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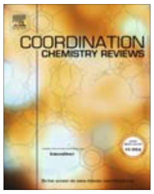

Review

Molecular approaches to heterogeneous catalysis ☆

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ABSTRACT

In most applications in industry involving catalysis, heterogeneous catalysts are preferred over their homogeneous counterparts when available. However, the former cannot be easily made as selective for complex chemical conversions as the latter. Selectivity requires control of the structural and electronic properties of the catalytic sites at a molecular level, and that is in general quite difficult to accomplish in solids. Nevertheless, a number of novel approaches have been advanced in recent years toward that goal. In this brief Perspective we provide a personal view of some of the avenues available to make highly selective heterogeneous catalysts. First, we discuss the possibility of tethering or otherwise immobilizing homogeneous catalysts on solid surfaces. Alternatively, molecular complexity can be added to solid surfaces via the adsorption of discrete modifiers. Isolated catalytic sites with unique molecular characteristics can also be created during or after the synthesis of heterogeneous catalysts. The structure of the exposed facets of solids can themselves be exploited to control catalytic performance. Finally, complex nanostructures such as Janus and core-shell nanoparticles can be synthesized and employed as scaffolds for multiple catalytic functionalities. A few examples of all of these methodologies, mainly from our own laboratory, are provided, and a discussion of the pros and cons of each approach is provided.

Contents

1. Introduction

Since the beginning of the incorporation of catalysis into industrial chemical processes more than a century ago, it has been realized that some compromises may be required in catalytic designs [1–3]. In particular, it has been long recognized that the use of solid catalysts is highly desirable, because those are easier to handle, separate from the reaction mixture, recover, and reuse than molecular counterparts, and therefore make process designing simpler. Solid catalysts offer additional advantages, including good stability, low toxicity, and the ability to resolve incompatibility problems associated with solubility and functionality. On the other hand, the design and preparation of catalysts with sites exhibiting well-defined structural and electronic characteristics is much more

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difficult in solids than with discrete molecules. This limitation has become more acute over the years, as the need for high selectivity in catalytic processes, to optimize the consumption of feedstocks, eliminate separation steps, and minimize the production of potentially polluting byproducts, has gained higher relevance and importance. The holy grail of catalysis is to achieve with heterogeneous (solid) catalysts the same level of catalytic selectivity in complex conversions afforded by homogeneous (molecular) catalysts [4,5].

In order to address this issue, it helps to think about it from a molecular chemistry perspective. Two parallel directions of research have been adopted to this end. On the one hand, great effort has been placed in understanding the molecular details of catalytic reactions on solids [6,7]. This has been aided by the advancement in the past few decades of a modern surface-science research approach that relies on the use of surface-sensitive analytical techniques together with simplified models of the relevant catalytic surfaces [8,9]. Recent development of spectroscopies and other characterization techniques that can probe catalytic sites *in situ* under realistic catalytic conditions, or even in *operando* mode during the course of catalytic processes, has further improved our understanding of the mechanisms of these catalytic reactions [10–12]. The challenge of determining mechanistic details of catalytic reactions using controlled environments (i.e., vacuum) and connecting them to true catalytic processes is what the surface-science community has dubbed "bridging the pressure gap" [13,14]. Additional improvements on the complexity that has been added to the model surfaces used for these studies to more closely resemble real catalysts by "bridging the materials gap" is further helping develop a more accurate molecular-level picture of heterogeneous catalysis [15,16]. Many advances have been made in these directions of research in the past few years.

In parallel to those surface-science studies, much emphasis has been placed on developing ways to prepare solids with sites on their surfaces displaying the same level of detail and tunability as discrete molecules, with the aim of emulating homogeneous catalysts or creating new heterogeneous catalysts with highly selective centers [17,18]. Recent advances in nanotechnology, in the synthesis of complex but well-defined nanostructures, have greatly helped in this endeavor [19,20]. It is now possible to, for instance, prepare solids with unique and sophisticated surface atomic ensembles or porous structures, or to modify those surfaces after synthesis to incorporate new molecular functionalities. The catalytic performance of surfaces can be tuned *in situ* during reactions as well, via the addition of molecular modifiers. In general, it has been useful to focus on the active sites of solid catalysts and to gradually build complexity on those to achieve the desired selectivities. This can be done at different levels, sometimes via the creation of homogeneous-heterogeneous catalysis hybrids. In this brief Perspective, we discuss some of the most prominent approaches that have been taken in recent years to address these issues, with focus on our own research. Our article is not intended to be comprehensive, but rather it has been conceived as a way to introduce the reader to some of the ideas that have arisen to develop new, highly selective heterogeneous catalysts. We also focus on the definition and characterization of catalytic sites on solid surfaces and only briefly mention aspects of coordination to those sites during catalysis, as that is a much less developed area in heterogeneous catalysis and not the main interest of this Perspective. With each new approach introduced, we provide a short overview of the state of the art and the ideas introduced in the last few years, followed by a few chosen examples, mainly from our own group. We conclude with some general remarks on our own view of the status of the field.

2. Immobilization of homogeneous catalysts on surfaces

Perhaps the most straightforward way to attain high selectivities with heterogeneous catalysts, comparable to those seen with their homogeneous counterparts, is to tether or otherwise immobilize the latter on solid surfaces. This idea has been explored, in particular with metalorganic complexes, for several decades [21–24]. Initial work focused on grafting metal complexes directly to surfaces, using surface sites as coordinating ligands [25,26], but that approach has proven limiting, as the surface modifies the electronic properties of the metal catalytic center, affecting its performance. Grafted metalorganic moieties can also leach out of the solid [27], or, conversely, undergo aggregation into metal nanoparticles (NPs) under reducing conditions [28]. More recently, it has become more common to tether these types of homogeneous catalysts via short organic linkers using "click" chemistry; several synthetic procedures have been developed for the covalent tethering of molecular functionalities on oxide surfaces in particular [29–31]. An example of this approach from our group is reported in Fig. 1 where an iron-coordinated cavitand was tethered to the surfaces of a SBA-15 mesoporous material to promote reversible redox reactions, specifically the selective room-temperature oxidation of C–H bonds in unactivated hydrocarbons [32]. An induction period was required for the activation of the catalyst during which a change in coordination of the iron ion takes place, but high activities and excellent recyclability were observed afterward.

Tethering of homogeneous catalysts to solid surfaces does not need to be limited to metalorganic complexes; other functionalities such as organic acidic or basic moieties can be incorporated as well [33–35]. Fig. 2 depicts heterogeneous catalysts made by tethering cinchonidine (Cd) onto a silica support in order to promote coupling reactions enantioselectively [36]. The resulting heterogenized catalysts showed performances comparable to the homogeneous analogs, but this study also highlighted some potential pitfalls associated with the presence of the surface of the solid, which clearly plays an active role in these tethered catalysts beyond providing a solid platform for the heterogenization of molecular catalysts [37]. Initially, a loss of enantioselectivity was observed upon tethering because of the nonselective catalytic activity of the solid itself and the possible inactivation of the Cd molecule via its bonding to the surface. Fortunately, these effects could be minimized, via silylation of the surface in the first case and by choosing appropriate solvents and selecting the best attaching position in the second; the latter procedure illustrated in Fig. 2.

One advantage of tethering molecular functionalities to solid supports is that it prevents those from reacting with each other. This helps avoid the annihilation of incompatible reacting groups such as acids and bases, or reducers and oxidizers, as it would occur if both were added to a single solution in homogeneous catalysis. Accordingly, the immobilization of two or more catalytic centers on a single solid can be used to carry out multiple-step reactions in cascade or tandem fashion, all in one pot [38,39]. In fact, the various functionalities may conceivably be placed strategically in specific spatial patterns within the structure of the solid in order to generate additional cooperative effects or to facilitate the transfer of unstable intermediates from one catalytic center to a second adjacent one, although this has proven difficult to accomplish; the successful implementation of this idea may still be in the future [40,41]. Our experience in the area of tandem catalysis with tethered molecular functionalities is illustrated by the synthetic strategy depicted in Fig. 3, where a number of steps, including group protecting and deprotecting, were devised to add both acidic and basic functionalities to one single mesoporous silica support without neutralizing each other [42]. Critically, the resulting anchored sulfonic acid and amino groups are spatially

