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PERSPECTIVE

New Challenges in Heterogeneous Catalysis for the 21st Century

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Abstract Heterogeneous catalysis has been around for a long time, but has still much room to grow. The empirical trial-and-error mode used to develop catalysts in early times has progressively made way for a more molecularly driven approach to their design. Modern surface-sensitive techniques have opened the way to a better understanding of the mechanisms of catalytic reactions and the demands imposed on catalytic sites. Computational studies have added insights into the structural and energetic details of surface species and the kinetic driving forces for specific surface reactions. Novel nanotechnology and synthetic advances have provided new methods to manufacture better-defined catalysts, with high concentrations of the active sites identified by fundamental mechanistic studies. All combined, these advances have led to the design of new catalysts by taking advantage of the size and shape of the nanoparticles used as active phases and of specific structures and the nature of the support. New research has also been directed to the development of more sophisticated nanostructures, to add new functionalities to simpler catalysts or to combine two or more primary functions into one single catalyst. Much progress has been made in these directions, but the new tools are yet to be fully exploited to resolve present limitations in a myriad of catalytic systems of industrial importance, for energy production and consumption, environmental remediation, and the synthesis of both commodity and fine chemicals.

Keywords Heterogeneous catalysis · Surface chemistry · Nanotechnology

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1 Introduction

The field of heterogeneous catalysis has a long and illustrious history. Soon after the introduction of the term by Berzelius in 1835 and the more scientific definition provided by Ostwald in 1895, many catalytic processes of great industrial importance were developed, including the oxidation of sulfur dioxide to sulfuric acid in 1875, which was initially catalyzed by platinum supported on asbestos, magnesium sulfate, or silica, the oxidation of methanol to formaldehyde in 1890, aided by silver gauze, the hydrogenation of olefins and edible oils and fats in the early 1900s, catalyzed by supported Pt or Ni particles, the Ostwald process to oxidize ammonia to nitric acid in 1906, using Pt–Rh alloys, and the Haber process to produce ammonia from N_2 and H_2 in 1913, promoted by iron-based materials [1]. This long list of commercial catalytic processes has continue to grow since, and include such well-known examples as the Fischer–Tropsch synthesis of fuels, the oxidation of ethylene to ethylene oxide to make anti-freeze liquids, the steam and catalytic reforming used for hydrogen and fuel production, the synthesis of vinyl acetate for polymer manufacturing, and the three-way catalytic converter for gas emission treatment in automobiles, to mention a few [2]. At present, catalysis is central to close to 80 % of all chemical industrial processes, and by some measures contributes to approximately 35 % of the world's GDP [3].

Historically, the development of catalytic processes has been accomplished primarily by empirical trial and error. This is not to say that there have not been fundamental studies directed at the basic understanding of the chemistry of catalysis. Early landmark contributions in this respect were provided by the works of Bodenstein, Ostwald, Sabatier, Langmuir, Rideal, Hinshelwood, Taylor, Eley, Horiuti, Polanyi, Ipatieff, Bond, Wells, and others [4, 5]. Those pioneers developed the basic kinetic and thermodynamic concepts associated with the adsorption, desorption, and surface reactions that explain heterogeneous catalysis, and added to our understanding of surface processes in terms of specific reactions such as the dissociative adsorption of H_2, O_2, and N_2, key reactants in many industrial synthesis, that occurs at specific sites conformed by unique ensembles of atoms at the surface of the catalyst. Nevertheless, the introduction of new catalytic processes by and large has preceded the corresponding molecular-level explanation of how they function.

The early picture of catalysis began to evolve and change in significant and fundamental ways toward the second half of the 20th century, an evolution that continues to this date. Better experimental and theoretical tools are being developed for the characterization of solid catalysts and for the study of reactions on solid surfaces [6–8], and new synthetic methodology is being incorporated to the preparation of better-defined and more complex solid catalysts [9–11]. In parallel, the paradigm of catalysis is shifting from a focus on increasing the rate of conversion of feedstocks to products in relatively simple reactions to an emphasis on improving the selectivity of catalysts to preferentially promote desirable reactions from complex manifolds of available pathways in more sophisticated synthetic processes [12, 13]. The demands of new industrial processes are ever increasing; witness, for instance, the desire to selectively synthesize enantiopure chiral compounds for pharmaceutical and agricultural applications and for uses in the food industry [14, 15]. It has also been realized that selectivity not only reduces the consumption of reactants and facilitates the isolation of the targeted products, but also helps make industrial processes greener, that is, more environmentally friendly. The catch is that this new emphasis on selectivity adds significantly to the requirements imposed on the catalyst [16]. A more extensive knowledge is require of the molecular details of catalysis, and better synthetic methods are also needed to prepare the catalyst that can satisfy the conditions identified by such basic studies. Increasingly, the old catalyst preparation protocols have proven inadequate for the needs of new catalytic processes.

Catalysis is now at a crossroad, where the old empirical procedures need to be substituted by a more molecularly driven designing approach. Once a desired catalytic process has been chosen, basic chemical criteria need to be identified to define the requirements for the catalyst. These criteria are to be derived from fundamental mechanistic studies of surface reactions, which are being aided by the increasingly large pool of surface-sensitive analytical techniques developed in the last few decades [6, 8, 17], and also by the significant progress made in recent years on computational methods based on quantum mechanics and kinetic modeling to predict and understand structures, energetics, and kinetics of adsorbed species and surface reactions [18]. Then, synthetic routes need to be devised to prepare those catalysts [9, 19]. They are likely to demand the presence of particular surface sites, capable of selectively promoting specific reactions, in large concentrations, and to require the minimization of other sites capable of promoting undesirable reactions. Accordingly, the resulting catalysts need to display well-defined structural characteristics in terms of the size and shape of the active phase, a task that may be accomplished by relying on novel materials-science synthesis based on sol–gel, colloidal, and other self-assembly methodology. We believe that it is this synergy between the fields of modern surface science, computational chemistry, and materials synthesis that will usher the field of heterogeneous catalysis into a new modality where catalysts will be designed at a molecular level to selectively promote specific reactions in complex systems.

2 Dependence of Catalytic Performance on Nanoparticle Size

Most heterogeneous catalysts are comprised of small nanometer-sized particles of an active phase, often a metal, finely dispersed on a cheaper high-surface-area support, commonly a porous oxide. The dispersion is used mainly to maximize the surface-to-volume ratio of the former. Traditionally, such catalysts have been prepared by impregnation of the solid with a salt of the metal followed by oxidation–reduction pretreatments. Unfortunately, that approach leads to the formation of nanoparticles with a wide range of sizes and shapes displaying a distribution of surface sites capable of promoting many different reactions. No molecular control on the nature of the active sites is exerted, which means that only limited control on the selectivity of reactions can be achieved.

Controlling the size of the nanoparticles used for catalysis can lead to profound changes in catalytic behavior. One very prominent example of this principle is that recently identified with gold: metallic gold is typically chemically inert, but when made into nanoparticles of only a few nanometers in diameter it can promote a great number of reactions under quite mild conditions [20, 21]. This means that it is critical to control particle size during the synthesis of those catalysts. In more general terms, it is important to develop an a prior understanding of the requirements in terms of particle size for a given catalytic process in order to aid in the design of the catalyst. Some surface-science work has recently focused on addressing this issue. In the case of gold cited above, for instance, a clear correlation has been reported between the size of gold particles dispersed on a titania support and both the magnitude of the electronic band gap of the metal and its catalytic activity for CO oxidation [22]. It was concluded that the observed trends are related to a quantum-size effect with respect to the thickness of the islands that gold forms on the support.

