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Nested Metal Catalysts: Metal Atoms and Clusters Stabilized by Confinement with Accessibility on Supports

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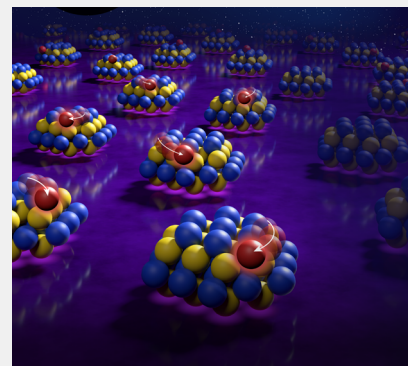
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ABSTRACT: Supported catalysts that are important in technology prominently include atomically dispersed metals and metal clusters. When the metals are noble, they are typically unstable—susceptible to sintering—especially under reducing conditions. Embedding the metals in supports such as organic polymers, metal oxides, and zeolites confers stability on the metals but at the cost of catalytic activity associated with the lack of accessibility of metal bonding sites to reactants. An approach to stabilizing noble metal catalysts while maintaining their accessibility involves anchoring them in molecular-scale nests that are in or on supports. The nests include zeolite pore mouths, zeolite surface cups (half-cages), raft-like islands of oxophilic metals bonded to metal oxide supports, clusters of non-noble metals (e.g., hosting noble metals as single-atom alloys), and nanoscale metal oxide islands that selectively bond to the catalytic metals, isolating them from the support. These examples illustrate a trend toward precision in the synthesis of solid catalysts, and the latter two classes of nested catalysts offer realistic prospects for economical large-scale application.



KEYWORDS: catalyst synthesis, supported metal catalysts, encapsulated catalysts, nested catalysts, atomically dispersed metal catalysts

Many catalysts incorporate active sites that are metals isolated as atoms or ions stabilized by surrounding ligands. Examples include the mononuclear metal complexes that are dominant in industrial homogeneous catalysis, exemplified by rhodium complexes for olefin hydroformylation¹ and iridium complexes for methanol carbonylation.² Metals in many of nature's catalysts incorporate isolated metal ions, exemplified by the iron in heme structures in cytochrome P450 enzymes,³ the vanadium in bromoperoxidases,⁴ and the zinc or cadmium in carbonic anhydrase enzymes.⁵ Many solid catalysts also incorporate isolated metal ions, with the ligands being supports: for example, chromium ions bonded to the surface of high-area porous SiO₂ are industrial catalysts for ethylene polymerization,⁶ and titanium ions bonded in the crystalline framework of the zeolite material silicalite catalyze industrial olefin epoxidation with H₂O₂.⁷ The recent catalysis literature reflects an intense, growing interest in noble metals that are atomically dispersed on supports—we address these in the following perspective.

Most catalysts used on a large scale are solids—because solids are readily and economically separated from fluid-phase reaction products, and many of them are inorganic materials robust enough to withstand high temperatures in long-term operation. (Liquid-phase catalysts are rarely used at high temperatures, because many are unstable and because high pressures are required to maintain the liquid phase, and high-pressure operation is costly.) Many catalysts incorporate metals dispersed on porous, high-area supports, which are typically metal oxides,

carbons, or zeolites. Such supported metal catalysts are the keys to efficient, economical petroleum refining, petrochemical conversion, and vehicle exhaust emission abatement. Many supported catalysts incorporate noble metals, commonly platinum. The metals are typically present as zerovalent clusters or nanoparticles dispersed on the internal surfaces of the porous supports.

Industrial supported metal catalysts are manufactured on large scales in economical processes that involve much less precise chemistry than the syntheses of molecular catalysts like those used for olefin hydroformylation and methanol carbonylation. The supported metal clusters or nanoparticles are nonuniform in size and structure, but there is a trend in research (that is beginning to be reflected in technology) towards more precisely synthesized solids, illustrated by crystalline aluminosilicates (zeolites) that are supports for the metals.

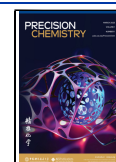
When the catalytic metals are expensive (e.g., palladium, rhodium, and platinum) they are often dispersed so highly that a large fraction of the atoms reside on a surface—accessible to reactants from a gas or liquid phase, and engaged in catalysis. In

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the limiting case of the highest dispersion, the metals are present as individual, isolated atoms or few-atom clusters that allow access of reactants to each atom. Such high dispersions optimize the metal utilization and are preferred—provided that the structures are stable, and provided that they have suitable activity and selectivity for desired products. Stabilization of active metal species is a major challenge in practice, and extensive research has focused on precision syntheses of highly dispersed metals that are somehow stabilized. Such syntheses and the resultant materials are the topic of our perspective.

The supports in practical catalysts are usually robust porous inorganic materials, exemplified by metal oxides that are inexpensive and have reproducible, tailorable physical properties—surface area, pore volume, pore size distribution, and robustness. Examples of widely used catalyst supports are transition aluminas (e.g., γ - Al_2O_3), SiO_2 , MgO , and mixed oxides such as silica–alumina. The surfaces of these materials are nonuniform in composition and structure, including defects on various scales and often impurity components. Zeolites are especially important supports, finding applications in many hydrocarbon conversion processes. Zeolites are more highly crystalline than common metal oxide supports, but they nonetheless have nonuniformities in composition and structure; these include defect sites such as grain boundaries and terminating SiOH functional groups, with variously placed aluminum and silicon atoms in the frameworks—and they can also incorporate amorphous impurities. Metal–organic frameworks, MOFs, are drawing wide attention among researchers as catalyst supports but are so far limited in catalytic applications—owing largely to their lack of stability. MOFs also have substantial nonuniformities (including missing nodes and linkers, and defects and local variations in node and framework compositions).

The nonuniformities of the supports imply nonuniformities of the metal species on them, including their immediate surroundings, which influence the catalytic properties, sometimes strongly. This point has been largely overlooked and, we posit, is central to the topic of precision synthesis of supported catalysts.