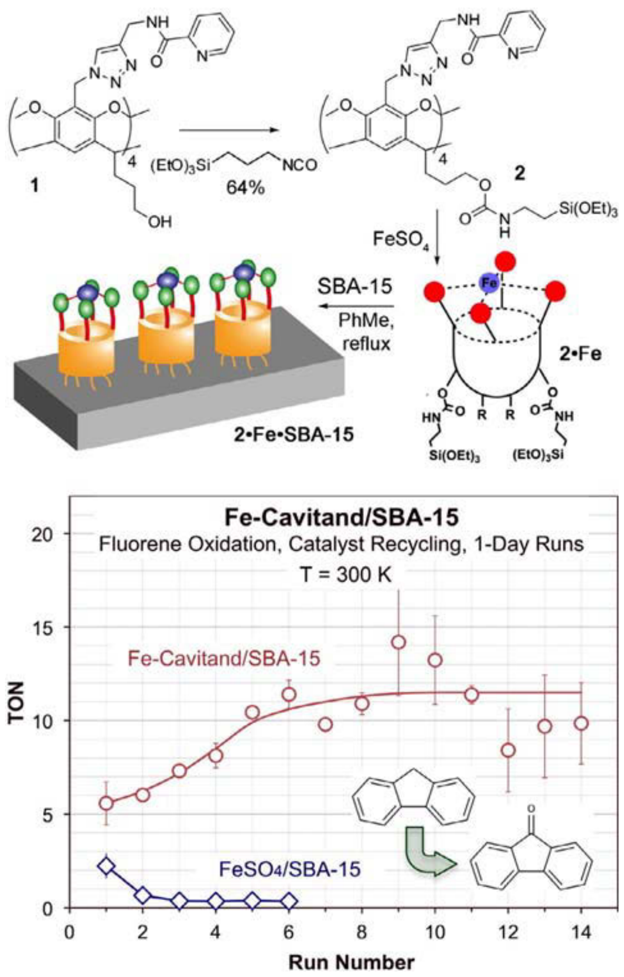


Fig. 1. Example of a tethered homogeneous catalyst [32]. Top: Synthesis of a Fe-containing cavitand catalyst tethered to a SBA-15 silica support. Bottom: Catalytic activity for the oxidation of fluorene versus run number to highlight both the induction period needed for full activation and the recyclability of this heterogeneous catalyst. Reproduced from Ref. [32] with permission, Copyright 2013 American Chemical Society.

separated, located mainly on the outer and inner surfaces of the pores, respectively, and therefore can react independently of each other. These catalysts were successfully tested for the promotion of a cascade process comprising of sequential deacetylation plus Henry reaction steps.

In summary, the tethering or immobilization of homogeneous catalysts on solids has much to offer as a way to make highly selective catalysts. On the other hand, this approach does suffer from some important shortcomings, mainly related with catalyst stability. Once the catalyst is deactivated, because of interactions of the molecular functionalities with the surface, leaching, or thermal or chemical decomposition, there are no easy procedures for their successful reactivation or recycling. Moreover, due to the fact that the preparation of these catalysts may require expensive synthetic steps, they may be useful only for high-cost processes, possibly for the synthesis of high-value sophisticated pharmaceuticals or fine chemicals.

3. *In-situ* molecular modification of solid surfaces

An alternative way to add molecular definition to catalytic sites on solid surfaces is via the adsorption of appropriate discrete molecules. These so-called modifiers, which can be incorporated *in situ* during catalysis (by adding them to the reaction mixture), may adopt specific bonding geometries and create unique chemical environments on the surface with molecular definition to help with selectivity during catalytic conversions [43]. In electro- and photo-catalysis, the use of discrete organic redox mediators is also common [44,45]. The adsorption of the modifiers tends to be reversible, so the original catalyst can be easily recycled. Having the modifier present in solution also helps with the potential preformation of modifier-reactant complexes prior to adsorption on the surface, affording easy association and the adoption of the appropriate configuration to facilitate selective conversion once bonded to the solid. Nevertheless, non-reversible adsorbates have also been used as catalyst modifiers, in particular self-assembled monolayers (SAMs) [46]. Examples of reactions where SAMs have been shown to add selectivity to catalysis include the hydrogenation of polyunsaturated fatty acids, aromatic oxygenates such as furfural, or unsaturated aldehydes such as cinnamaldehyde, as well as the ring-opening or ring-closing of epoxides (Fig. 4a) [43,47]. In one case from our laboratory, the addition of alkyl thiol SAMs to colloidal platinum NPs was shown to lead to significant improvements in both activity and selectivity during the hydrogenation of α-keto esters with cinchonidine as a chiral modifier [48]. The effect on catalysts made out of supported Pt NPs proved to be subtler, with compromises required between activity and enantioselectivity, but acceptable performances were proven possible still, with all-heterogeneous catalysts made out of cinchonidine-terminated thiol SAMs reaching almost the same enantioselectivities (albeit with lower activity) as the best solution-modified catalysts (Fig. 4b) [48]. Several mechanisms may be operational to control selectivity in these cases, including the SAMs ability to selectively block specific surface sites, to introduce new steric constrains for molecules approaching the surface (via crowding, forcing them to adopt particular orientations), to directly interact with the reactants to provide a level of molecular recognition, or to kinetically control the residence time of other modifiers [43,48].

A particularly interesting subset of the catalyst modification using molecular adsorbates approach that has proven possible but that has yet to become general is the addition of chiral modifiers to the solution of reactants to bestow enantioselectivity to hydrogenations promoted by metal NPs dispersed on high-surface-area supports [49,50]. The prototypical example in this category is the Orito reaction, in which cinchona alkaloids are added to the solution to bestow enantioselectively to the Pt-catalyzed hydrogenation of α-ketoesters such as ethyl pyruvate, as already illustrated in the example reported in Fig. 4 [51,52]. Unfortunately, the scope of this reaction is quite limited. Great effort has been dedicated by the surface-science community to understand how these chiral modifiers operate in order to extend their effectiveness and range [53–55], but the advances in this direction are still not sufficient to afford the design of different modifiers in order to promote enantioselectivity in other reactions.

Much molecular understanding on the adsorption of chiral modifiers comes from studies on flat surfaces and under ultrahigh vacuum (UHV) conditions, which have permitted the use of spectroscopies such as reflection–absorption infrared absorption spectroscopy (RAIRS) [56,57], near-edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy [58], scanning tunneling microscopy (STM) [54,57,59,60], temperature programmed desorption (TPD) [61,62], and molecular beams [61,63]. Additional information has been extracted from quantum mechanics calculations [59,64,65]. It has been determined that, under vacuum at least, binding of the chiral modifier involves its aromatic ring, with its plane oriented parallel to that of the surface. Moreover, coadsorption of the chiral modifier with the reactant leads to the formation of a 1:1 complex on the surface involving

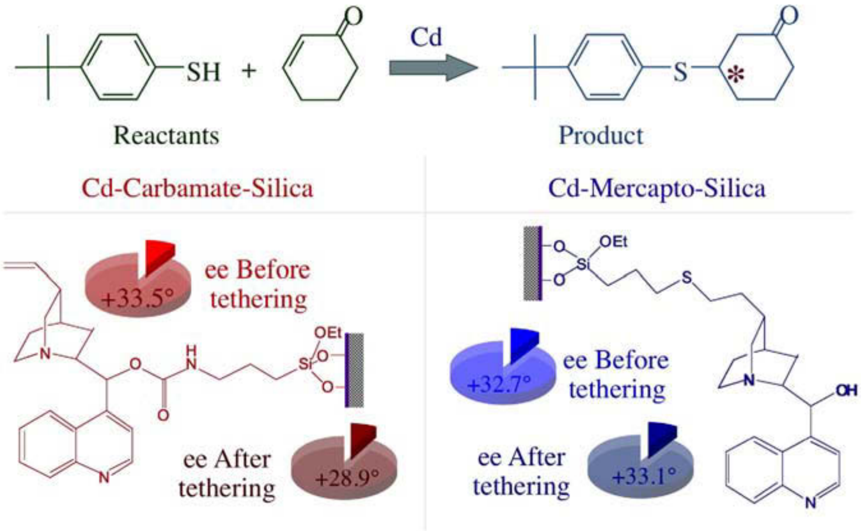
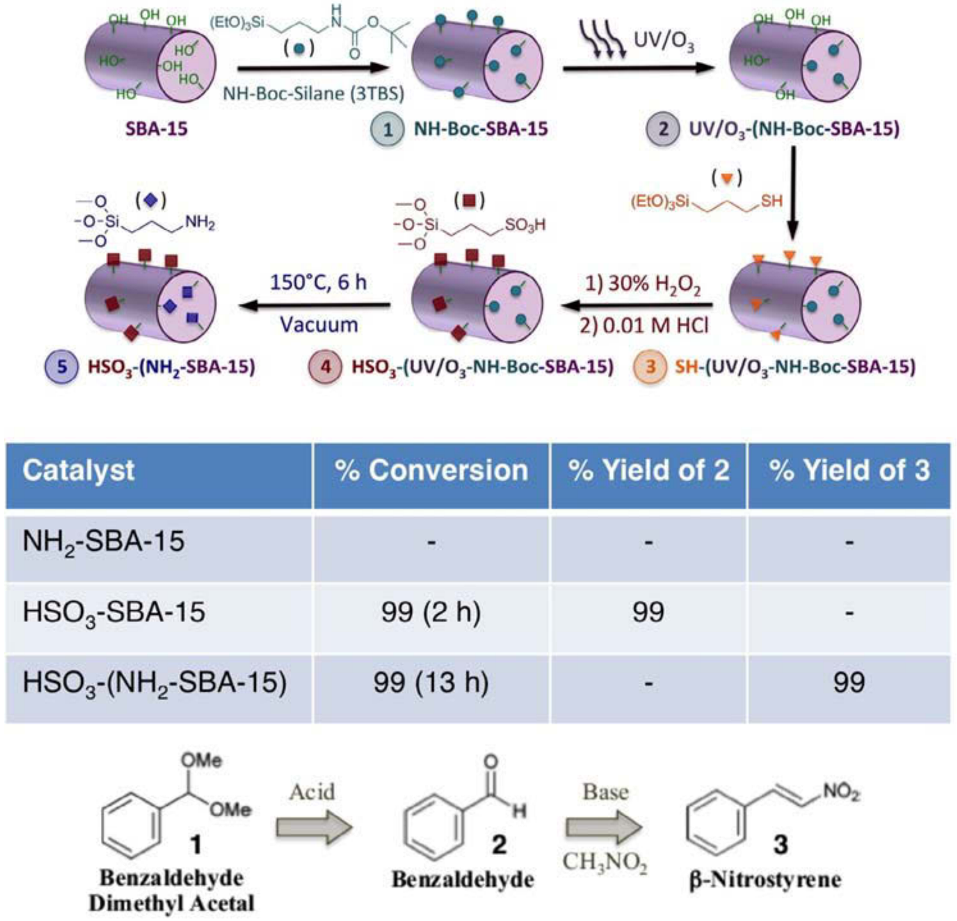