Another example of surface-science studies of reactivity dependence on nanoparticle size is that reported for CO and O_2 adsorption on Pd/Fe_3O_4 model catalysts [23]. An atypically weak CO adsorption state was identified on very small Pd particles, on the order of a couple of nanometers in diameter (Fig. 1), attributable to a strong interaction with the support; those particles also displayed facile oxidation and reduction. A similar increase in the ability to form oxides with decreasing nanoparticle size was reported for a model $Pt/SiO_2/Si(100)$ system [24]. It has become clear that metal nanoparticles of dimensions of around a few nanometers are particularly active and can display much different chemistry than that observed with bulk samples of the same element. Much of the surface-science work in this area to date has focused on simple oxidation reactions, but the potential is there to extend the research to other more complex catalytic systems [25, 26]. It would be particularly interesting to direct this type of fundamental studies with surface-science tools and model catalyst samples to the investigation of changes in selectivity with particle size.

The nanoparticle size effects in catalysis identified by the fundamental studies described above are being translated into the preparation of high-surface-area catalysts with well-defined dispersed nanoparticles. Fortunately, metal nanoparticles can now be made with quite narrow size distributions by using colloidal [27, 28] or dendrimer-based [29, 30] chemistry. In fact, nanoparticles made using those approaches have already been tested for catalysis in solution and in electrochemical systems [31]. The challenge, if heterogeneous catalysts are to be made this way, is to disperse the colloidal nanoparticles on high-surface area supports and to activate them without loosing the original size (and shape) distribution. A nice example on how this can be made to work and how nanoparticle size can be used to control catalytic selectivity is provided by the work of Somorjai et al. [32]. Figure 2, for instance, shows how the selectivity for the hydrogenation and hydrogenolysis of pyrrole on platinum catalysts shifts from close to 100 % conversion to *n*-butylamine with large nanoparticles to the production of significant quantities of pyrrolidine if nanoparticles on the order of ~1 nm in diameter are used instead.

Catalyst activation in the last example was accomplished by reduction in a hydrogen atmosphere [33]. Other treatments involve a mixture of reduction and/or oxidation steps, the latter typically using air, oxygen, or ozone [34, 35]. These are required because the synthesis of well-defined nanoparticles using colloids, dendrimers, or other self-assembly methods involves the use of organic agents, and those need to be removed if the surface of the metal is to be exposed and made available for catalysis. A balance needs to be struck in order to be able to clean the surface while still preserving the desired size and shape of the nanoparticles [36]. Although this issue has not been fully

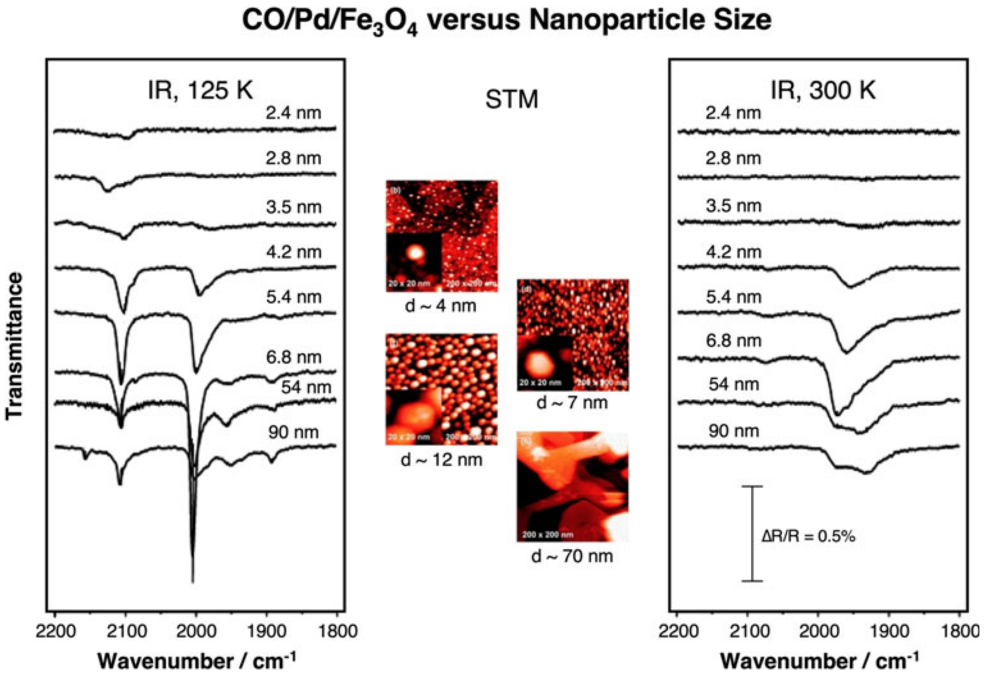

Fig. 1 Evidence for the effect of size on chemisorption for the case of a model system comprised of palladium nanoparticles dispersed on a Fe_3O_4 thin film [23]. *Left and right* infrared (IR) absorption spectra in the C–O stretching region for saturation coverages of carbon monoxide on several samples with different nanoparticle average size at 125 K (*left*) and 300 K (*right*). A unique weak adsorption state on particles with diameter below ~3 nm is indicated by the peak at 2,130 cm^{-1} evident at 125 K but not at 300 K. *Center* scanning tunneling microscopy (STM) images of representative samples. Figure courtesy of Joerg Libuda and Hajo Freund, adapted from Ref. [23] with permission. Copyright 2007 the PCCP Owner Societies

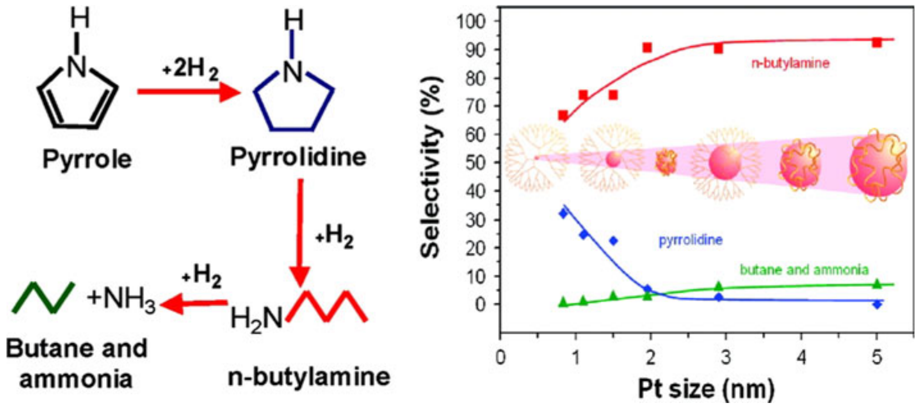

Fig. 2 Pyrrole hydrogenation selectivity at 413 K (4 torr pyrrole, 400 torr H_2, 2 % conversion) as a function of the size of the Pt nanoparticles, dispersed on a HY zeolite, used as catalysts [32]. Hydrogenation to pyrrolidine is facile in all cases, but further hydrogenolysis to *n*-butylamine can only be partially avoided if small nanoparticles, of diameters on the order of ~1 nm, are used. Figure courtesy of Jeong Park and Gabor Somorjai, reproduced from Ref. [32] with permission. Copyright 2009 American Chemical Society

settled, it appears that mild reduction treatments may be preferred in many instances, even if those leave some of the organic matter behind [30]. In fact, it is possible that the remaining carbonaceous deposits may actually help with the performance of the catalyst, at least in the promotion of mild reactions such as olefin hydrogenations [37]. Access to the metal inside dendritic or colloidal structures may also be possible in liquid solutions [38], in which case the catalyst may not even require special activating treatments. The issue of the activation of heterogeneous catalysts prepared by these new self-assembly methodologies requires further studies.