The metals in molecular metal complexes are isolated by the ligands, which may hinder reactions that lead to the formation of structures with metal–metal bonds (clusters or nanoparticles). Metal particles have atoms buried in their interiors, inaccessible to reactants and unavailable for catalysis. Thus, stabilization of isolated metal atoms may be strongly advantageous, and multidentate or macrocyclic ligands may be effective in providing this stabilization, as illustrated by the hemes in cytochrome P450 enzymes. Comparable multidentate bonding of metals also occurs on solid surfaces, for example, when metals are embedded in them. Strong bonding of metals to supports may be helpful in stabilizing them (making them resistant to sintering), but this benefit often comes at the cost of limiting the accessibility of the metal sites to reactants for bonding and catalysis; we elaborate on this point below.

This point about catalyst stability is of enormous practical importance, because supported metals, especially noble metals, often sinter in catalytic operation. That is, the metals migrate on support surfaces (or in the gas phase) and aggregate into clusters or particles. Sintering of metals means loss of metal surface area and catalytic activity, and it is a common cause of catalyst deactivation and a major economic burden in large-scale applications.

If metals are initially dispersed on supports as isolated cations, then the sintering is triggered by reduction of the metals⁸—which is important because many practical reactions (illustrated by hydrocarbon conversions) take place in reducing atmospheres. Hydrogen is often applied at high pressures for high reactivity in processes including hydrogenation, hydroisomerization, and hydrotreating.

Researchers have worked for decades to stabilize highly dispersed metals on supports without compromising accessibility and catalytic activity. Here we summarize some recent research presenting synthetic strategies that address this issue. These strategies afford metals that are stably confined in solids and—the focus of our perspective—in *necks* on support surfaces.

We thus illustrate materials syntheses that are much more precise than the preparations of industrial solid catalysts, which almost always include multiple steps and changes in phases, compositions, and material properties. But we emphasize that even the most precise syntheses of catalytic materials—including those described here—fall far short of the precision of synthesis of molecules. The materials we describe represent research catalysts that are made more precisely than industrial solid catalysts, but much less precisely than molecular catalysts. The latter are usually made with solution chemistry that benefits from product purification by column chromatography, distillation, (re)crystallization, etc. Such methods are not available in syntheses that involve modifications of the composition and structure of a solid.

We describe catalyst supports that incorporate *necks*, with sites that are, to a degree, optimized to contain highly dispersed metals and hold them in place—while still providing access to reactants for bonding. Thus, the metals in these *necks* are catalytically competent. The *necks* are ligands. They fall into the following categories:

- molecular-scale pore mouths of regular, crystalline porous materials exemplified by zeolites
- cups (“half-cages”) that are exposed at surfaces of crystalline solids (exemplified by zeolites) that in the bulk incorporate regular molecular-scale cages
- nanosized islands (of metals or metal oxides) dispersed on support surfaces that host and stably isolate highly dispersed metals

The synthesis strategies summarized here have the aim of placing metal atoms/clusters on better-defined support locations than are attainable with conventional catalyst supports—they afford metals that are stably confined in relatively well-defined *necks* on support surfaces. There are still only a few examples of catalysts in these classes, and our purpose is to stimulate interest in the subject and suggest some paths forward for research. Before describing the nested catalysts, we summarize work with comparable, but less precisely synthesized, catalytic materials incorporating supports that *encapsulate* metals, but in structures that are more confining than the *necks*.

■ SUPPORTED METALS CONFINED IN SOLID SUPPORTS

Metal particles in catalysts usually reside on the surfaces of porous supports, but the metals may instead, to some degree, be encapsulated within layers on the supports or within the supports. These statements pertain to atomically dispersed metals, to few-atom metal clusters, and to metal nanoparticles. By and large, the syntheses of such catalysts are not highly precise.

Metals on Supports Enveloped in Bulky Ligands

The need for molecular approaches to stabilize metal clusters was articulated some years ago by Burch et al.,⁹ who stated that the field of metal-cluster catalysis “must await design of more robust, catalytically active coordinatively unsaturated clusters.” An emerging approach to accomplish this goal is to use bulky ligands—calixarenes—to stabilize metal clusters on supports. Examples include coordinatively unsaturated clusters incorporating hydride ligands—which, without the calixarene sheaths, have a strong tendency to aggregate and become deactivated as catalysts. Because the protection is associated with the bulkiness of the calixarene ligands, the strength of the interactions of the metal with the support is relatively unimportant, and tetrairidium clusters have been stabilized even on a weakly interacting support such as silica.¹⁰ The bulky calixarene ligands even freeze intramolecular CO exchange processes, which otherwise occur rampantly, on tetrairidium carbonyl clusters.¹¹ This class of catalyst includes a silica-supported di-iridium cluster (Figure 1), which could be reversibly decarbonylated in

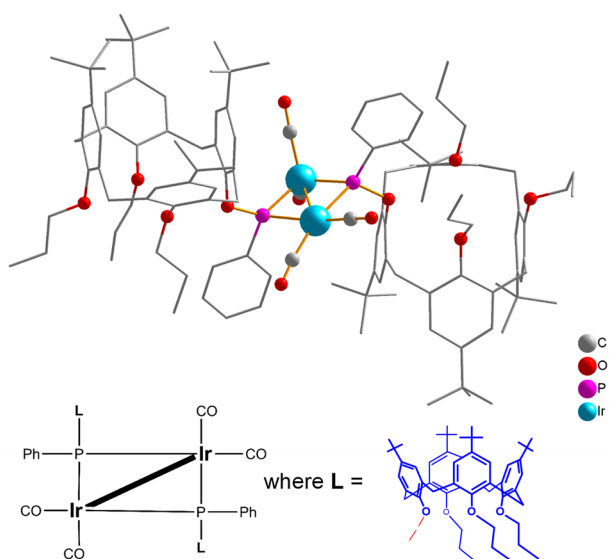


Figure 1. Molecular structure of di-iridium cluster with two bulky calixarene phosphine ligands. On a weakly interacting support (SiO_2), this catalyst remains stable for ethylene hydrogenation at 50 °C and atmospheric pressure in a flow reactor.¹²

the presence of H_2 to synthesize a cluster hydride that was a stable catalyst for ethylene hydrogenation, in contrast to comparable catalysts lacking the calixarene ligands, which sintered.¹²

Metals on Supports Enveloped in Ionic Liquid Sheaths

A stabilization strategy related to that just stated involves formation of metals on porous supports such as metal oxides and enveloping the metals with thin layers (e.g., monolayers) of ionic liquids. These sheaths protect the metals and limit metal sintering, and they offer less mass transfer resistance (which often is apparently negligible) than bulk polymers. Enormous numbers of ionic liquids are available for fine tuning of the electronic properties of the metals and thereby the catalytic properties.^{13,14} When the metals are atomically dispersed, the choice of the electron-donor/acceptor properties of the support and the ionic liquid imply substantial precision in the catalyst synthesis.