Fig. 2. Enantiomeric excess (ee) results obtained for the addition of p-*tert*-butylbenzenethiol to 2-cyclohexene-1-one (top) using two types of catalysts, with cinchonidine (Cd) tethered to a silica mesoporous material (SBA-15) via its OH (carbamate, left) and vinyl (mercapto, right) moieties (bottom) [36]. Upon careful tuning of the surface and reaction conditions, catalytic performances comparable to those obtained with free Cd were possible. Adapted with permission from Ref. [36], Copyright Springer Science + Business Media, LLC 2011.



Catalyst	% Conversion	% Yield of 2	% Yield of 3
NH_2-SBA-15	-	-	-
HSO_3-SBA-15	99 (2 h)	99	-
HSO_3-(NH_2-SBA-15)	99 (13 h)	-	99

Fig. 3. Top: Synthetic strategy to make acid-base multifunctional solid catalysts [42]. Bottom: Catalytic results for a tandem process that includes deacetylation followed by a Henry reaction: only the bifunctional catalyst, the last entry in the table, promotes full conversion to the desired product. Reproduced from Ref. [42] with permission, Copyright 2018 American Chemical Society.

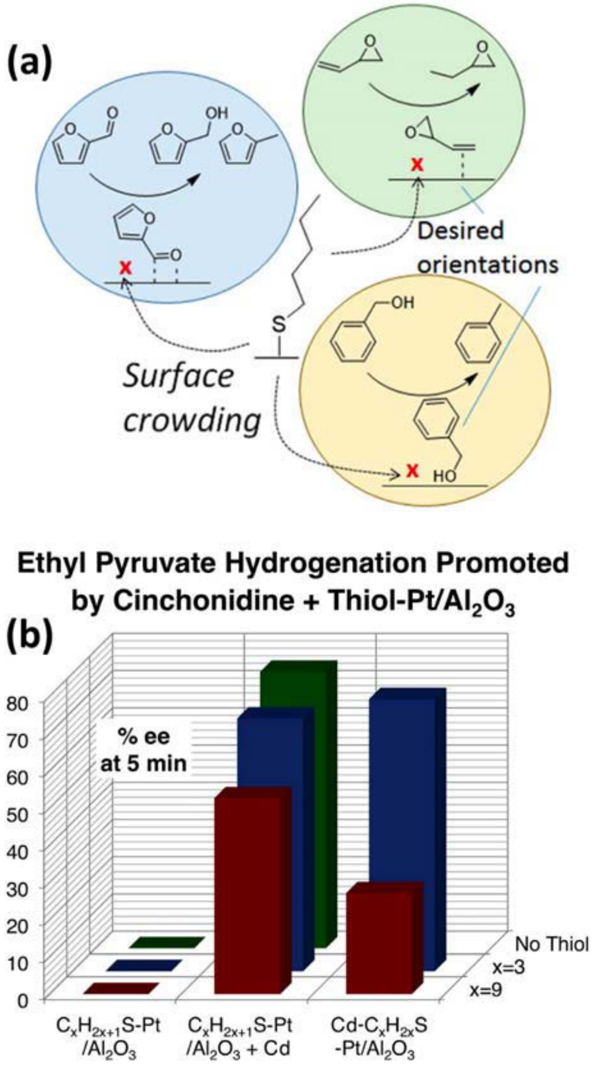


Fig. 4. (a) Examples of catalytic reactions where the modification of surfaces with SAMs has been used to improve selectivity [47]. Reproduced from Ref. [47] with permission, Copyright 2015 American Chemical Society. (b) Example where the enantioselectivity excess (%ee) during the hydrogenation of ethyl pyruvate with 1 wt% Pt/Al$_2$O$_3$ was modified by SAMs [48]. The performance of the original catalyst (green bars) is contrasted with samples treated with regular (C$_x$H$_{2x+1}$SH, two left rows, without and with cinchonidine –Cd– added in solution, respectively) and cinchonidine-derivatized (Cd-C$_x$H$_{2x}$SH, right row) thiols of two alkyl chain lengths (x = 3, blue, and x = 9, red). The all-heterogeneous Cd-C$_3$H$_6$SH catalyst reached enantioselectivities comparable to the best solution-modified case, albeit with lower overall activity. Reproduced from Ref. [48] with permission, Copyright 2014 American Chemical Society.

bonding at three points (Fig. 5a) [66,67]. Interestingly, with 1-(1-naphthyl)ethylamine (NEA), a simpler prototypical chiral modifier, an effect of surface coverage on enantioselectivity has also been observed, similar to what is known with smaller chiral adsorbates [53,68]: titration of enantiopure NEA layers on Pt(111) surfaces with enantiopure propylene oxide (ProO), for instance, have led to the identification of a unique enhancement in titrant uptake at approximately half of NEA monolayer saturation, but only with homochiral (SS or RR), not with heterochiral (SR or RS), modifier-titrant pairs, and only for the ProO more strongly bonded to the surface (Fig. 5b) [50,61,69].

All this is useful knowledge when discussing chiral modification in catalysis, but cannot be directly extrapolated to real catalytic systems. It needs to be remembered that practical metal catalysts do not display many flat surfaces, but are rather comprised of small metal NPs dispersed on porous materials. More critically, these reactions are carried out in liquid phase, and the solvent has been proven to play a crucial role directing the catalytic reactions [71–75]. Basic *in situ* characterization of the adsorption of cinchona modifiers from solution have shown a change in adsorption geometry, from the flat-lying configuration seen under UHV with diluted solutions to a more tilted arrangement as the concentration of the modifier is increased and the surface becomes more crowded, that correlates with changes in enantioselectivity in catalysis in ways still being debated in the literature [56,76–80]. There is also a large conformational space available to some of these modifiers, cinchona alkaloids in particular, and catalytic chiral modification appears to depend on the conformation adopted by the adsorbed modifiers on the surface [65,73,81,82]. More recently, we have challenged the accepted idea that bonding of the modifiers to the surface involves primarily the aromatic ring; spectroscopic data acquired *in situ* with a family of modifiers based on NEA, using systematic substitutions to block specific functionalities, points to bonding via the amine nitrogen atom instead [83,84]. As shown in Fig. 6, adsorption is only possible with primary amine groups. Also indicated in Fig. 6 is the fact that enantioselectivity in catalysis is only possible with the chiral modifiers that bind to the surface.

The full understanding of how these chiral modifiers adsorb on metal surfaces and contribute to the bestowing of enantioselectivity to catalytic reactions is far from settled, and extending this knowledge to the design of other modifier is still farther in the future. Nevertheless, the molecular-level information extracted from surface-science studies of these systems is expected to be useful in the design of molecular modifiers for catalytic processes. Although the examples available to date are few, they do show that such modifiers can create unique local environment when adsorbed on heterogeneous catalysts, and thus define catalytic sites with molecular precision. What is needed is a better ability to chose modifiers in terms of their adsorption properties and their ability to both create the desired surface catalytic sites and interact with the reactants to direct them toward the right reaction pathways.