When considering nanoparticle size in heterogeneous catalysts, one extreme is catalysis by one single atom, or perhaps by a small number of atoms in a well-defined molecular cluster. The behavior of the catalyst in such cases may resemble more closely that of homogeneous catalysts, where selectivity can sometimes be controlled at a molecular level. In fact, the heterogeneous catalysts can be prepared by starting with the corresponding discrete molecular clusters [39]. However, the interaction of the atoms of the catalytic phase with the support is rarely negligible, and needs to be considered. The final structure of the surface species may also dynamically change as the pretreatment or reaction conditions are changed, and the final active phase may exhibit very different characteristics to those of the original organometallic precursors. An interesting example of a change in the structure of the catalyst leading to changes in reaction selectivity has been recently reported for the conversion of ethylene on supported rhodium catalysts [40]. In that case, the initial $Rh(C_2H_4)_2$ complexes bonded to a crystalline zeolite HY support could be made to remain isolated and to display high selectivity for the dimerization of ethylene to butenes and butane under most conditions, except upon exposure to highly reducing environments, after which they were seen to form small metal clusters and to preferentially promote hydrogenation to ethane instead. Curiously, this transformation was shown to be reversible: the isolated-Rh dimerization sites could be regenerated upon exposure of the catalyst to ethylene-rich mixtures. In general, the use of small molecular clusters as precursors for the preparation of heterogeneous catalyst could be quite useful if issues of stability and selectivity can be worked out.

3 Nanoparticle Shape

Perhaps more interesting than controlling the performance of catalysts by controlling the size of the nanoparticles of the active phase is the idea of exerting that control via the selection of their shape. It has been long known that some catalytic processes are structure sensitive, which in traditional catalysis has come to mean that their performance in terms of activity or selectivity changes significantly with the method used for their preparation. However, this behavior has been justified on the basis of the associated changes in the distribution of particle size in the resulting catalysts [41]. It has only been recently, with the incorporation of methods to better control particle size and shape independently of each other, that the effects of those two parameters have started to be untangled.

In surface science studies using model system, structure sensitivity has traditionally been probed by comparing chemical reactivity on single crystals exposing surfaces with different orientations [5, 8]. Initial studies on chemisorption were later extended to catalytic rate measurements using so-called "high pressure cells" [42–44]. Those studies have been quite useful, but also revealed some intrinsic limitations, in particular the fact that they cannot always reproduce the behavior of small nanoparticles or mimic the effect of the support. Newer surface-science work has focused on mimicking more realistic systems consisting of metal nanoparticles dispersed on oxide model surfaces [25, 45]. A particularly relevant example here is that of the group of Roldan Cuenya, the key results of which are summarized in Fig. 3 [46]. In that work, platinum nanoparticles with similar size distributions, around ~1 nm in diameter, but different shapes were dispersed on a γ-alumina support. The shape of those nanoparticles was characterized, and their catalytic activity in promoting the oxidation of 2-propanol evaluated. A correlation was identified between the number of under-coordinated atoms at the surfaces of the nanoparticle and the onset temperature for 2-propanol oxidation.

In terms of testing supported catalysts, another recent example highlighting the difference between size and shape effects in controlling hydrocarbon conversion reactions is the study by Somorjai and co-workers [47] on the use of Pt nanoparticles for the conversion of methylcyclopentane with hydrogen. A weak dependence of catalytic activity and selectivity on particle size was identified, with small nanoparticles promoting ring opening to 2-methylpentane over the whole temperature range studied but large nanoparticles producing primarily benzene at temperatures above 515 K. Independently, another correlation was highlighted with particle shape, with Pt(100) nanocubes producing the largest fraction of cracking products and Pt(110) nanooctahedra the largest fraction of the ring-opening product hexane (and the smallest fraction of 2-methylpentane); Pt spheres and truncated octahedra showed higher overall turnovers.

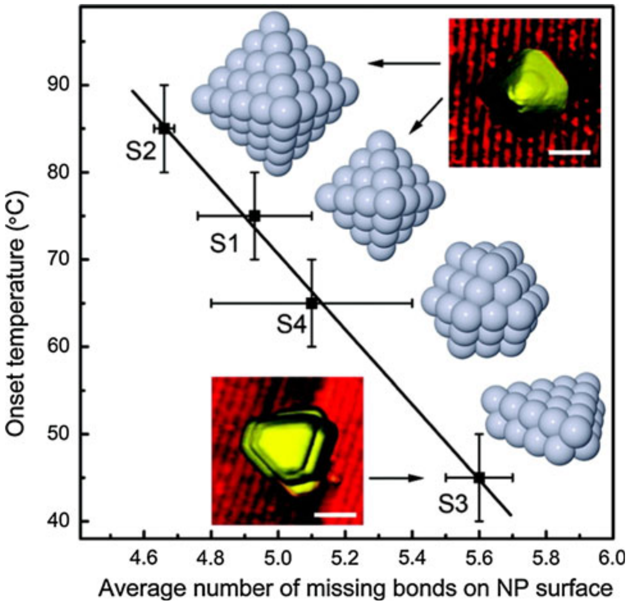

Fig. 3 Onset temperature for 2-propanol oxidation over Pt nanoparticles (NPs) dispersed on a γ-Al_2O_3 nanocrystalline support versus the average number of missing bonds at the NP surface, calculated by using the idealized model shapes shown in the insets [142]. Typical particle shapes are also shown in the reported STM images, obtained on a $TiO_2(110)$ surface (the *scale bars* represent 5 nm). A correlation was identified between the ease with which 2-propanol is oxidized (the extent to which the reaction onset temperature is lowered) and the increase in the number of coordinatively unsaturated sites on the Pt nanoparticles (an increase in the number of missing bonds). Figure courtesy of Beatriz Roldan Cuenya, reproduced from Ref. [142] with permission. Copyright 2007 Springer

We in our group have also addressed this issue of the effect of surface structure and nanoparticle shape on catalytic performance, in our case by focusing on the selectivity associated with the isomerization of olefins. Extensive surface-science [48–51] and theoretical [52] work led us to the conclusion that *cis* olefins are more stable than their *trans* counterpart when adsorbed on flat platinum surfaces, specifically on Pt(111) planes, even though the opposite is true in gas phase. Catalysts were then made using Pt nanoparticles with tetrahedral shapes [which only expose (111) facets] to take advantage of this unique trend [36], and their performance was evaluated and contrasted against that of similar catalysts containing more rounded nanoparticles of the same average size [53]. As predicted, it was found that *cis*-to-*trans* isomerization is favored on the tetrahedral particles, whereas *trans*-to-*cis* conversion, the behavior typically seen with commercial catalysts, dominates on other rougher particles (Fig. 4) [54]. The power of this work is that catalytic selectivity was first predicted based on results from basic surface-science studies with model systems and DFT calculations and then realized by taking advantage of new colloidal chemistry to make nanoparticles of specific shapes. This synergy between basic mechanistic studies with model systems and new synthetic nanotechnology offers great opportunities for the design of new, highly selective catalysts in the 21st century [19].