Metals on Supports Enveloped in Polymer Sheaths

Metal catalysts, such as nanoparticles, have been stabilized and tuned by polymers enveloping the catalyst particles on supports.¹⁵ For example, a porous polymer layer was used to control the selectivity of TiO_2 -supported ruthenium; the catalyst was used for CO_2 hydrogenation, with the polymer envelope markedly favoring the selectivity for C_{2+} products; the polymer was found to modify the catalyst performance by favoring the adsorption of reactants and intermediates near the catalytically active species that it enveloped.¹⁶

A related benefit of polymers near catalytic sites on a surface was illustrated when poly(vinylpyrrolidone) was introduced into the pores of a mesoporous silica that was functionalized with catalytically active acidic groups. Addition of the polymer, which was stabilized by crosslinking in the pores, was found to favor the selective dehydration of fructose, a simple carbohydrate that can be obtained from cellulose, to give a potentially valuable platform chemical, 5-hydroxymethylfurfural.¹⁷ The aprotic environment of the pores, caused by the presence of the polymer, facilitated the selective catalytic reaction.¹⁷

The polymer matrices in these catalysts may help to stabilize the metals that they encapsulate and may favorably influence catalyst selectivity, but, because they hinder transport of reactants and products, they are typically expected to slow down the catalysis, although the effects are often small. The polymer matrices have stability limitations, and removal—by burning—of carbonaceous deposits (coke) formed on the catalysts during operation will destroy the polymer and limit catalyst regeneration/recycle. There is a lack of large-scale applications of such catalysts.

Metals Encapsulated in Metal Oxides

Metal catalysts have been encapsulated within particles of robust metal oxides with sufficient porosity to allow access of reactants to the metals. When the encapsulating material is aluminum oxide, for example, the resistance to sintering of the metal is markedly increased, and the material is stable at high temperatures (e.g., 1100 °C).¹⁸ Again, the protective sheaths present mass (and heat) transport resistance, and there is a lack of applications of such materials.

Comparable to these materials are a large group of solid catalysts—exemplified by metal oxides—into which metals have been doped; these materials, and their catalytic properties, are beyond the scope of this perspective.¹⁹

Metals Encapsulated in Zeotype Materials

Methods have been developed for enveloping catalytic nanoparticles of metals within the bulk structures of zeotype materials. One synthesis involved incorporating the metal in zeolite seed crystals and then growing zeolite sheaths around the seeds.^{20,21} In another synthesis, the metal precursor (e.g., Au^{3+}) was stabilized by 3-mercaptopropyltrimethoxysilane, a ligand that was chosen to have a composition that helped facilitate the growth of titanium-containing silicalite-1 around the gold nanoparticles that formed in the synthesis mixture;²² the procedure led to the formation of gold nanoparticles smaller than those that formed when the stabilizing ligand was absent.

The zeolite-encapsulated materials include metal species of various sizes and shapes that are stabilized by the surrounding zeolite matrix yet still accessible via the zeolite pores.²¹ Because of the encapsulation, metals in such catalysts are highly resistant to sintering, and the zeolite matrix also hinders the formation of carbonaceous deposits during catalysis, which is often a major cause of catalyst deactivation.²¹

The syntheses may sometimes be precise in terms of the catalyst structure/transport properties. Thus, the regular molecular-scale pores of an encapsulating zeolite may align reactant molecules in such a way as to facilitate selective catalysis, as illustrated by the selective reduction of the nitro group in compounds such as *p*-chloronitrobenzene—the selectivity is associated with the preferential (stronger) bonding of the nitro rather than the chloro group to the encapsulated metal (e.g., palladium nanoparticles).²³ It was inferred that the reactant molecules were aligned in the narrow pores of the zeolite (zeolite Beta) with the nitro groups strongly bonded to the palladium being the ones that react. In contrast, when comparable catalysts were made that allowed facile bonding of both functional groups on the aryl ring with the metal, the catalysis was unselective.²³

Metals Entrapped in Cages of Zeotype and Related Materials

Zeolites and related (zeotype) materials that incorporate molecular-scale cages as part of their porous crystalline structures have also been used to stabilize metal catalysts by encagement. Some such syntheses are precise—for example, catalysts have been made that consist of metal clusters that just fit in the zeolite cages but are too large to fit through the apertures connecting the cages. Examples of such clusters are $\text{Ir}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$, with diameters of about 9 and 12 Å, respectively, which have been made by ship-in-a-bottle syntheses from smaller molecular precursors.²⁴ Encaged bimetallic clusters have also been reported.²⁵ The metal carbonyl clusters are catalysts for some reactions,^{24,25} and they can sometimes be decarbonylated to give clusters that are catalysts, but often the structures of the decarbonylated clusters do not retain the metal frames of the precursors and give structurally complex catalysts. The ship-in-a-bottle synthesis strategy has been extended to mesoporous materials, illustrated by FSM-16.²⁶ These encaged catalysts are essentially molecular, and the activity of $\text{Ir}_4(\text{CO})_{12}$, for example, is increased by removal of the CO ligands (with the cluster frame intact), which are catalyst poisons for many reactions.²⁷ The transport restrictions of the zeolite supports are expected to be substantial, and catalysts in this class lack large-scale applications.