4. Preparation of isolated single catalytic sites on surfaces

Single isolated catalytic sites can also be built within the structure of solid surfaces. Much emphasis has been placed in recent years into adding such so-called single sites to appropriate solid materials to promote specific reaction selectively [85–89]. One way to accomplish this is to adsorb metalorganic precursors, as done when grafting homogeneous catalysts (see discussion above), and then partially or fully decompose the associated ligands to create new surface structures [90–92]. The distinction here is somewhat arbitrary, but when thinking about single-site catalysis the focus is on creating new surface structures rather than on relying on the coordination chemistry of the original grafted metalorganic complex. The new sites are typically dependent on the chemical behavior of a single metal ion coordinated to a surface site, often on an oxide such as silica or alumina, but more complex multi-atom ensembles can also be devised this way. An example is provided in Fig. 7, a case where well-defined isolated Pt(IV)-hydride sites were stabilized by neighboring Zn(II) surface species on a SiO$_2$ support to promote both the selective partial hydrogenation of butadiene to butene and the reduction of nitrobenzene derivatives to anilines under mild reaction conditions [93]. New acidic sites can also be tuned this way: witness, for instance, the case where the surface silanol groups in silica were converted into strong Brønsted acid sites via the addition of weakly coordinating

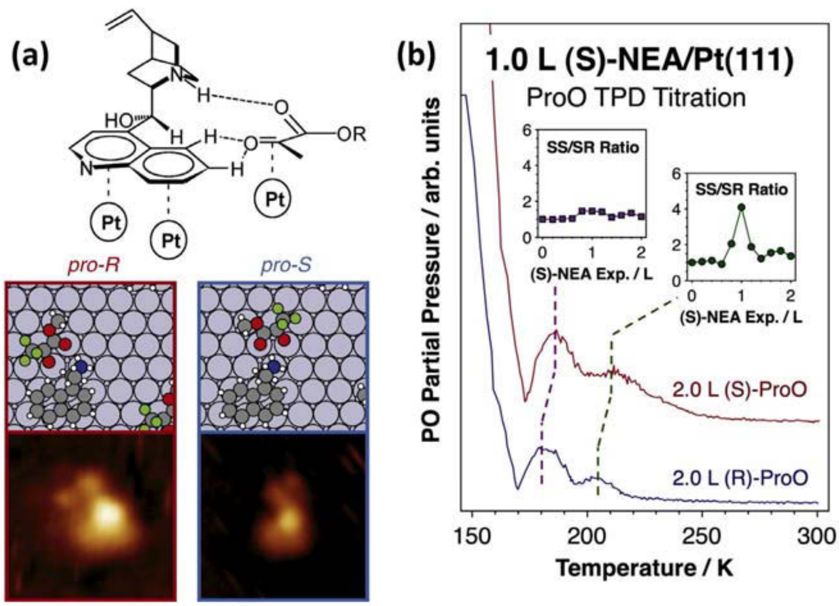
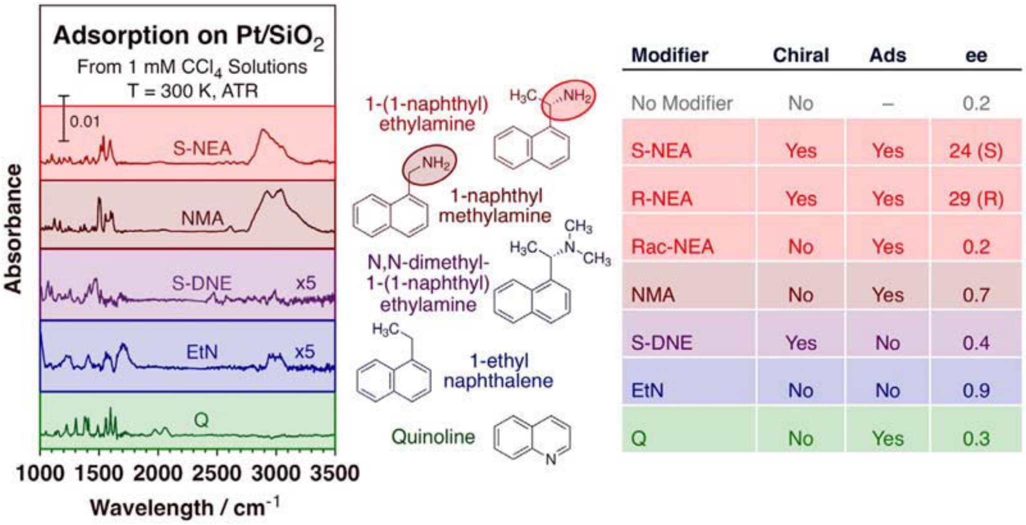


Fig. 5. (a) Scanning tunneling microscopy (STM) images and corresponding DFT atomic illustrations (middle) and schematic representation (top) of the most stable surface complexes that form on Pt(1 1 1) surfaces upon coadsorption of 3,3,3-methyltrifluoropyruvate (the reactant) and (R)-NEA (the chiral modifier), highlighting the three-point interaction between the two molecules believed to help define catalytic enantioselectivity [67]. Reproduced from Refs. [70] and [67] with permission, Copyright 2007 and 2014 American Chemical Society. (b) Propylene oxide (ProO) TPD titration data from Pt(1 1 1) surfaces chirally modified with (S)-NEA [61]. Clear differences are observed in the traces obtained with (S)-ProO versus (R)-ProO: the (S)-ProO enantiomer appears to adsorb more strongly (it desorbs at higher temperatures), and reach higher uptakes in the high-temperature state at intermediate (S)-NEA coverages (around 1 L exposure, which corresponds to approximately half of monolayer saturation; insets). These results identify a second enantioselective mechanism for the NEA modification of Pt that depends on coverage, in addition to that illustrated in (a). Reproduced from Ref. [69] with permission, Copyright 2008 American Chemical Society.



Modifier	Chiral	Ads	ee
No Modifier	No	–	0.2
S-NEA	Yes	Yes	24 (S)
R-NEA	Yes	Yes	29 (R)
Rac-NEA	No	Yes	0.2
NMA	No	Yes	0.7
S-DNE	Yes	No	0.4
EtN	No	No	0.9
Q	No	Yes	0.3

Fig. 6. Left: *In situ* attenuated total reflection infrared absorption (ATR-IR) spectra of NEA and related modifiers adsorbed on a supported Pt/SiO$_2$ catalyst from CCl$_4$ solutions [56]. Right: Corresponding catalytic enantiomeric excesses (ee) measured during the catalytic hydrogenation of ethyl pyruvate [84]. Adapted from Ref. [56] with permission, Copyright 2017 Elsevier B.V.

$Al(OC(CF_3)_3)_3$*PhF anions, to form bridging $\equiv Si{-}OH\cdots Al(OC(CF_3)_3)_3$ silanol moieties [94]. Single-site catalysts can be made out of supports other than oxides as well: carbon-based materials are particularly popular here, as the oxidation of graphene, for instance, creates molecular sites such as hydroxide and carboxylic groups that can be used to coordinate the desirable catalytic elements such as metal ions [95,96].

Monoatomic dispersion of metals on solid supports can be achieved by other means too, beyond simple impregnation or coprecipitation using metal salts. In fact, although impregnation and coprecipitation are methods long used to make more conventional supported metal catalysts, they had to be adapted for the preparation of single-site catalysts to obtain the desired metal atom isolation, by, for instance, reducing the metal loading [97–101]. Other more sophisticated approaches include ion exchange, chemical etching, ionic-liquid self-assembly, mass selected soft landing of cluster ions, and atomic layer deposition (ALD), among others [19,101–104]. For example, a Fe-Co dual-metal site used

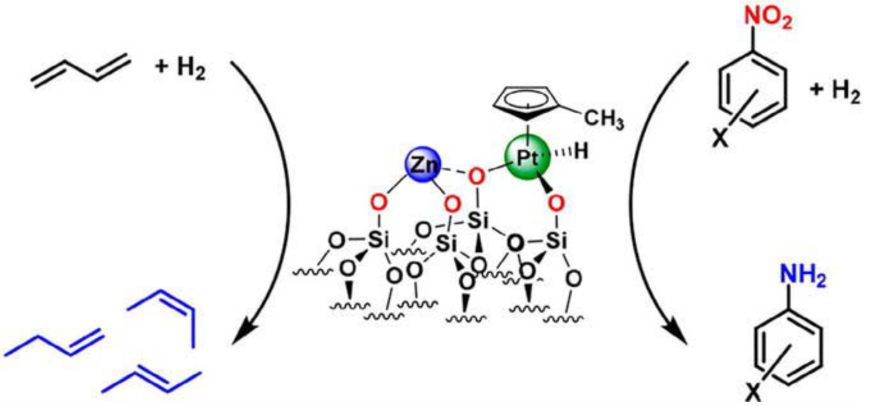


Fig. 7. Single-site catalyst comprised of a Zn–O–Pt–H core ensemble built on a silica surface for the selective promotion of hydrogenation and reduction reactions [93]. Reproduced from Ref. [93] with permission, Copyright 2018 American Chemical Society.

to promote the oxygen reduction reaction (ORR) in fuel cells was embedded into the atomic network of N-doped porous carbon by following the three-step procedure shown in Fig. 8 [105]. According to quantum mechanics calculation, this bimetallic site opens up a low activation barrier path for the binding of O_2, the formation of an OOH adsorbed intermediate, and the dissociation of the O–O bond in that species, not available with single-metal catalysts. It should be indicated that, with metals in particular, there is always the chance that the atomically dispersed atoms may sinter and form NPs on the surface upon high temperature treatments or exposure to certain chemical environments, including the reaction mixture [106,107]. Supports that interact strongly with the individual metal atoms may minimize this problem, but at the expense of significantly modifying the electronic properties of the catalytic centers, and with that the behavior of the catalyst [108]. These factors need to be balanced and adjusted for each individual catalytic system being considered to optimize performance.