To reiterate, once potential effects in catalysis in terms of activity or selectivity versus surface structure are identified, preferably via basic studies using surface-science research and/or theoretical calculations, those surface structures may be realized by using the growing variety of synthetic routes available to make nanoparticles with specific shapes [27, 28, 55]. There are some intrinsic limitations to this approach, though: because such self-assembly methodology for particle growth rely on relative differences in rates for surfactant adsorption and reactivity versus surface facet, the resulting particles tend to expose the most thermodynamically stable surfaces, (111) and (100) facets for face-center-cubic (fcc) materials, for instance. If improved catalytic activity or selectivity is promoted by a less stable surface plane, it may not be easy to make such catalysts with the preparation procedures available in the

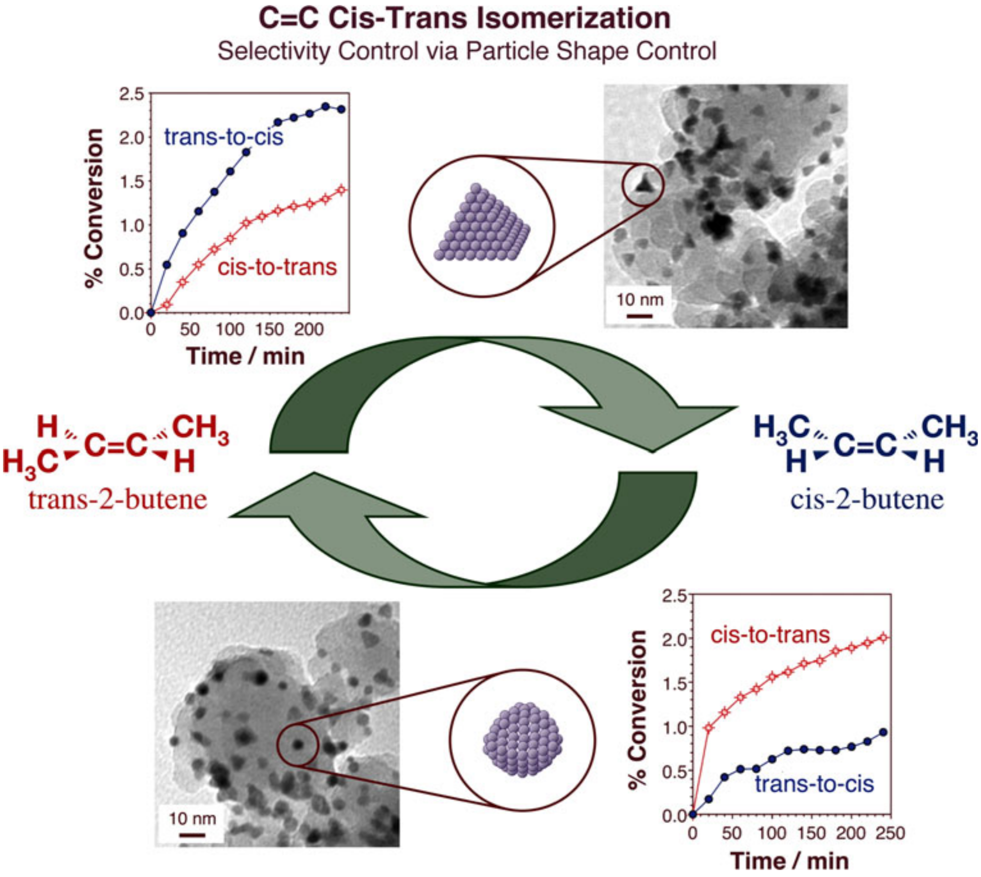

Fig. 4 Kinetic catalytic data and transmission electron microscopy (TEM) images to indicate the correlation that exists between the structure (*shape*) of platinum nanoparticles and their selectivity in alkene *cis–trans* isomerization conversions [16]. It can be seen that tetrahedral platinum particles, which only expose (111) facets, preferentially promote the formation of the *cis* isomer (*top*), whereas other more rounded structures display a reversed selectivity toward the *trans* isomer (*bottom*). Reproduced from Ref. [16] with permission. Copyright 2009 American Chemical Society

literature. It would be highly desirable to have ways to produce nanoparticles with preferential exposure of high Miller index planes.

It is also important to note that most of the reports on nanoparticle synthesis to date focus on metals. There are now some reports on the making of nanoparticles of oxides and other compounds with well-defined shapes [56–58], but much more research is still needed in this direction. An interesting non-metallic system where surface-science, theoretical, and catalytic work has been combined to obtain a molecular-level description of catalysis and to design a new practical catalyst is that based on MoS_2 platelets as the active phase for hydrodesulfurization (HDS) reactions. Initial studies with single-slab MoS_2 triangular model structures made on a Au(111) substrate indicated that edge sulfur atoms can be removed via reaction with hydrogen atoms to create sulfur vacancies (Fig. 5) [59]. Further scanning tunneling microscopy (STM), density functional theory (DFT), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) work tested the role of those vacancies in HDS. Interestingly, it was concluded that it may not be the vacancies but rather new special brim sites unique to these triangular 2 to 3 nm size MoS_2 structures that carry out the catalytic cycle [60–62]. The knowledge derived from these basic studies was later used to develop a new industrial-style MoS_2 nanocatalysts [63].

4 Structure and Modification of Supports

Typically, heterogeneous catalysts are viewed as containing an active phase dispersed on a high-surface-area support, as mentioned before. The support is often considered inert, but, in fact, it may be a factor in controlling activity and selectivity. One traditional way in which supports can affect catalytic performance is via control of the access of the reactants to the active phase or of the products to the outside environment. With the introduction of crystalline zeolites and, more recently, ordered mesoporous materials, it has been possible, in a few cases, to direct selectivity in catalytic reactions by engineering the shape of their pores [64–66]. More recently, the design of such pores has been advanced by the introduction of templating-directing agents during the synthesis of the solids [67, 68]. Quite elaborate structures can already be produced this way, including chiral pores [69, 70], but their use to control selectivity in catalysis is still unproven.

The size and structure of pores in such zeolite and mesoporous materials can also be changed by further

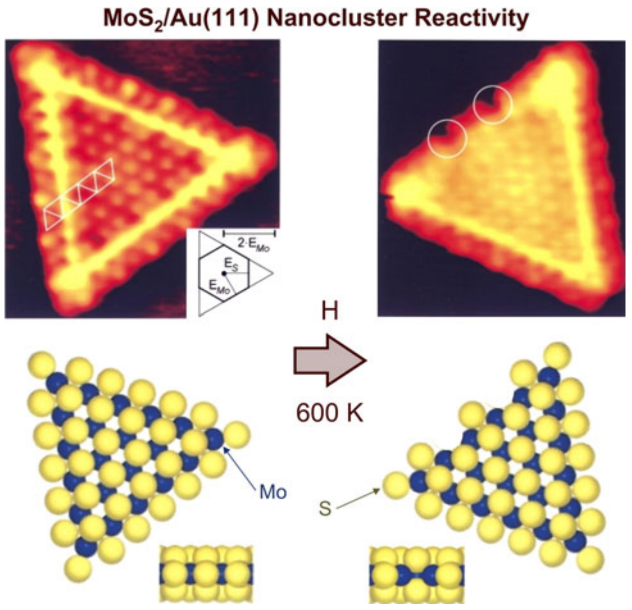

Fig. 5 Atom-resolved STM images of MoS_2 nanoclusters supported on a Au(111) surface before (*left*) and after (*right*) reaction with atomic hydrogen at 600 K [59]. The *grid* in the *left image* shows the registry of the edge atoms relative to those in the basal plane of the MoS_2 *triangle*, and the *circles* in the *right image* highlight the sulfur vacancies created at the edges by the reaction with hydrogen. *Bottom* schematic representation of the *top* and *side views* of the MoS_2 slabs. Subsequent experiments have indicated that the bright "brim" sites rather than the sulfur vacancies produced after hydrogen treatment are likely to be the sites for hydrodesulfurization catalysis. Figure courtesy of Jeppe V. Lauritsen and Flemming Besenbacher, reproduced from Ref. [59] with permission. Copyright 2000 American Physical Society