Metals within Surface Layers of Metal Oxides

Metals on metal oxide supports are typically bonded to oxygen ions at the support surfaces. The metal–oxygen distances are typically cation–anion bonding distances (as shown by extended X-ray absorption fine structure (EXAFS) spectroscopy). When metals are atomically dispersed on a support, they usually bear positive charges similar to those of cations in metal oxides or metal salts (as shown, for example, by X-ray absorption near-edge spectroscopy).

Thus, it is not surprising that the metals may be bonded at defect sites on supports, so that they are not so much on the support surface as partly enveloped by the surface. For example, Hoffman et al.²⁸ characterized iridium cations isolated on high-area MgO powder (which is highly crystalline) and showed that, by varying the calcination conditions, it was possible to bond each iridium cation to more or fewer support oxygen ions—with the MgO calcined at higher temperatures having more defects than the others and having more, and stronger, Ir–O bonds—with the iridium being in the first layer of the MgO lattice near Mg^{2+} vacancies.²⁹ EXAFS data and models based on density functional theory led to approximate structural models of the iridium ions in the first MgO layer.²⁹ The greater the degree of

encapsulation by the support, the greater the tendency of the iridium to resist reduction and sintering in the presence of H_2 , but the lower the catalytic activity of the iridium for ethylene hydrogenation.²⁸

These examples lead into the subject of more precisely synthesized metals on supports—metals in nests on supports—examples of supported catalysts that we posit can be considered to be examples of precisely synthesized materials.

■ NESTED SUPPORTED METALS

Pegboard Catalysts (Metal Complexes Anchored in Uniform Nanoscale Pore Mouths)

To anchor metal complexes—without fully encapsulating them—in nearly identical isolated sites on support surfaces, a little-explored strategy is to use crystalline materials with uniform pore openings—such as zeolites—as pegboards. For example, some zeolites, exemplified by mordenite (MOR), have straight, parallel pores, and the crystal faces with pore openings offer a regular array of sites for insertion of molecules. Researchers have adsorbed organometallic compounds (dineopentylmagnesium³⁰ and trimethyltin³¹), evidently at the pore mouths. These molecules have been shown to plug the pores, hindering transport into and out of them.

We suggest that if the organometallic molecules have ligands that are relatively long chains that fit snugly into the pores and have a strong affinity for the pore walls, and if the other ligands on the metal make the whole molecule too large to fit into the pore, then the molecule might become stably rooted in the pore with the metal exposed at the surface—where it could be a stable catalyst with a unique, essentially molecular structure. Synthesis of such materials might be expensive and tricky, and questions would arise about regenerability of the materials as catalysts.

Metals Anchored in Uniform Nanoscale Cups (Half-Cages) on Zeolite Surfaces

When a zeolite crystal derived from a lamellar precursor is cleaved perpendicular to the *c* direction (or, equivalently, the *z* axis), supercages in the bulk become exposed as half-cages at the cleaved surfaces. These are cups in which metal complex catalysts can be anchored and readily accessed by reactants. For example, the external surfaces of a siliceous deboronated B-SSZ-70 zeolite, shown schematically in Figure 2, incorporate 12-membered ring pockets with surface silanol groups (Si–OH groups). Calix[4]arene-Ti(IV) complexes were anchored in these nests (Figure 2).³² For comparison, the titanium complex catalyst was also supported on amorphous silica, giving samples that are models of commercial SiO_2 -supported catalysts used for the production of propylene oxide from propylene.³³ The two supported catalysts were indistinguishable on the basis of X-ray absorption spectra recorded at the Ti K edge,^{32,33} demonstrating that the titanium had the same inner-sphere oxo-coordination environment in each. To investigate the effect of the different outer spheres, controlled by the support environment, the materials were used for olefin epoxidation catalysis by the Ti(IV) sites. The partial confinement of the catalytic groups in the zeolite nests rather than on the amorphous silica led to a five-fold increase in the rate constant for cyclohexene epoxidation with *tert*-butyl hydroperoxide present in the liquid phase, an effect attributed to a more favorable entropy of activation of the reaction in the nests rather than on the conventional support—that is, a more favorable reorganization of the required solvation sphere in the transition state in the rigid zeolite pockets relative to that on the amorphous silica support.³³ Although stability

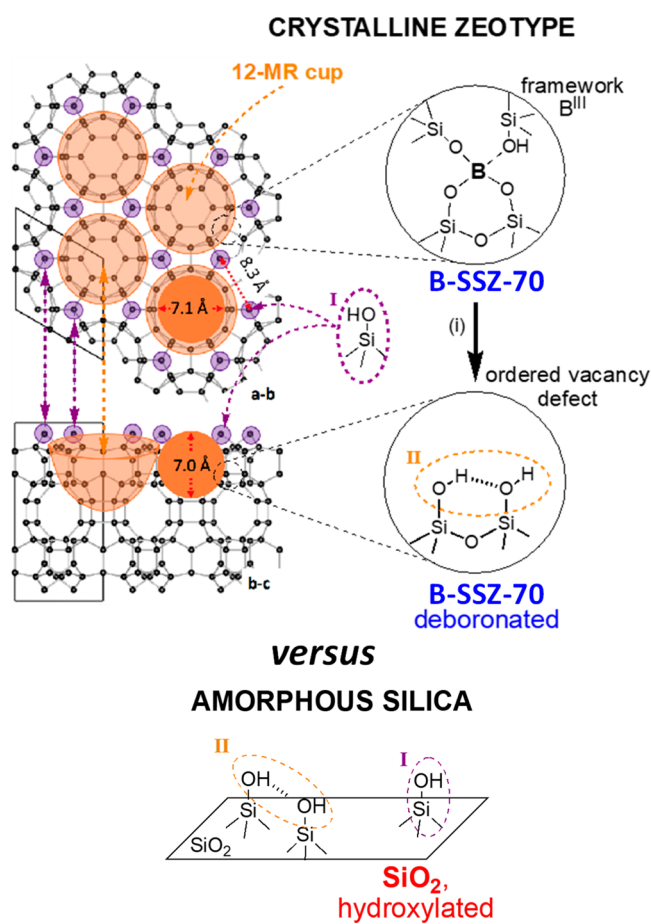


Figure 2. Schematic representation of siliceous surfaces of crystalline deboronated B-SSZ-70 (top panel) and amorphous silica (bottom panel).³²

characteristics of these nested catalysts require further investigation, preliminary data point to the possibility of stability enhancements relative to those characterizing amorphous catalysts lacking cups.³⁴

In an example involving hydrogenation catalysis, the iridium cluster shown in Figure 1 was anchored to a surface containing similar regular nanoscale cups, on Si-SSZ-70 (which is isostructural to B-SSZ-70 of Figure 2, but with a silicon atom replacing boron in the cups). Again, an amorphous silica support was used for comparison. In hydrogenation of ethylene as one of the gas-phase reactants, the nested catalyst was twice as active as the conventionally supported catalyst,¹² an enhancement attributed to the partial confinement of the catalyst in the 7-Å pockets.