One particularly interesting family of single-site catalysts is that derived from diluted metal alloys [109,110]. In these so-called single-atom alloy (SAA) catalysts, the single sites are minority metal atoms embedded within NPs made out of a different metallic element, typically dispersed on porous supports. The main element is presumed to be responsible for most of the catalytic reactions of the targeted process, but the second component, highly diluted and present in isolated atomic form on the surface, is believed to be needed in order to help with a crucial step not feasible on the original metal [109,110]. Perhaps the best-studied SAA system in recent years is that based on Pt (or Pd) atoms diluted in Cu NPs, for which much basic surface-science research has been carried out to unravel the mechanistic details of the catalysis [111]. The data point to the role of individual Pt atoms on the surface being the activation of H–H bonds, so selective hydrogenations can then occur on the milder Cu surface [112]. However, this simple picture has been recently challenged by us, because we have found that

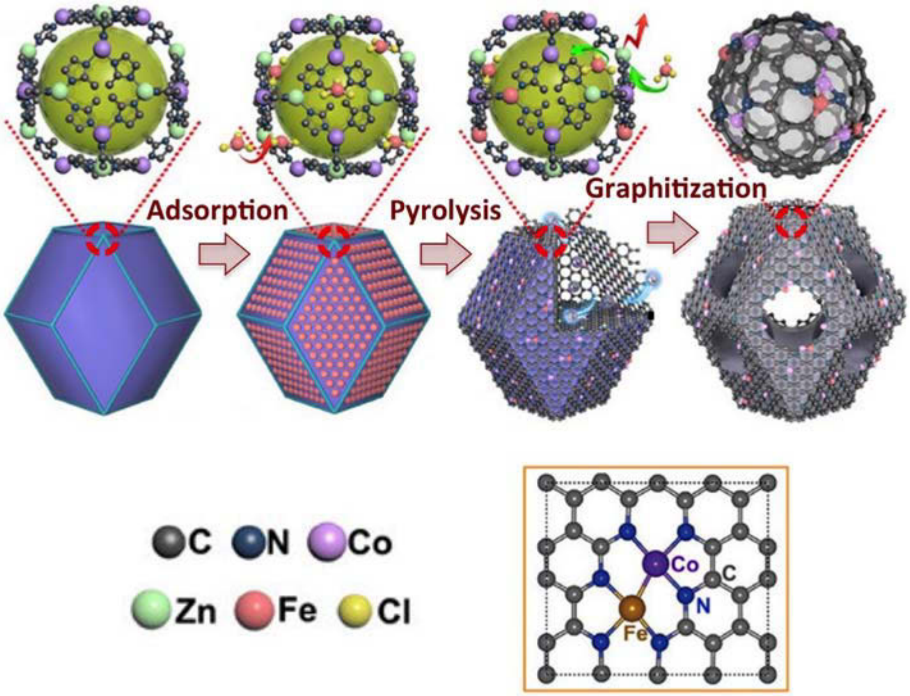


Fig. 8. Synthetic approach for the creation of Fe-Co dual-metal single sites to facilitate the dissociation of O–O bonds in oxygen reduction reactions [105]. Reproduced from Ref. [105] with permission, Copyright 2017 American Chemical Society.

under reaction conditions the metal NPs tend to oxidize and form an outer copper oxide layer, possibly preventing the Pt atoms from reaching the surface [113]. Moreover, the activity and selectivity of the hydrogenation reactions, for the specific case of the hydrogenation of carbonyl groups in unsaturated aldehydes at least, has been shown to be affected by the composition of the alloy, as indicated in Fig. 9 [114]; this is not expected if the hydrogenation steps all take place on the Cu surface. More studies to characterize the nature of the catalytic phase *in situ* under reaction conditions are needed to better understand how SAA catalysts function.

In general, there are many ways to create unique catalytic sites with well-defined characteristics at an atomic level, by adsorbing and decomposing molecular precursors on the surfaces of appropriate solids or by incorporating the key elements during the synthesis of the catalysts. These sites may be isolated on surfaces, displaying specific electronic characteristics associated with the catalytic elements themselves, or may be embedded in a larger solid matrix, as in metal alloys, in which case the electronic effects may be extended over many atomic units. Catalytic sites may be made out of single atoms, by themselves or with organic ligands, or may involve multi-atomic ensembles. The preparation of these sites in a reproducible fashion on surfaces is a challenge, but new synthetic approaches and nanotechnologies are being developed for this purpose at a rapid pace. The single-site approach to heterogeneous catalysis is in its infancy, but offers great promise.

5. Controlling the structure of the exposed surfaces in solids

Ideally, surface sites for heterogeneous catalysis should be able to have the same level of molecular definition and complexity as in homogeneous catalysis, which is why the ideas introduced so far are based on the incorporation of discrete molecules or atomic ensembles into the structure of those sites. However, as also discussed in the previous sections, this is not always possible. Moreover, molecular functionalities are often fragile, and only survive in catalytic processes requiring relatively mild conditions. It would be highly desirable to be able to construct sophisticated surface sites out of the solid constituent elements instead. This is not straightforward, but new synthetic nanotechnologies have in recent years significantly widened the range of solid structures that can be made [115].

One interesting development from basic surface-science studies with model systems is the realization that catalytic performance often depends on the structure of the surfaces exposed. It has long been recognized that some reactions are "structure sensitive" [116,117], but the new work has provided further insights into the nature of the surfaces that promote specific catalytic reactions [118–120]. The challenge has been to translate that knowledge into realistic catalysis systems by synthesizing catalysts with structures exposing the desired surfaces. Colloidal and other self-assembly approaches have been recently incorporated to achieve this so-called "shape selectivity", especially in cases where the active phase is a metal [18]: metallic NPs of many sizes and shapes, not only simple cubes and octahedra but more sophisticated forms such as stars, can now be produced this way [121–124]. The colloidal particles can be used in solution, in particular for electrocatalysis [125–129] as well as for organic conversions such as C–C bond formations [130–132]. However, they are perhaps more useful in heterogeneous form, dispersed on an appropriate support [10,17,133]. An example from our group concerns olefin *cis*–*trans* interconversions: although the trans isomers of alkenes and other unsaturated organic molecules are the most thermodynamically stable and the preferred products with most metal-based heterogeneous catalysts, our extensive surface-science [134–136] and quantum-mechanics [134,137–139] research has indicated that on the (1 1 1) facets of Pt the cis isomer, which is the desirable product in food processing and other applications, dominates. On the basis of that conclusion, new catalysts were prepared using tetrahedral Pt colloidal particles, and their selectivity for *trans*-to-*cis* conversions in olefins corroborated (Fig. 10) [134,140,141].

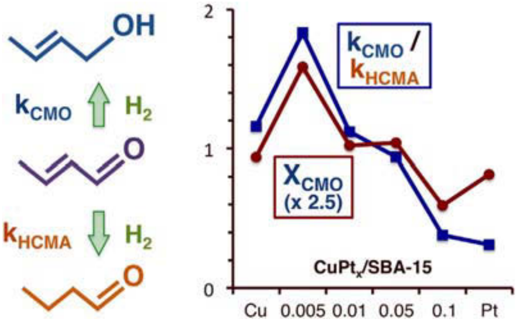


Fig. 9. Kinetic trends in the hydrogenation of unsaturated aldehydes with Cu-Pt SAA catalysts as a function of alloy composition [114]. Selectivity toward the desired product (X_{CMO}), varies with the Cu-to-Pt ratio because of relative changes in the reaction constants for the formation of the unsaturated aldehyde (k_{CMO}) versus the hydrogenated aldehyde (k_{HCMA}). This is not the behavior expected, and indicates that the isolated Pt atoms in the Cu-Pt alloy not only help with H_2 activation but also affect selectivity. Reproduced with permission from Ref. [114], Copyright 2020 American Chemical Society.

Shape control is only meaningful for metal NPs of a certain minimum size, on the order of a few nanometers; smaller NPs have only a limited number of stable structures. Nevertheless, in many catalytic applications small NPs are desirable, to maximize surface exposure and to provide unique low-coordination sites. One way to produce small metal clusters with well-defined numbers of atoms is by using dendrimers as templates, a method pioneered by Crook and coworkers [142,143]. The resulting dendrimer-encapsulated NPs (DENs) can be made in the ~ 1–2 nm range [144,145], and have been used to promote a number of reactions, both in solution and after dispersing them on solid supports. Examples of DENs applications in heterogeneous catalysis include hydrogenations [146–148], isomerizations [149], C–C couplings [150], and C–C [151] and C–N [152,153] bond activations in organic feedstocks, and also many redox reactions [154]. It should be noted that in solution the dendrimer structure is flexible and can adopt open or close configurations, controlling the mass transfer of reactants and products to and from the metal NPs, respectively (Fig. 11) [155–157], and hence potentially modulating the catalytic performance of the DENs [158–162]. The dendrimer themselves can also contribute to the catalytic chemistry, either by complexating metal ions or other homogeneous catalysts [163,164], or via their exposed or added organic functionalities [165]. Thanks to the precise control afforded by this dendrimer-based synthetic route, it has also been possible to test subtle trends in catalytic activity as a function of metal NP size [166–168].