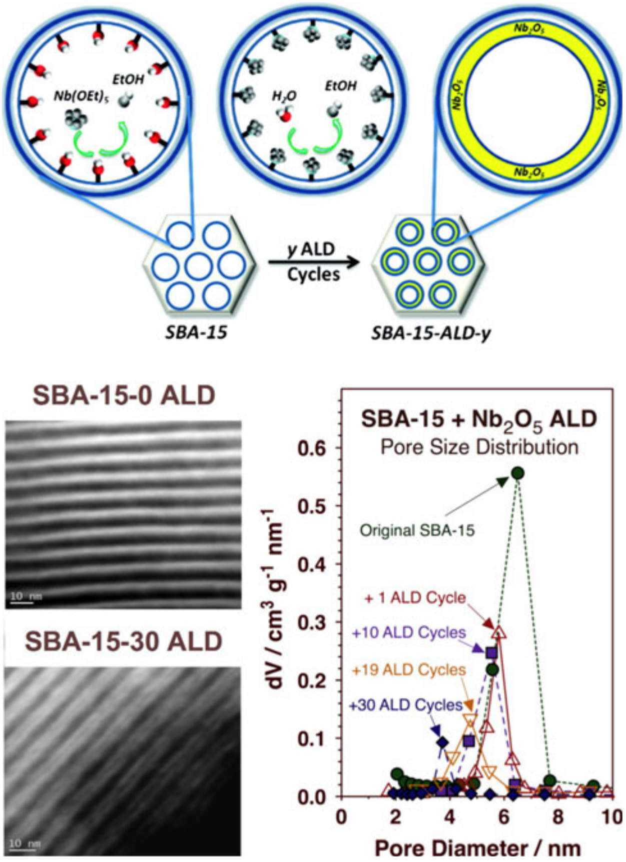

Fig. 6 Example of deposition of a thin film of an active phase on the surface of the pores of a high-surface-area support by atomic layer deposition (ALD). In this case, films of Nb_2O_5 of different thicknesses were grown in a controlled fashion by choosing the number of ALD cycles [75]. *Top* schematic representation of the two half-reactions used for each ALD cycle. *Bottom left* TEM images of the silica-based SBA-15 mesoporous material used in these experiments before (0 ALD cycles) and after (30 ALD cycles) niobium oxide deposition. *Bottom right* pore distributions measured for samples with different Nb_2O_5 thicknesses, showing a decrease in pore size with increasing number of ALD cycles. Figure courtesy of Christopher Marshall, Jeffrey Elam, and James Dumesic, reproduced from Ref. [75] with permission. Copyright 2011 American Chemical Society

modification using organic functionalization [71], or, alternatively, via the deposition of additional material on their surfaces. The latter may be accomplished by controlled growth of thin films conformally using a new approach know as atomic layer deposition (ALD), where the deposition chemistry is split in two self-limiting and complementary half-reactions in order to control the film growth at a monolayer level [72, 73]. This procedure can in fact be also used to deposit nanoparticles of the active catalytic phase [74], or to create a thin layer of a new active material covering the inside surface of the pores of the support [75]. Illustration of the latter application is provided in Fig. 6 for the case of the deposition of a thin layer of niobia inside the pores of a SBA-15 mesoporous material [75].

The deposition of thin films on catalysts can also be performed after dispersing the active metal nanoparticles on the high-surface-area support as a way to protect those nanoparticles and prevent them from sintering. This can be accomplished by using ALD, as recently shown for the case of a Au/TiO_2 catalyst (where the metal was covered by a thin silica layer [76]), or, alternatively, by using more conventional sol–gel chemistry. The latter approach was recently tested in our laboratory by dispersing platinum nanoparticles on silica beads and then covering them with a layer of mesoporous silica [37, 77, 78]. The challenge proved to be the removal of enough of the newly grown material to regain access to the platinum surfaces without loosing the structural advantages in terms of sintering provided by the encasing of the nanoparticles inside the new silica layer. A novel surface-protected etching procedure was developed for this purpose [77], and significant thermal stability of the Pt nanoparticles was obtained without sacrificing catalytic performance, which could be reinstated after proper etching (Fig. 7) [37]. The use of organic growth-directing agents may potentially add control of the directionality and/or shape of the pores of the newly deposited mesoporous material [79].

Much of the new nanomaterials synthetic methodology that has been developed over the last few years can be implemented to design complex nanoarchitectures for catalysis as well [28]. One pair of designs that has received particular attention is core@shell and yolk@shell nanostructures, where one or more nanoparticles of one material are encapsulated inside a shell of a second element, with or without a void space in between [77, 80–82]. The shells in these nanostructures add a number of functionalities to the catalyst, such as protection of the core from the outside environment, increased compositional and structural integrity, sintering prevention, selective percolation of molecules, increase in solubility for liquid-phase processes, and addition of new physical or chemical properties. In the case of the yolk@shell structures, they also create individualized nanoreactors around the core nanoparticles. The performance of this type of catalysts is illustrated in Fig. 8 with gold nanoparticles embedded inside hollow titania shells [83]. In that case it was demonstrated that, while the yolk@shell structure prevents the gold particles from sintering upon annealing to high temperatures, as it happens with regular Au/TiO_2 dispersed catalysts, it does not affect their catalytic activity toward carbon monoxide oxidation. We have also recently demonstrated that diffusion of gases in and out of the inside of the shells occurs freely even in liquid solutions [84].

Catalytic sites can in principle be encased in a solid environment after dispersion on the support, and cavities around them may be generated with specific shapes by using sacrificial organic templates. The potential for imprinting catalytic cavities this way has been recently demonstrated by using specific ligands on anchored organometallic complexes and polymers as the material for the cavity formation [85]. Figure 9 shows the schematics of the synthetic route used to prepare a Ru-based catalyst on a silica surface for the selective reduction of specific acetophenones [86]. Even chiral pockets may be produced this way, as was shown by using (R)-1-(2-fluorophenyl)ethanol as the templating agent to produce a catalyst to promote the asymmetric hydrogenation of acetophenones [87]. Only a handful of examples of this approach are available at present, though, and it is not clear yet how general it may turned out to be.