Metal Nanoparticles in Wide-Mouthed Cups

Platinum nanoparticle catalysts (in dendrimer sheaths) were supported on three-dimensionally assembled silica nanosheets that were synthesized to incorporate high densities of compartments (bowls), 60–80 nm deep with wide openings (10–80 nm in diameter).³⁵ These bowls contained the catalytic metal nanoparticles, with the confinement to some degree limiting sintering of the metal by keeping the nanoparticles widely spaced from each other. However, these bowl-supported catalysts, like those anchored in zeolite half-cages, evidently do not provide a stabilization comparable to what has been mentioned above for encapsulated metals.

Noble Metals Isolated in Nanoscale Nests of Oxophilic Metals on Supports

A contrasting approach, not involving zeolites, but rather more open-pored materials, involves catalysts made from bimetallic clusters on supports, synthesized from organometallic precursors that contain both a noble and an oxophilic metal. The syntheses yield samples incorporating clusters of the noble metal on islands of the oxophilic metal, the latter present as cations and bonded strongly to a metal oxide support—the oxophilic metal is sandwiched between the noble metal and the oxide support. Such catalysts have been synthesized from Pd–Mo,³⁶ Pt–W,^{37,38} and Pt–Re³⁹ precursors. The idea is to have the oxophilic metal bond strongly to the support and at the same time bond to the noble metal, keeping it dispersed—stably isolated on the oxophilic metal rather than on the support.

Examples of such catalysts were synthesized from Pt[W(CO)₃(C₅H₅)₂(PhCN)₂] and Pt₂W₂(CO)₆(C₅H₅)₂(PPh₃)₂ (Ph is phenyl); for comparison, samples were synthesized from a mixture of monometallic precursors, PtCl₂(PhCN)₂ and W(CO)₆.^{37,38} The precursors were adsorbed from organic solutions on a high-area porous γ -Al₂O₃ support, and the supported species were characterized by EXAFS spectroscopy (at both the Pt L_{II} and the W L_{III} edges) and by chemisorption of H₂, CO, and O₂. Low-resolution microscopy was also used, not sufficient to resolve individual atoms. The samples had been reduced with H₂ at 400 °C prior to the characterizations. EXAFS data show that tungsten in either of the bimetallic precursors helped to maintain the platinum in a highly dispersed state on the support during exposure to H₂, giving platinum clusters incorporating only about 4–6 atoms each, on average. EXAFS Pt L_{II} edge spectra indicate substantial Pt–W contributions in samples synthesized from the bimetallic precursors, but not in those synthesized from the monometallic precursors. The Pt–W coordination numbers in the former samples were about 2 and 1, respectively, at an average Pt–W distance of 2.71 Å. W L_{III} edge EXAFS data correspondingly indicate substantial W–Pt interactions in the samples prepared from the bimetallic precursors, with an average W–Pt coordination number of about 1.0 at a distance of 2.71 Å. The data imply that W–Pt–W (or Pt–(W)₂–Pt) moieties in the precursors were largely retained in the supported species following removal of the organic ligands by reaction with H₂. EXAFS data also show that the Pt–W interactions in samples prepared from the bimetallic precursors were strong enough to be largely maintained even under oxidation/reduction conditions at temperatures as high as 400 °C. However, in addition to the metal–metal contributions, the EXAFS data show substantial interactions of both tungsten and platinum with oxygen atoms of the γ -Al₂O₃ support. The platinum clusters in the bimetallic cluster-derived samples are inferred to have been stabilized in their highly dispersed state by interacting with tungsten cations held in nests by strong bonding with support surface oxygen atoms (as indicated by the EXAFS data). In contrast, the sample prepared from the monometallic precursors and largely lacking Pt–W interactions contained relatively large platinum nanoparticles. The supported platinum clusters made from bimetallic precursors are characterized by lower capacities for chemisorption of CO or of hydrogen and by lower catalytic activities for toluene hydrogenation but higher activities for crotonaldehyde hydrogenation than the samples made from the monometallic precursors.

An important point is that all the data support the inference that tungsten in the bimetallics formed isolated nanoscale islands (or rafts) of cationic tungsten on γ -Al₂O₃, which helped

to isolate the platinum and strongly influence the adsorption and catalytic properties. The structures were no doubt mixtures, with the characterization data providing only average structural information, and there are no high-resolution images to provide evidence of the individual atoms and the degree of uniformity of the samples; nor do the data determine whether some of the platinum was present on the support surface where tungsten was absent—and the EXAFS data indicate some direct bonding of platinum to oxygen atoms of the alumina support. Thus, we infer that the nesting provided by the tungsten did not meet a high standard of precision in the synthesis.