One general concern with catalysts made out of self-assembly using organic surfactants or dendrimers is that those are bonded to the surface and interfere with catalytic reactions, or at the very least block surface sites. This issue has been addressed extensively by many research groups [170–173], but has not been full resolved. The organic residues from the colloidal or dendrimer synthesis of metal NPs may in some instances help with selectivity, as with the use of SAMs and other modifiers discussed above, but more often are detrimental to catalytic performance. An example from the Somorjai group shows that cleaning of poly(N-vinyl-2-pyrrolidone) (PVP)-stabilized Pt NPs, by UV radiation or thermal oxidation, is incomplete but significantly affects catalysis, enhancing ethylene hydrogenation but poisoning methanol oxidation (Fig. 12a and 12b) [174]. Often the problem is that the conditions

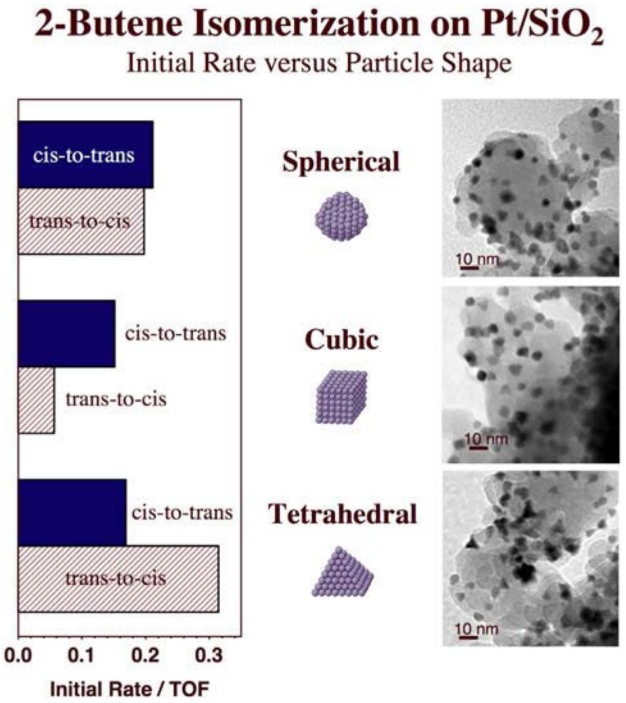


Fig. 10. Example of shape selectivity in catalysis, in this case for the preferential isomerization of trans olefins (*trans*-2-butene) to their *cis* counterparts [115]. The initial reaction rates (TOFs) reported on the left for three different Pt NPs shapes (microscopy images provided on the right) show that this can be accomplished by using tetrahedral shapes, which primarily expose (1 1 1) facets; other morphologies enhance the production of the *trans* olefins instead. Reproduced from Ref. [115,134] with permission, Copyright 2011 the Owner Societies.

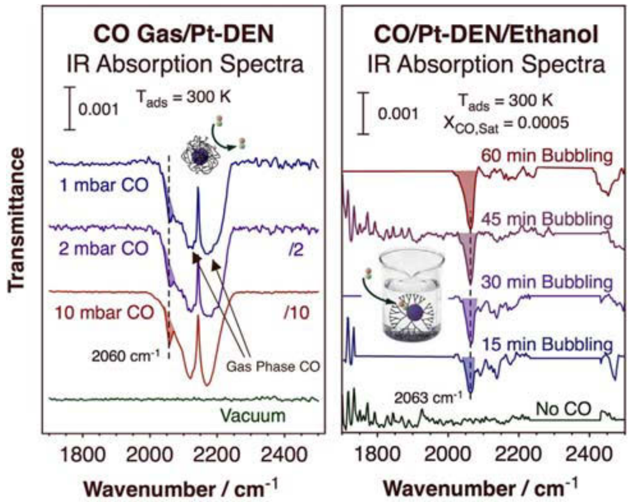


Fig. 11. *In-situ* carbon monoxide infrared absorption titrations to test the accessibility of Pt-DENs to chemical reactants in gas (left) and liquid (right) phases [155,169]. Virtually no CO uptake (shaded peak at 2060 cm^{-1}) can be seen in the gas phase because of the collapsed configuration of the dendrimer, whereas in solution significant CO adsorption is easily detected (shaded peaks at 2063 cm^{-1}). Reproduced from Ref. [169] with permission, Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

required to remove all of this organic matter from the surface of the catalysts are quite aggressive: for instance, calcination of the surfactants used to make colloidal Pt NPs once dispersed on an oxide support such as silica may require temperatures as high as 675 K (Fig. 12c) [140,141]. This brings about the issue of NP stability, since shape in particular is difficult to preserve due to the propensity of surfaces to reconstruct or NPs to sinter upon exposure to thermal treatments or chemical environments [175–178]. Because of this, shape selectivity is probably the most promising for mild reactions, those that take place at relatively low pressures and temperatures and in non-aggressive environments (possibly gas rather than liquid phases). Nevertheless, the use of supported NPs with specific shapes could address selectivity problems in catalysis such as the preferential production of *cis* olefins shown above that are difficult to solve by other means.

6. Post-synthesis modification of solid surfaces

Adsorption sites on solid surfaces can be modified or blocked after catalysts have been synthesized via further chemical processing. A common example in this category is that of silylation, by which solid oxides are treated with capping organic agents (silyl groups, typically $-Si(CH_3)_3$ or another $-SiR_3$ moiety) to deactivate surface hydroxyl groups, silanols in the case of silica [31,180,181]. The chemistry involved in surface silylation is akin to, but perhaps simpler than, that mentioned before in connection with the tethering of molecular functionalities to oxide surfaces, and is also quite common in organic synthesis, where silyls are often used as protective groups [182,183]. Some of the common silylation agents used in this chemistry include silyl halides such as trimethylchlorosilane (TMCS) and octadecyltrichlorosilane (ODTS), silyl amines such as hexamethyldisilazane (HMDS), and trimethylsilyl ether (TMS) [184].

Silylation is useful in catalysis because hydroxyl surface sites tend to be somewhat active as Brønsted acids; silyl groups can be used to block that functionality when it is not desirable [185–187]. Even Lewis acid sites may be blocked by silylation [188]. Silylation also makes hydrophilic surfaces hydrophobic by changing the surface termination from hydroxyl groups to aliphatic hydrocarbon moieties such as methyl groups [189–192]. One example from our group involving the use of silylation has to do with the catalytic use of cinchona alkaloids tethered to silica surfaces already illustrated in Fig. 2 [37]. It was found that heterogenized cinchonidine is not as enantioselective as the free molecule in the promotion of the addition of aromatic thiols to conjugated cyclohexanones because of interference from surface silanol groups, which can behave as nonselective catalytic sites and also bind and inactivate the tethered cinchonidine molecules. A combination of surface silylation and the use of non-protic solvents during reaction were found to solve this problem (Fig. 13) [37].

A more recent and versatile procedure for post-synthesis modification of catalysts is via the deposition of additional material by chemical means, using so-called chemical vapor deposition (CVD) methods. Ample technological skills have been developed for the chemical growth of well-defined thin films on solids in other applications, and have more recently been implemented for use in catalyst preparation as well [193–195]. A particular modality offering perhaps the best control in terms of film thickness and conformality is atomic layer deposition (ALD), a procedure where the reactants are introduced separately, in sequence, to attain self limited growth because of monolayer saturation during each of the corresponding half-reactions [196–199]. In some applications, ALD is used to deposit a metal on a high-surface-area support, but because metals typically display low surface tension, they tend to sinter and form 3D NPs rather than thin films on the surface. It is still useful to use ALD in those cases to tune the rate of metal deposition, and even to grow core–shell-structured bimetallic NPs [200–202], but control on their catalyst surface morphology is lim-