5 Multiple Catalytic Functionality

Because there are only a limited number of materials useful in heterogeneous catalysis, it is not always possible to promote a particular reaction by using one single solid. Consequently, most catalysts are comprised of several

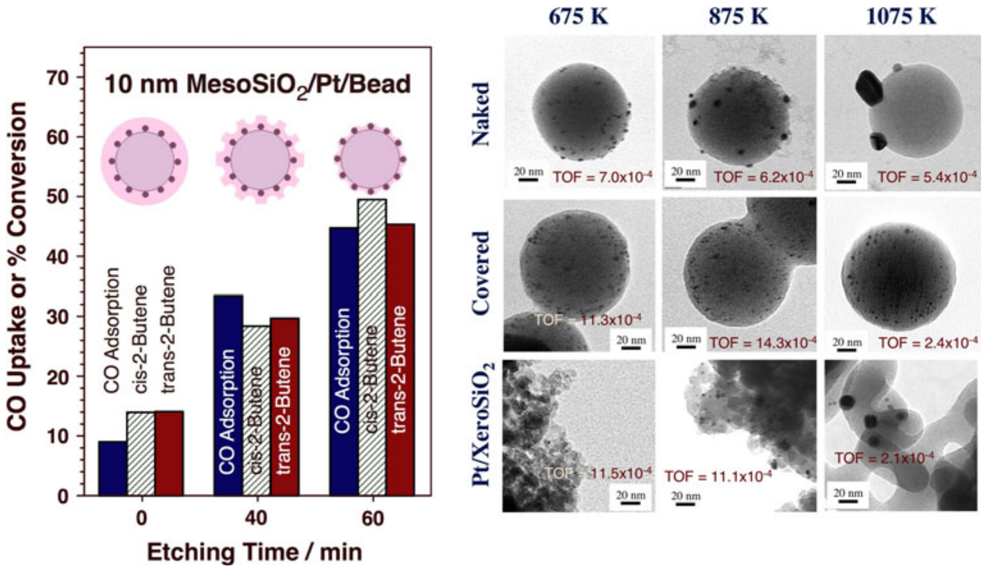

Fig. 7 Use of mesoporous silica films to increase catalyst stability [37]. *Left* summary of the performance of catalysts prepared by depositing 5-nm Pt nanoparticles on 100-nm silica beads, growing a 20-nm thick mesoporous silica layer using sol–gel chemistry, and etching that back using NaOH for the indicated times. Results are reported for the extent of carbon monoxide uptake at 200 K (*solid blue bars*) and for the catalytic activity toward the conversion of *cis*- and *trans*-2-butene at 375 K (*hatched-green* and *solid red bars*, respectively). *Right* test of the thermal stability of the silica-encased Pt catalysts. Shown are TEM images as a function of calcination temperature for three samples, ''naked'' (i.e., uncovered) nanoPt/SiO_2-beads (*top row*), mesoSiO_2/nanoPt/SiO_2-beads (*middle row*), and platinum nanoparticles dispersed on a homemade xerogel (*bottom row*). The silica-protected catalysts show increased stability without sacrificing activity. Reproduced from Ref. [37] with permission. Copyright 2011 the Owner Societies

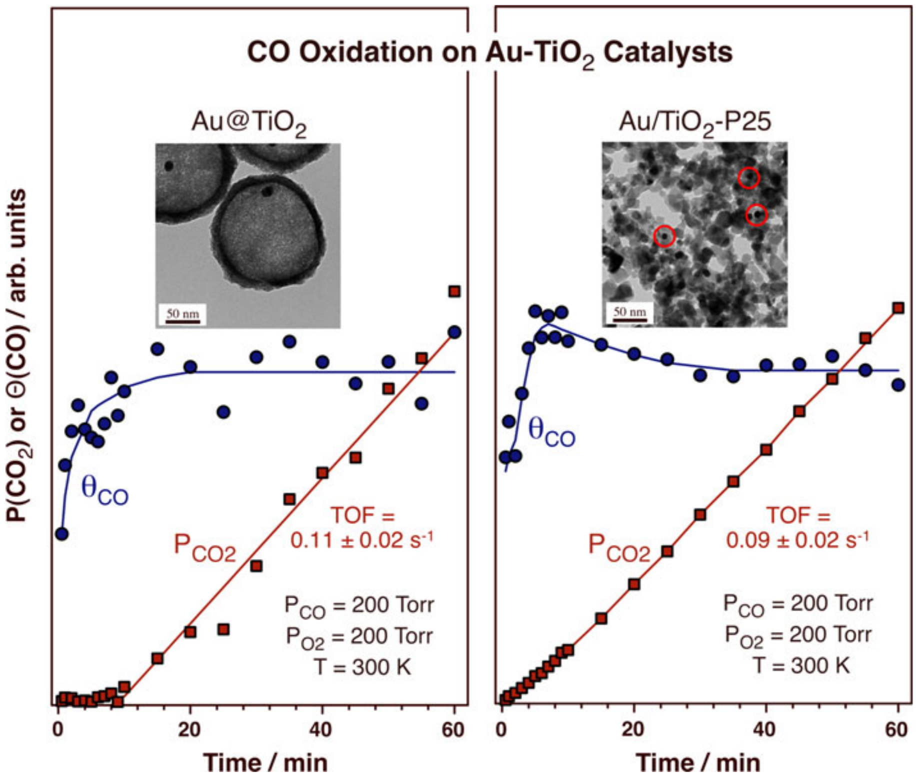

Fig. 8 Contrasting of performance between a Au@TiO$_2$ yolk@shell nanostructure (*left*) and a regular Au/TiO$_2$-P25 dispersed catalyst (*right*) [83]. Shown are time-dependent data for the uptake of carbon monoxide on the gold (θ_{CO}, *circles*) and the production of carbon dioxide (P_{CO_2}, *squares*) during the room-temperature oxidation of CO with O$_2$. Similar performance was seen with both catalysts, normalized to the surface area of the gold nanoparticles, but sintering was observed with the regular catalyst but not with the yolk@shell nanostructure after calcination at 775 K (not shown). Also shown are TEM images of the catalysts. Reproduced from Ref. [83] with permission. Copyright 2011 John Wiley and Sons

