pd crystallites. The highly porous structure (surface area of 64 m² g⁻¹) led to the high catalytic activities and stabilities displayed by the hollow spheres for the Suzuki coupling reaction. Schüth and co-workers took the approach an additional step further by covering the Au particles with a thick silica layer first, followed by a thin ZrO₂ layer. By etching away the silica interlayer, hollow spheres of zirconia containing Au particles enclosed within were obtained. The authors reported that there was minimal growth of the encapsulated Au particles after heating the system to 800 °C, an outstanding result considering the low melting point of Au. The presence of small gaps between the ZrO₂ crystallites that formed the shell allowed the particles to be exposed to reactants so that the material was active for CO oxidation, despite the large Au particle size (~15 nm).

Similar hierarchical architectures that take advantage of the synergy between the component parts were prepared using multwall carbon nanotubes (MWCNTs) as the support. The synthetic procedure was based on oxidized MWCNTs that exposed carboxyl groups on the surface in order to bind the core-shell structures. The resulting architecture had nanocrystalline oxide layers (TiO₂, ZrO₂ or CeO₂) wrapped around MWCNTs, with metal particles (Pd or Pt) embedded within the oxides (Figure 6). Because this particular architecture allows electronic interactions between the MWCNTs and the oxide, these catalysts were active and stable for a variety of reactions, including water–gas shift reaction, photoconversion of methanol to produce H₂, and Suzuki coupling reactions.

The use of carbon nanotubes as an electronically active substrate, wired to polyoxometalate (POM) clusters, demonstrated how effective hierarchical structures can be for catalysis. The connection between the two components was provided by electrostatic interactions between charged groups at the surface of carbon nanotubes and in the coordination sphere of the Ru-based POM. The water oxidation activity of the POM was greatly increased by the presence of carbon nanotubes due to the facilitated transport of charge to the ITO electrodes. Indeed, comparison with the same POM deposited onto electrically inactive materials demonstrated the pivotal role played by the POM-carbon nanotube architecture on the high water oxidation activity.

The advantage of hierarchical structures is that the different component building blocks can provide multifunctional properties to the final material. A clear example of this is the preparation of metal-organic framework (MOF) materials encapsulating nanoparticles. Various types of nanoparticles with different compositions, sizes and shapes were successfully encapsulated inside the structure of ZIF-8. Among the functional properties of this type of hierarchical structure, the demonstration of size-selective catalysis in the hydrogenation of n-hexene versus cis-cyclooctene using embedded Pt nanoparticles, was the most interesting. The coupling between the catalytic properties of the Pt core and the sieving characteristics of the MOF make this hierarchical structure ideal for selective transformations.

### 5. Conclusions and Perspectives

Catalysis can greatly benefit from the synthetic procedures recently developed in the field of nanotechnology. The coupling between these two disciplines has already produced materials with tailored structures and properties that led to improved catalysts and to well-defined systems for studying structure–activity relationships under industrially relevant conditions. In this Concept, some key advances were discussed that take advantage of this new paradigm. These examples demonstrate to the reader how new synthetic insights can advance catalytic science and technology.

It is important to notice that the preparation of precise architectures is pointless if the structures are not stable under reaction conditions. This implies that there is a wide space for the exploration of new concepts that combine a careful design with the appropriate stability required for the desired application. Reconstruction of surfaces/interfaces under reaction conditions cannot be neglected when rigorous structure–activity
relationships are to be studied. The potential for the use of nanotechnology tools in catalysis is huge and exploration is just beginning. The intimate connection between the two fields can definitely improve our understanding of catalysts and allows the preparation of new materials that will contribute to sustainable industrial processes.

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CONCEPTS

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Catalysts with improved activity, stability and selectivity can be prepared by synthetic techniques that produce uniform building blocks, such as clusters and nanocrystals, and by appropriate manipulation and assembly at the nanoscale.