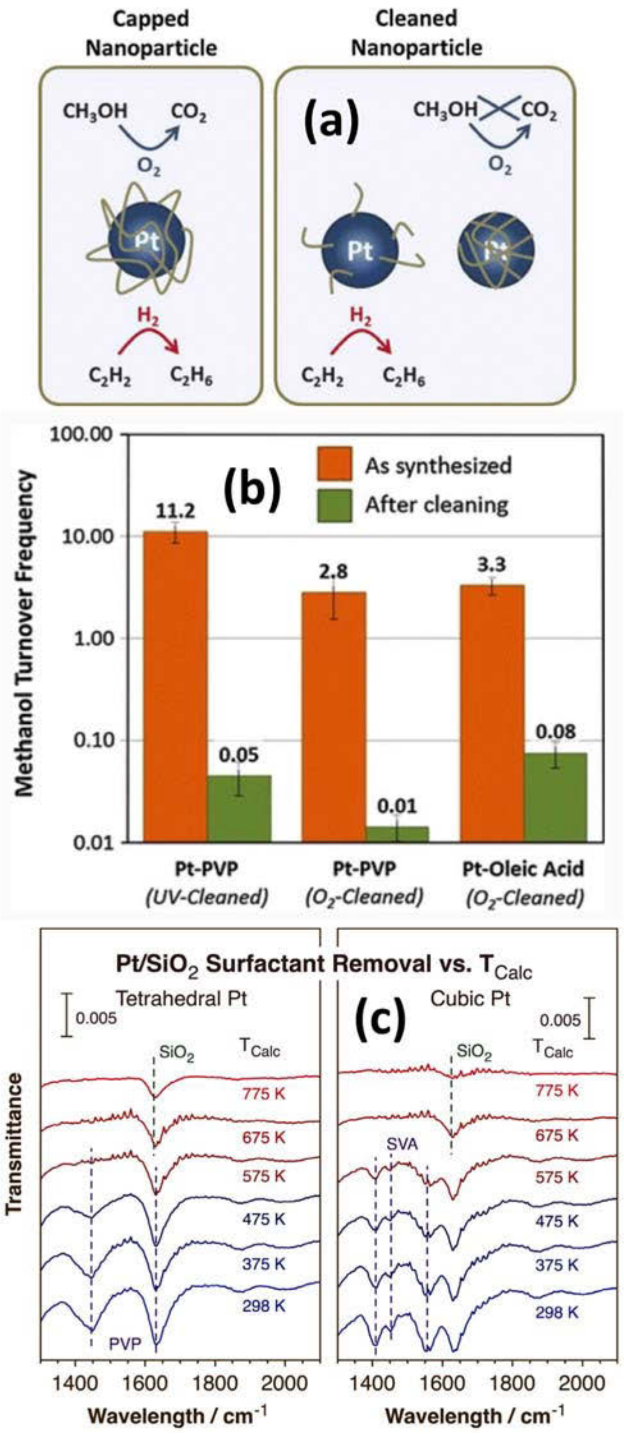


Fig. 12. (a) Schematic representation of the effect of capping Pt NPs with organic matter on their catalytic activity for the promotion of methanol oxidation versus ethylene hydrogenation [179]. (b) Methanol oxidation turnover frequencies before and after cap removal, relative to that of ethylene hydrogenation on the same catalyst. Data are shown for three types of cleaning procedures, i.e., UV treatment of Pt–PVP, thermal treatment of Pt–PVP, and thermal treatment of Pt–oleic acid [179]. The Pt activity for methanol oxidation is shown to decrease by a factor of between 50 and 250 following the removal of the organic matter. Reproduced from Ref. [179] with permission, Copyright 2012 Springer Science + Business Media, LLC. (c) Infrared absorption spectra of catalysts made with colloidal Pt NPs dispersed on a silica support as a function of the calcination temperature used for their cleaning [140,141]. Data are shown for two NPs shapes, tetrahedral (left), and cubic (right). The removal of the surfactants used, PVP and sodium polyacrylate (SPA), respectively, required calcination temperatures of approximately 675 K or higher; only under those conditions the peaks due to the organic matter completely disappear.

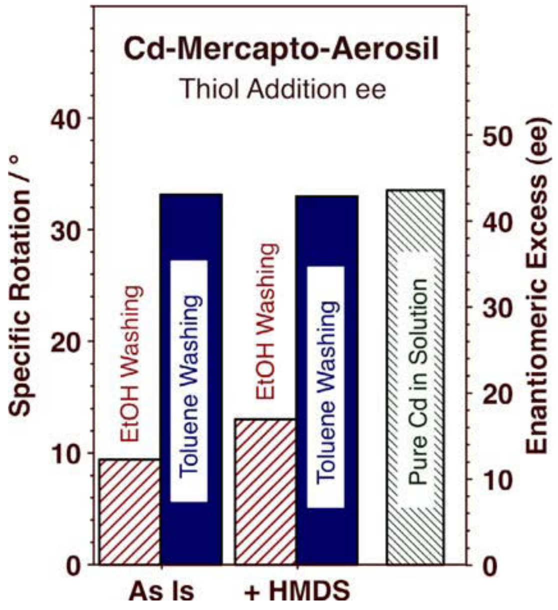


Fig. 13. Catalytic performance of cinchonidine (Cd) tethered to silica surfaces (using a mercapto linker attached at the vinyl group of Cd) in terms of enantioselectivity for the addition of p-tertbutylbenzenethiol to 2-cyclohexene-1-one [37]. Silylation of the catalyst with HMDS, in conjunction with the use of toluene as a washing agent, leads to improvements in reaction selectivity. Reproduced from Ref. [37] with permission, Copyright 2012 American Chemical Society.

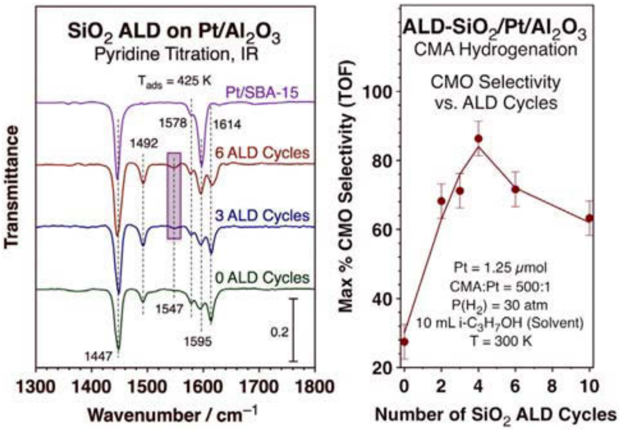


Fig. 14. Example of catalysts with mixed-oxide sites made by ALD, in this case by depositing silica on Pt/Al_2O_3 [220]. Left: Data from pyridine-infrared absorption spectroscopy titrations of acid sites indicating the formation of new strong Brønsted (1547 cm^{-1}, highlighted) and Lewis (1620 cm^{-1}) sites on the surface. Right: Maximum selectivity for the production of cinnamyl alcohol (CMO, in terms of turnover frequencies –TOFs) from cinnamaldehyde (CMA) hydrogenation as a function of the number of SiO_2 ALD cycles used. Optimum performance was seen after 4 SiO_2 ALD cycles, which was estimated to correspond to a SiO_2 coverage of approximately half a monolayer. Adapted from Ref. [220] with permission, Copyright 2018 American Chemical Society.

ited [203–206]. Alternatively, ALD can be used to stabilize those metal NPs against sintering [207–209], or to tailor the chemical nature of interfaces in catalysts where the active phase is dispersed on the surface of a second material [210,211]. However, the most promising application of ALD in catalysis is, in our opinion, for the growth of well-defined films of materials such as metal chalcogenides [212] or metal oxides [213]. In fact, because ALD can be designed to deposit submonolayer quantities of a material, it affords the creation of new mixed-oxide surface sites [214–218]. This is an idea that we have explored in detail in our laboratory [219–222]. In one example, mixed –Al–O–Si– sites with Brønsted-acid properties were created by adding submonolayer coverages of silica to Pt/Al_2O_3 catalysts, as identified by infrared-absorption spectroscopy titration experiments using pyridine as the probe molecule (Fig. 14, left panel). These new sites proved to help increase selectivity during the hydrogenation of unsaturated aldehydes (cinnamaldehyde, CMA) to the desired unsaturated alcohol products (cinnamyl alcohol, CMO), as shown in the right panel of Fig. 14. A similar trend was observed when alumina films were grown via ALD on Pt/SiO_2 catalysts [221]. The optimum selectivity performance (albeit at the expense of a loss in total activity) was in both cases seen at coverages of approximately half a monolayer of the new oxide film [221]. Unique mixed-oxide redox sites can also be added to metal oxide supports such as silica via the ALD of reducible oxides such as titania [222]. Exploration of the use of ALD in catalysis has just only started.

7. Use of complex nanostructures in catalysis

So far we have discussed different approaches on how to create unique surface sites in heterogeneous catalysts with well-defined molecular characteristics. The emphasis has been on designing and producing ensembles of atoms on surfaces to create sites with the structural and electronic properties required to selectively promote specific reactions. In addition, it is also possible to design catalysts using nanomaterials with structures defined at a larger scale, on the order of nanometers. The scale of the features in these nanostructures may preclude them from directly contributing to the definition of the catalytic sites, but may still help create unique environments around them to aid with, for instance, minimizing metal sintering or controlling the mass transport of reactants and products [20]. Solids with well-defined structures such as zeolites [223–225], ordered mesoporous materials [226–228], and metal–organic frameworks (MOFs) [226,229–233] can indeed be used either as supports or as catalytic phases [234]. More complex architectures include Janus nanostructures such as dumbbells [235], useful in biphasic catalysis (Fig. 15a) [236,237] and to create self-propelling NPs (Fig. 15b) [238,239] or solid interfaces with unique synergies [240] or electronic properties [241], especially for use in photo-(Fig. 15c) [242,243] or electro-catalysis [244,245].