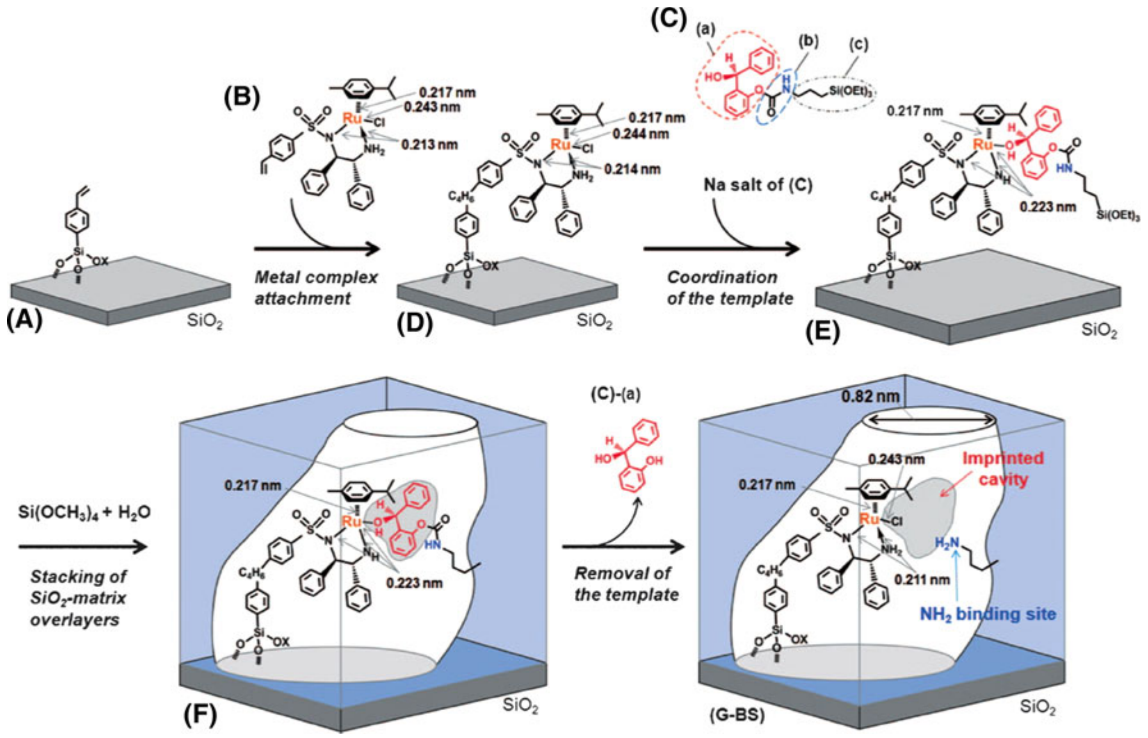

Fig. 9 Schematic illustration of the synthetic methodology used to imprint well-defined cavities around a coordination site in an anchored ruthenium organometallic catalyst [86]. A ligand with an *o*-hydroxybenzhydrol moiety is initially coordinated to a Ru complex anchored to a silica surface, and used as a templating agent to create a specific cavity during a subsequent encasing adding a polymer film. After removal of the template, a site is generated for the hydrogenation of *o*-fluorobezophenone. Figure courtesy of Zhihuan Weng and Mizuki Tada, reproduced from Ref. [86] with permission. Copyright 2011 John Wiley and Sons

elements. In the case of metals, for instance, the electronic structure may need to be fine-tuned to promote specific pathways. This can be accomplished by using alloys [88, 89]. Based on theoretical calculations, it has been argued that the reactivity of metal catalysts can be roughly correlated to the center of the d-band with respect to the Fermi level, and that this center can be shifted by mixing two or more metals [7].

Thanks to new synthetic methodology in materials chemistry, it is now possible to prepare bimetallic nanoparticles with specific distributions of the constituent elements, in well-mixed alloys or in layered arrangements, for instance [90–92]. These structures can in principle be used to promote specific reactions selectively, taking advantage of the local electronic structure created by the unique distribution of metal atoms within a given nanoparticle. However, this approach may be limited by the high mobility of atoms in such small particles. Indeed, the distribution of metals within a given particle can easily change upon thermal treatment or because of the chemisorption of reactants, which means that it may not be possible to retain specially tailored compositional profiles in bimetallic catalysts. An elegant example of this atom mobility is provided in Fig. 10, which shows the reversible segregation of Rh and Pd atoms to the surface of $Rh_{0.5}Pd_{0.5}$ nanoparticles under alternating oxidizing and catalytic conditions during the conversion of NO with CO [93]. Nevertheless, it is clear that bimetallic nanoparticles can display unique catalytic behavior, and that such behavior can change depending on the way they are prepared. A full understanding of why such differences may be seen in spite of the dynamical compositional and structural changes that can occur on metal nanoparticles under catalytic conditions awaits further research.

The properties of the active phase of a catalyst can also be altered via the addition of small amounts of other elements, which can act as promoters, inhibitors, poisons or, in more general terms, modifiers. Classic examples here include the addition of alkali metals as promoters in ammonia [94] and Fischer–Tropsch [95] synthesis and the use of sulfur as a selective poison in hydrocarbon reforming [96]. A subtler version of this idea is the recent use of chiral molecules as modifiers to bestow enantioselectivity to regular hydrogenation catalysts [14, 15]. Unfortunately, this latter approach has so far been shown to work for a fairly restricted set of molecules, and its extension to more general cases has proven difficult, in part al least because of the limited understanding available on how the catalyst modification operates at a molecular level [97]. Much more research is needed in this area to take full advantage of the idea of using reversibly adsorbed discrete molecules as modifiers, to define complex catalytic sites on surfaces and, with that, increase selectivity for complex reactions.

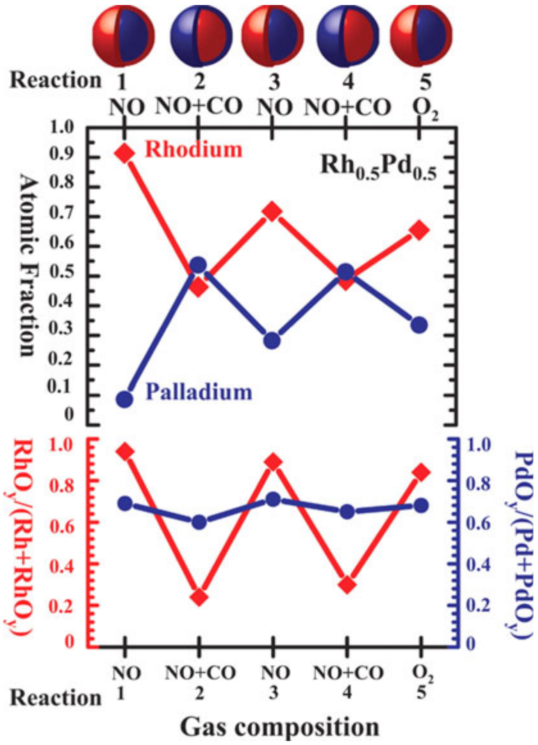

Fig. 10 Example of the dynamic behavior of bimetallic nanoparticles under reaction conditions. Shown are data for the evolution of the total atomic fractions for Rh and Pd (*top*) and of their fraction in oxidized form (*bottom*) in $Rh_{0.5}Pd_{0.5}$ nanoparticles upon exposure to alternating NO and NO + CO atmospheres at 575 K [93]. The schematic diagrams shown on *top* highlight the reversible segregation of Rh and Pd under alternating oxidizing and catalytic conditions. Figure courtesy of Miquel Salmeron, reproduced from Ref. [93] with permission. Copyright 2008 the American Association for the Advancement of Science

Many heterogeneous catalysts require multiple functionalities to promote different individual reactions within a multiple-step process. This can be seen, for instance, in the use of platinum-based particles dispersed on high-surface-area acidic supports to promote hydrocarbon reforming: the metal phase is used mainly to promote hydrogenation–dehydrogenation reactions, whereas acidity in the support is added to catalyze isomerization steps [96]. In some instances, catalyst are designed so the reactant, first activated on one part of the surface of the catalyst, then migrates to a second site for further reaction, a phenomenon know as spillover [98, 99]. Such division of labor is particularly common in photo- and electrochemically driven catalysis, processes that have regained much interest in recent times in connection with the harvesting and use of energy. In fuel cells, for instance, the oxidation of hydrogen (or methanol) and the reduction of oxygen are carried out separately, on different catalysts, and electron transfer is driven electrically through an external circuit [100]. Many issues remain unresolved in fuel cells [101], but, fortunately, those can be addressed independently: electrocatalysts can be designed and optimized separately for each half-reaction.