A related set of samples was made similarly from $\text{Re}_2\text{Pt}(\text{CO})_{12}$ on $\gamma\text{-Al}_2\text{O}_3$ and characterized by EXAFS spectroscopy at both the Re L_{III} and Pt L_{III} edges with the sample in the presence of H_2 .³⁹ The data form the basis of a simplified model of the supported bimetallic structures, consisting of Re_4Pt_2 entities, with oxophilic Re in a low positive oxidation state interacting strongly with the oxygen atoms of the $\gamma\text{-Al}_2\text{O}_3$ support and stabilizing the dispersion of the Pt atoms (Figure 3). Like the

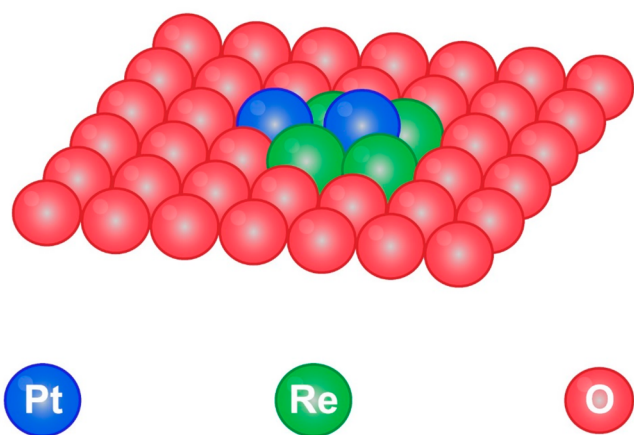


Figure 3. Simplified structural model of Re_4Pt_2 clusters on $\gamma\text{-Al}_2\text{O}_3$ based on EXAFS data (average coordination parameters) obtained at the Re L_{III} and Pt L_{III} edges. The clusters are presumed, for simplicity, to reside in registry with the [111] surface of the $\gamma\text{-Al}_2\text{O}_3$ support.²⁵

catalysts mentioned in the preceding paragraph made from Pt–W clusters, this one incorporates a highly dispersed noble metal in a nest of oxophilic metal ions bonded to the metal oxide support. The platinum in this catalyst was found to be more resistant to deactivation during catalytic dehydrogenation of methylcyclohexane than catalysts prepared conventionally from rhenium and platinum salt precursors and not having the platinum nested in few-atom clusters; the observations suggest that strong bonding of the platinum to the rhenium hindered migration and aggregation of the platinum on the $\gamma\text{-Al}_2\text{O}_3$, an important goal in practical catalysis. The structure shown in Figure 3 might resemble those in industrial Re–Pt catalysts used for naphtha reforming—catalysts that have stability advantages that facilitate operation at low hydrogen partial pressures, a significant economic advantage. The industrial catalysts are no doubt made from inorganic precursors (metal salts) and are less nearly uniform than the samples made from $\text{Re}_2\text{Pt}(\text{CO})_{12}$.

Noble Metals Isolated in Nanoscale Nests of Non-noble Metals on Supports

Supported clusters of a metal with relatively low activity for some reactions (e.g., copper) have been mounted on metal oxide supports, and isolated noble metal atoms (e.g., rhodium) have

been incorporated in low loadings by a galvanic displacement method, so that they are stabilized as isolated (even atomically dispersed) sites on the islands. These metal-nanoparticle-nested noble metals offer catalytic properties that in some ways make them superior catalysts, even with potential for large-scale applications, as described below.⁴⁰

The group of Sykes and Flytzani-Stephanopoulos⁴¹ reported the synthesis of palladium dispersed atomically on supported non-noble metal nanoparticles. A galvanic replacement method was used to add minor amounts of palladium to copper nanoparticles supported on $\gamma\text{-Al}_2\text{O}_3$. The isolated palladium atoms reacted with H_2 , which underwent dissociation and migration (spillover) onto the surrounding copper surface, where it reacted with adsorbed phenylacetylene, hydrogenating it. These catalysts were selective for hydrogenation to give styrene—markedly more selective than palladium alone.

Comparable catalysts were synthesized with platinum atoms on copper nanoparticles.⁴² Images determined by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) show the presence of atomically dispersed platinum on the nanoparticles on a $\gamma\text{-Al}_2\text{O}_3$ support (Figure 4). Platinum on copper catalysts are selective for partial hydrogenation of 1,3-butadiene.⁴¹ Atomically dispersed platinum on copper catalyzes C–H activation—without the formation of coke deposits that takes place on platinum surfaces and poisons

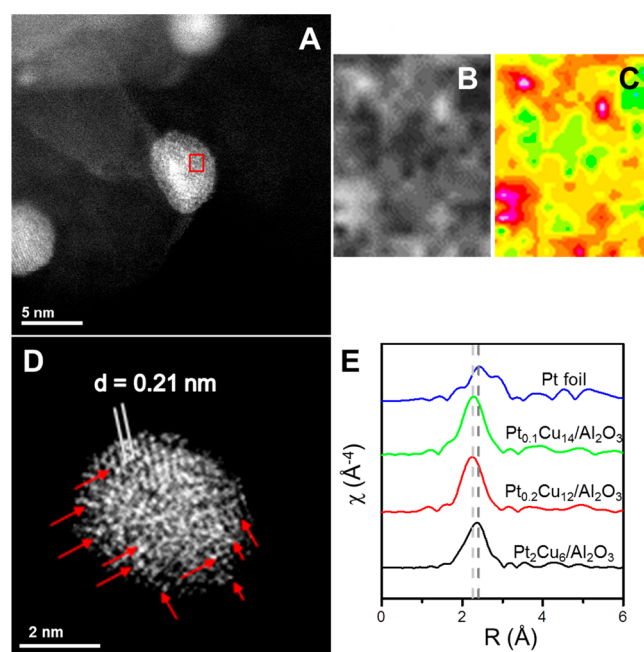


Figure 4. Characterization of copper nanoparticle catalyst with platinum dispersed atomically on the copper.⁴² (A–D) HAADF-STEM images with (C) colored intensity map from selected region, and (E) EXAFS data collected at the Pt L_{III} edge: k^3 -weighted Fourier transforms of reference platinum foil and supported catalysts with various compositions. (A,D) Regions of the sample $\text{Pt}_{0.1}\text{Cu}_{14}/\text{Al}_2\text{O}_3$ showing copper nanoparticles with isolated platinum atoms on them (denoted with arrows). Scale bars: 5 nm (A) and 2 nm (D). (B) Enlarged image and (C) intensity map of highlighted region showing isolated platinum atoms. (E) EXAFS data were collected at the Pt L_{III} edge at room temperature with platinum foil and in H_2 atmosphere at Pt L_{III} edge at room temperature with pre-reduced $\text{Pt}_{0.1}\text{Cu}_{14}/\text{Al}_2\text{O}_3$, $\text{Pt}_{0.2}\text{Cu}_{12}/\text{Al}_2\text{O}_3$, and $\text{Pt}_2\text{Cu}_6/\text{Al}_2\text{O}_3$. Reproduced with permission from ref 42. Copyright 2015 Springer Nature.