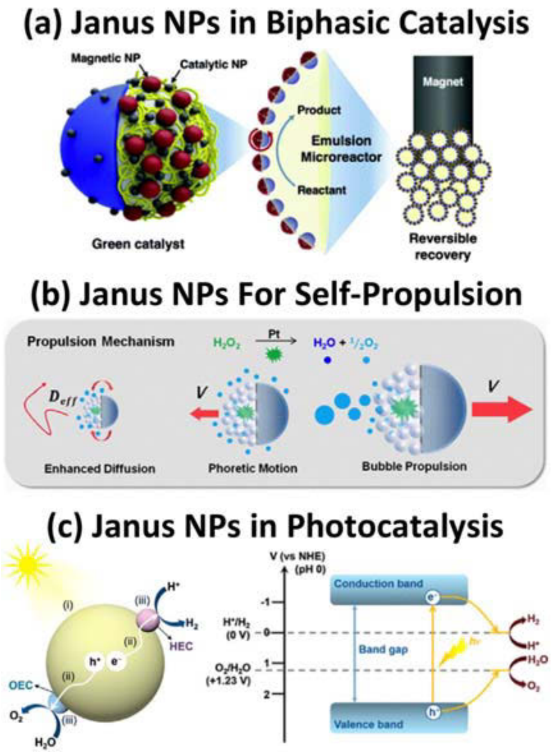


Fig. 15. (a) Example of the use of a Janus nanostructure in biphasic catalysis: Pd clusters dispersed in the hydrophobic poly(tetradecyl acrylate) (left) side of NPs promote the oxidation of organic reactants in organic solvents while the Fe_2O_3 magnetic clusters dispersed on the hydrophilic poly(styrene-co-vinyl alcohol) (right) side afford easy separation for catalyst recycling [237]. Reproduced from Ref. [237] with permission, Copyright 2018 The Royal Society of Chemistry. (b) Schematic representation of the different types of propulsion mechanisms based on catalytic reactions, on the catalytic decomposition of hydrogen peroxide in particular, that apply to Pt-based Janus NPs [246]. Reproduced from Ref. [246] with permission, Copyright 2016 American Chemical Society. (c) Janus scheme comprised of semiconductor NP photoabsorbers decorated with appropriate components for charge trapping and redox reaction promotion, to be used in photocatalytic processes such as water splitting into H_2 and O_2 [246]. The corresponding energy diagram is shown on the right. Reproduced from Ref. [246] with permission, Copyright 2016 American Chemical Society.

Another set of popular nanostructures in catalysis is based on core–shell and yolk–shell architectures, which can be used as nanoreactors to design multi-step processes. Bimetallic core–shell structures, for instance, can be used to tune the electronic properties of the external metal by the one located at the core of the NPs [247]. This type of nanostructures are expected to exhibit catalytic performance different to that seen with alloys [248], although it is important to keep in mind that the initial core–shell composition profile may not be preserved once the catalyst is exposed to the reaction conditions because metals have the tendency to diffuse in and out of the bulk depending on temperature and chemical environment [249,250]. Yolk–shell nanostructures, comprised of metal NPs encapsulated inside the void space of shells made out of metal oxides, have also become popular [20]. For instance, we in our laboratory have developed Au@void@TiO_2 and Pt@void@TiO_2 nanostructured catalyst [251] for both the promotion of oxidation reactions at cryogenic temperatures [252–255] and to investigate the mechanism of H_2 photoproduction from water [254,256]. Fig. 16 shows some results from the latter study, where the ability to control the structural parameters, shell diameter and shell thickness in particular, afforded the identification of a H· radical diffusion step between the reduction of protons on titania and the recombination of the resulting atoms on the surface of the metal to produce molecular hydrogen [257]. This observation was used to support a mechanism previously proposed by us where the role of the metal is to catalytically promote H–H bond activation rather than electron trapping after photon excitation, as commonly believed [258]. Additional studies were carried out to evaluate the accessibility of the metal phase in these nanostructures [259,260].

Much synthetic work has been dedicated in recent years to the preparation of increasingly more complex nanostructures, beyond simple dumbbells and core–shell arrangements. Many of these have been tested in connection with catalysis, but often as an afterthought; the focus has often been on the synthetic challenges associated with making more and more beautiful and interesting shapes. There is no doubt that honing on the synthetic skills to make complex nanostructures will ultimately be useful for catalysis, but more targeted research directed by specific catalysis hypotheses may help advance the field faster. It is important to clearly state the goals in terms of improvements in catalysis before embarking on a particular nanostructure synthetic quest and to set concrete benchmarks to be surpassed to really make progress from a catalysis point of view.

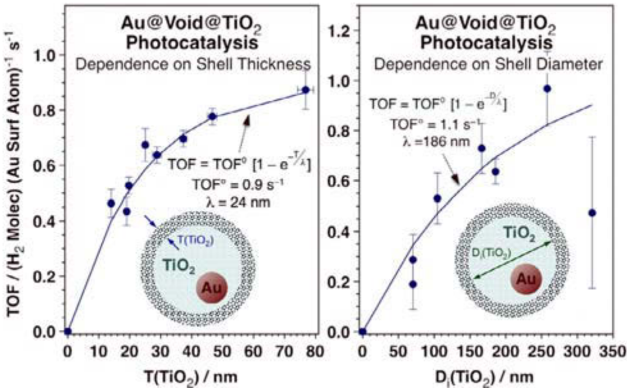


Fig. 16. Use of Au@void@TiO$_2$ yolk–shell nanostructures to test the mechanism of hydrogen photocatalytic production from water [254,257]. Turnover frequencies (TOFs) are plotted as a function of the thickness T(TiO$_2$) (left panel) and the diameter D$_i$(TiO$_2$) (right) of the titania shells to highlight the different characteristic distances associated with the two parameters. The large value in the second case argues in favor of a process limited by atomic hydrogen diffusion from the titania surface to the gold NP. Reproduced from Ref. [254] with permission, Copyright 2017, Springer Science Business Media, LLC.

8. Concluding remarks

The field of catalysis has been developing for more than a century, and has long constituted an essential part of the chemical industry. Catalytic processes greatly influence our way of life, and contribute enormously to the world economy: by some estimates, catalysis contributes to more than a third of the world's gross domestic product (GDP) [261–263]. Much of this activity is concentrated in a few large industries working with bulk chemicals, including the refining of crude oil and the synthesis of key commodity chemicals such as ammonia, sulfuric acid, methanol, propylene, ethylene oxide and acetic acid [2]. Although improvements continue to be made in those catalytic processes, they are in general well established and are not particularly demanding in terms of selectivity. With perhaps very few exceptions, all of those systems use heterogeneous catalysts. Additional new challenges continue to emerge in bulk-chemical catalysis, to process new biofuels or address environmental remediation, for instance, but, again, those involve relatively simple reactions that can be promoted with solid catalysts.

On the other end of the spectrum, the manufacturing of pharmaceuticals, agrochemicals, and other fine chemicals involve complex reaction networks and require exquisite selectivity. The volumes of these chemicals produced are orders of magnitude smaller than those of the bulk chemicals mentioned above, but their added value is much greater. Because of the intricacies of the chemistry involved, resolution at a molecular level is required, and this is most often achievable only with homogeneous (or enzymatic) catalysts. As mention in the introduction, though, homogeneous catalysis brings with it a number of inconveniencies and expenses, including the need of additional separation and purification steps. For instance, many pharmaceuticals are made using highly toxic metalorganic catalysts that need to be completely eliminated from the final products, a requirement that adds considerably to the cost of the synthetic process. Many of these issues could ideally be avoided by using heterogeneous catalysts instead.

The arguments outlined above provide the impetus for designing highly selective heterogeneous catalyst to rival their homogeneous counterparts. Making solid catalysts with selectivities comparable to those attainable in solution continue to be an unmet challenge, but newer synthetic procedures and nanotechnologies have infused new life into this challenge. In this Perspective we have briefly introduced some of the approaches available and tested to address this issue. They range from the use of homogeneous catalyst in heterogenized form, via their tethering or otherwise immobilization, to the creation or modification of surface sites on solids with a high level of molecular detail and to the use of novel nanostructures to direct mass transport and the sequence of multi-step reactions. Our discussion centers on our own approach and is not meant to be exhaustive, but hopefully illustrates the many new tools and ideas that have become available in recent years to tackle the goal of designing and making highly selective heterogeneous catalysts. This research is in its infancy, and much more is likely to come in the near future.

As research groups join this effort, it is perhaps useful to provide a couple of cautionary comments. First, the approaches discussed above, as well as many others, are quite promising, but also exhibit their own limitations. For instance, homogeneous catalysts tethered or immobilized on solid surfaces may not be very stable and are difficult to recycle, which means that they may only be good for a limited number of turnovers; they may be the most useful for promoting mild reactions and for making valuable chemicals. At the other end, intrinsic surface sites and solid nanostructures may be much more stable, but more difficult to make with the well-defined and complex ensembles of atoms required to create sophisticated catalytic sites. These can nevertheless be used to combine tandem reactions, solve problems of solubility or separability, and provide unique interfacial properties (for photo- and electro-catalysis, for instance). It is important to keep these issues in mind when embarking on the design of new catalysts to choose the right approach.

Finally, as already indicated above, it is important to define a chemical target for the catalysis of interest before starting the appropriate research effort. These days, synthetic chemists are capable of making solid materials with unique and amazing structures or physicochemical properties, and are often ahead of the catalytic community. It is highly desirable to have access to such materials, but their incorporation into catalytic processes can only be successful if they address specific issues associated with the catalytic reactions of interest. This is to say that it is important to identify a catalytic problem, develop a hypothesis on how it can be solved, and then search for the materials that may work for this, rather than to proceed in reverse and make catalytic materials first and then try to identify their potential uses. Also, when evaluating catalytic performance, it is important to have meaningful benchmarks to compare against, the activities and selectivities obtained with the best performing conventional catalysts, to be able to assess true progress in catalytic performance. Only by making catalytic performance and not catalysis synthesis the center of attention will real progress in catalyst development be made.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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