them.⁴² A further stability advantage of such catalysts is that poisoning by CO is minimized, because CO bonds less strongly to the alloy than to the pure noble metal. Thus, catalysts in this class offer multiple stability advantages, as illustrated further for dehydrogenation of light alkanes catalyzed by rhodium atoms embedded in supported copper nanoparticles.⁴³

The intriguing and valuable catalytic properties of these nested metal catalysts could lead to large-scale applications. The opportunities afforded by these materials are contrasted with those offered by the aforementioned metal oxide-supported analogues. Like the catalysts on oxophilic metal hosts, those supported on metals such as copper in bimetallic alloys are present in clusters or nanoparticles that have irregular sizes and structures. But when the active noble metal atom is present in only a low concentration in the host metal, then the surroundings of the noble metal may be almost uniform, and the structure may be quite stable. In these catalysts, the host metal (e.g., copper) is typically present in the zerovalent state, whereas in the catalysts mentioned above that have oxophilic host metals (e.g., tungsten), the host metal is typically present in a positively charged state.

Noble Metals Isolated in Nanoscale Metal Oxide Nests on Supports

A next logical step in the development of this field emerged from insights about how to isolate and stabilize highly dispersed noble metals in metal oxide nests on supports.⁴⁴ The synthesis is shown schematically in Figure 5; a key idea was to bond platinum in salt precursors selectively to nests of isolated cerium oxide (CeO_x) and not to the silica support on which the nests were formed. The synthesis of such nested metal atoms was

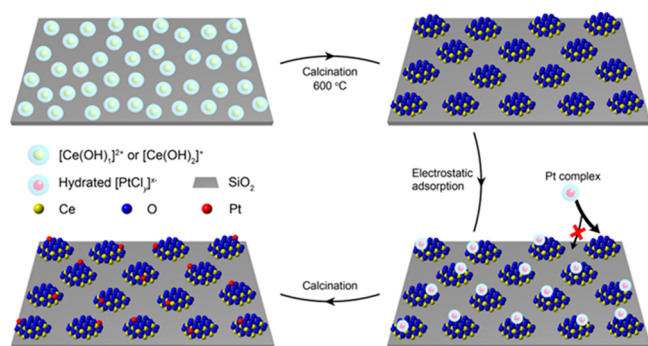


Figure 5. Schematic representation of the synthesis of $[\text{Ce}(\text{OH})_2]^+$ and $[\text{Ce}(\text{OH})_3]^+$ precursors on a silica support from Ce^{3+} reacting with OH^- species in a weakly basic solution. Conditions were chosen so that cerium-containing cationic species electrostatically adsorb on the negatively charged SiO_2 support in contact with an aqueous solution. High-temperature calcination caused the atomically dispersed cerium species to self-assemble into CeO_x nanocrystallite islands, which serve as functional nanogluers to localize catalytic noble metal atoms. Adjusting the aqueous solution pH so that the CeO_x nanoclusters were positively charged facilitated selective adsorption of negatively charged platinum-containing species on the CeO_x nanoislands. Subsequent washing and high-temperature calcination removed solution residues, including chloride, and facilitated confinement of platinum atoms in isolated CeO_x nanoclusters. The platinum loading was chosen so that there was less than one platinum atom per island, leading to nanostructures that incorporated predominantly single platinum atoms; infrared spectra of adsorbed CO and EXAFS spectra showed that the platinum was almost all atomically dispersed. Reproduced with permission from ref 44. Copyright 2022 Springer Nature.

accomplished by strong electrostatic adsorption of the metal precursor species, whereby negatively charged $[\text{PtCl}_6]^{2-}$ was attracted to the positively charged CeO_x nests and repelled by the silica with the same negative charge—the solution pH was adjusted to meet this criterion. The synthesis chemistry is straightforward and readily scaled up, suggesting good prospects for applications of this class of catalyst.

STEM images show that the isolated CeO_x nanoislands were about 2 nm in diameter, without much variation, and the platinum loading was chosen so that less than one platinum atom was present per CeO_x island.⁴⁴ These islands—called nanogluers—confined the noble metal atoms, which were shown not to migrate onto the silica support or to be transported between islands. This design of atomically dispersed metal catalysts allows metal atoms to move around in their respective CeO_x nests, but not to agglomerate outside the nests to form larger particles. Microscopic images and EXAFS and infrared spectra of the pre-catalyst and the catalyst itself confirmed the practicality of this design strategy: the platinum dispersion did not change under either harsh oxidative conditions (annealing in air at temperatures up to $600\text{ }^\circ\text{C}$) or harsh reductive conditions (heating in H_2 at temperatures up to $500\text{ }^\circ\text{C}$). Indeed, hydrogen reduction of the catalyst markedly increased its activity for CO oxidation, with the platinum remaining isolated as single atoms in the nests during the catalytic reaction.

In contrast, platinum atoms that were dispersed on large CeO_2 or silica particles, without the isolated CeO_x nanoislands, were characterized by inferior stability as the platinum sintered over time.⁴⁴ The stability of the nested catalysts is a major practical advantage that should allow the most highly dispersed noble metals to be used as catalysts in a range of applications.

The metals could still be susceptible to unwanted changes in oxidation state, especially at elevated temperatures under oxygen-rich conditions, and it might be of advantage to include a second metal component to bond with the first one (making bimetallic clusters) and modify the electronic structure and reactivity of the confined metals. It is expected that uniform, ultrasmall, and isolated metal oxide nests can host various monometallic, bimetallic, or multimetallic species and provide a platform for investigating the fundamental processes of heterogeneous catalysis.

Summary

The idea of isolating catalytically active metals in cups and on islands is gaining traction among researchers, and evidence implying the generality of the strategies of noble metal stabilization in metal or metal oxide nanoparticles on supports suggests that one might expect rapid progress going forward, with the prospect of practical applications. Some of the catalysts written about here provide benefits of efficient use of expensive metals, stability, selectivity, and activity.

The class of nested supported metal catalysts is still small, and many questions remain about their syntheses, structures, and properties, as summarized in Table 1. But some give prospects of relatively low-cost large-scale synthesis and properties that might make them suitable as practical catalysts—with advantages (e.g., in stability) that might some day lead to new technology.

It is selectivity that often is a distinguishing advantage of molecular metal catalysts used in technology (and biology)—and high selectivities are usually associated with uniformity of catalytic sites. As synthesis of solid catalysts becomes more precise, we may expect them to become more selective. We posit

Table 1. Nested Supported Metal Catalysts

type of supported metal catalyst	principal experimental characterization methods reported (and potentially valuable)	structural characteristics and properties that are well-established	structural and performance characteristics that remain to be established	synthesis methods and limitations	comments
metal complexes in zeolite pore mouths	IR and NMR spectroscopy; DFT modeling	presence of metal complexes in pore mouths, blocking entry into pores	precise structures; images of metals and surrounding atoms; evidence of catalysis; regenerability	few examples to evaluate precision and reproducibility of syntheses	only few citations of these materials, none used as catalysts; how stable are samples? is economical synthesis realistic?
metal complexes and clusters in zeolite cups	EXAFS and IR spectroscopy; catalyst performance for olefin hydrogenation and epoxidation	presence of metal complexes in cups	interactions of metals with zeolite surfaces (and bonding); stability in long-term operation; regenerability	few citations for evaluating synthetic yields	only few citations of these materials; are anchored metals stable, especially in the presence of liquid-phase reactants?
noble metal clusters dispersed on layers of oxophilic metals on supports	EXAFS spectroscopy; H ₂ , CO chemisorption; catalyst performance for toluene hydrogenation and crotonaldehyde hydrogenation	evidence of average majority structures; evidence of catalytic properties for various reactions; some evidence of stability	uniformity of samples; degree of isolation and stabilization of noble metals and their interactions with support in addition to nest; atomic-resolution imaging	several example of synthesis from bimetallic (noble metal-oxophilic metal) clusters suggest some generality of syntheses	organometallic precursors are expensive and may be impractical in potential applications; structures offer valuable catalytic properties, associated with small noble metal clusters, but questions remain about stability and regenerability
atomically dispersed metals in metal nanoparticles	STEM imaging, IR spectroscopy (EXAFS spectroscopy and other in operando structure data)	presence of isolated noble metals in non-noble metal; evidence of catalytic activity, selectivity, and stability for a number of reactions	stability; resistance of noble metals to sintering and transport into supported nanoclusters under forcing conditions; evidence of fluxionality and structural nonuniformities	only few examples known; opportunities for deeper understanding of how galvanic replacement syntheses can be done and how reproducible they are	offer prospects for large-scale catalytic applications, but questions remain about stability and regenerability
atomically dispersed metals and metal clusters in nanoscale metal oxide islands	operando EXAFS and XANES spectroscopies; IR spectroscopy with CO probe molecules (imaging of noble metals)	dispersion of noble metals in island nests and demonstration of stable confinement under forcing oxidative and reductive conditions; evidence of stable catalysis of CO oxidation at high temperatures	molecular-level structures of nests and evidence of structural nonuniformities; locations of individual noble metal atoms in islands and their changes under various treatment and catalytic conditions	synthetic method appears to be generalizable to other metal/support combinations, but experimental verification needed to determine generality of method	offer prospects of high stability and regenerability for large-scale catalytic applications, but questions remain about details of catalytic species, such as changes in metal oxidation state during catalysis in some reactions

that this is a direction for improvement in nested catalysts—and in catalysis science broadly—leading to better use of resources and minimization of harmful waste products. We suggest that the nested catalysts described here may help to show the way to future research in catalysis.

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Notes

The authors declare no competing financial interest.

Biographies



Bruce C. Gates has been a professor of chemical engineering at the University of California, Davis, since 1992, and has just entered emeritus status. His research group has recently focused on supported metal catalysts, including structurally well-defined mononuclear metal complexes and clusters. They collaborate with numerous research groups and have strived to combine skills for precise synthesis bolstered by multi-technique structure investigations that provide spectroscopic and microscopic evidence of catalysts in the functioning state bolstered by catalyst performance evaluations and electronic structure calculations. They investigate catalytically important metals, especially noble metals, emphasizing supports that are crystallographically well-defined, including zeotypes, metal–organic frameworks, and crystalline metal oxides such as MgO.



Alexander Katz has been on the faculty of the Chemical and Biomolecular Engineering Department at the University of California, Berkeley, since 2000; he currently holds the title of Professor. Since its inception, his research group has been focused on supported molecular catalysts, with an emphasis on synthetic approaches that can be used to enforce site isolation in this class of materials. Toolkits used by the Katz group rely on both organic and inorganic components, benefiting from collaborations involving spectroscopic characterization and electronic structure calculations. Much of the group's recent effort has been devoted to site-isolated iridium clusters (2–4 metal atoms), with a goal of deepening the understanding of hydrogenation catalysis, because this is key to many technological reactions limited by hydrogen transfer and involving supported noble metal catalysts.



Jingyue Liu has been a professor of physics at Arizona State University since 2011. His research group has focused on developing nanostructures for heterogeneous catalysis, energy, and sustainability, with an emphasis on synthesizing and evaluating functional properties of atomically dispersed species on high-surface-area supports. They utilize the capabilities of atomic-resolution electron microscopy techniques to explore synthesis–structure–performance relationships, and they collaborate with spectroscopy experts to gain insights into the nature of atomically dispersed metal species and how these surface moieties interact with their supports. The overall goal of Liu's research group is to develop scalable synthesis strategies to construct atomic-scale functional entities with targeted physicochemical properties.

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