Photocatalytic processes also often involve different sites for oxidation and reduction steps, although in principle those sites do not need to be physically apart. In fact, much effort is still being placed on identifying a single material to carry out all functions. In the case of water splitting to generate hydrogen fuel out of the decomposition of water, for instance, materials have been long sought capable of both absorbing light, preferably in the visible range, and promoting the subsequent redox reactions required to make $H_2 + O_2$ [102]. Such efforts have, however, yielded limited success; more promising is the modern research directed at the design of clever nanoarchitectures to separate the different functionalities and optimize each independently [103, 104]. A few examples of this are illustrated schematically in Fig. 11. Notice that, in all the arrangements shown in that figure, light absorption and hydrogen and oxygen production are typically carried out by different phases, on GaN:ZnO, RuO_2 and Mn_3O_4 in the example for a one-step process, respectively (Fig. 11, top left), or on $Pt/ZrO_2/TaON$ and Pt/WO_3 in a two-step Z-scheme (to gain flexibility in designing materials for light absorption over a wider range of energies, Fig. 11, bottom). Further improvements can also be achieved by modifying each individual phase, as in the example where a Cr_2O_3@Rh a core@shell structure is used to prevent the reduction site from promoting recombination with oxygen (Fig. 11, top right). There is much room for improvement in the design of these nanostructured photocatalysts still.

Finally, new types of catalytic sites may develop at the interface of two or more different solid phases. This may result in a desirable synergy leading to new catalytic reactions. A well-known version of this behavior is the so-called strong-metal-support-interaction (SMSI), seen when certain high-surface-area oxide supports are used to dispersed metal nanoparticles [105, 106]. Much discussion can be found in the literature about the causes of such effect, with explanations that include changes in the electronic properties of the metal, the formation of new mixed intermetallic phases, and the encasing or decoration of the metal by the oxide, but this issue is not entirely settled yet. SMSI has recently been invoked [107] as a possible explanation for the unique behavior of the gold/titania materials that have proven so versatile in low-temperature catalysis [20], but the formation of new interfacial sites may be a more likely explanation in that case [108, 109].

6 Molecular Functionalization

As mentioned above, the ultimate goal of the design of many new catalysts is to achieve high selectivity in complex reactions. This may require a level of molecular

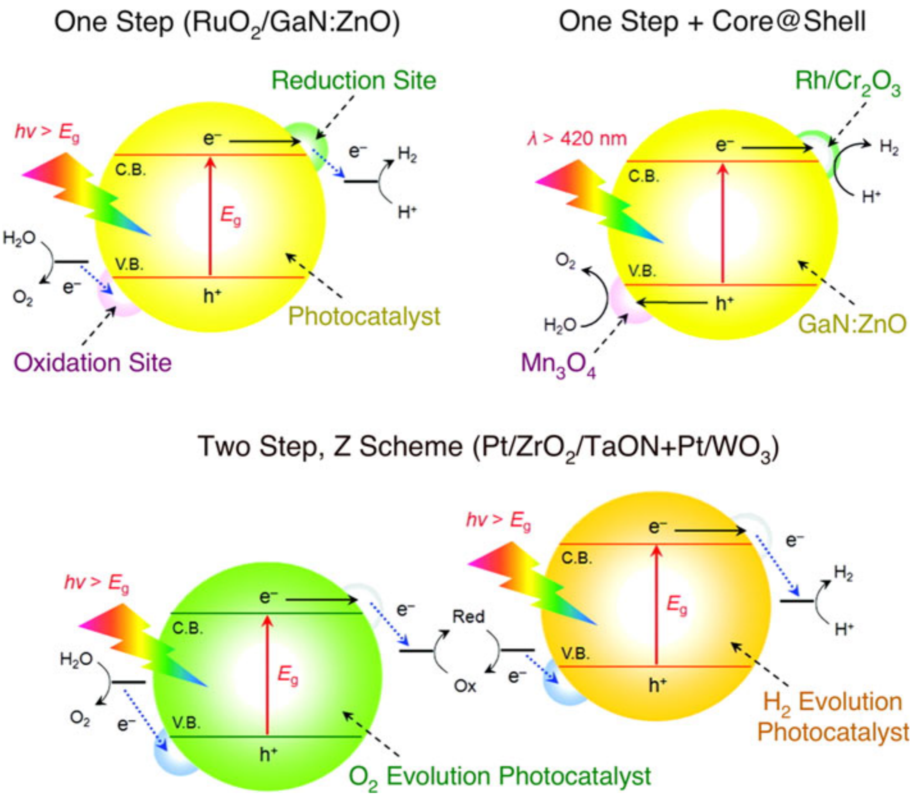

Fig. 11 Schematic representation of different nanoarchitectures proposed for the photocatalytic splitting of water. Three basic designs are depicted. *Top left* one-step system, where light harvesting and hydrogen reduction and oxygen production are carried out by three different connected solid phases. *Top right* improved version of the one-step system where a core@shell structure was added to the reducing site to prevent recombination of the H_2 produced with O_2. *Bottom* two-step (Z-scheme) system, where two different light absorbers are used for the H_2 and O_2 production in order to increase the light spectral range available for photocatalysis. Figure courtesy of Kazuhiko Maeda and Kazunari Domen, reproduced from Ref. [104] with permission. Copyright 2010 the American Chemical Society

control on the active site still not available by solid-state synthetic means. An alternative approach may be the derivatization of solids, to add specific molecular functionality by anchoring or tethering specific discrete molecules to them. Much work has been done already on anchoring homogeneous catalysts onto the surface of porous materials [110], but that idea has achieved limited success because: (1) the rigidity added by anchoring and the confined environment of the pores where the catalyst resides may degrade the performance of the catalyst, and (2) the lability of the ligands used for anchoring may lead to leaching of the catalyst out of the support.

Surface derivatizations can also been used to modify the catalytic performance of the solid itself, by adding a particular functionality to it. This may involve the addition of acid or basic sites, for instance. In one example from our laboratory, cinchonidine molecules were tethered to silica supports to impart enantioselectivity to catalytic reactions involving tertiary amines [111]. This tethering of specific moieties to surfaces, to oxides in particular, has been greatly facilitated by the development of so-called "click" chemistry, by which common terminal groups are used to react with each other in the assembly of the desired structure one piece at a time: typically, the desired catalytic functionality is bonded to the surface via a linking agent [112–114]. Still, only a few studies are available to date where a direct comparison of free versus anchored catalytic functionalities has been provided.

In addition to providing a more convenient way to handle catalysts, making their separation from the reaction mixture easier, the heterogenization of homogeneous catalysts or catalytic centers can potentially afford the assembly of multiple cooperative functionalities [115]. In fact, this procedure can be used to prepare catalysts with two or more antagonistic functions that may not be able to coexist in solution, such as acidic and basic sites [116]. Some interesting synthetic procedures have been reported to accomplish this task, including the use of partial titration of the basic sites via controlled addition of the acid [117] and the deposition of the acid and basic sites in the inner and outer surfaces of mesoporous nanoparticles, respectively [118]. Nevertheless, a major challenge in preparing this type of bifunctional materials remains the control and optimization of the relative positions of the two types of sites; most often, each anchored or tethered functionality is distributed randomly throughout the surface of the support, and performs its catalytic function independently of the other functionality [119]. A few ideas have been put forward to anchor both catalytic functionalities on surfaces in a correlated way [115, 120], but this issue is still, in general, unresolved.

A related approach to the molecular design of catalytic sites on surfaces is to tether a complex organic structure first and use that as a framework to define an environment on which to add the active phase, perhaps a metal ion or a small nanoparticle. Calixarenes in particular have been used recently to mimic sites similar to those seeing in enzymes [121]. Another option is to use such calixarenes as bulky ligands in organometallic catalysts anchored to high-surface-area supports to help defined the sterics of the catalytic site [122]. An example of the latter idea is provided in Fig. 12, where the activity of Al(III) ion sites anchored on a silica support was tuned by the way they coordinate to the calixarene ligand: only open sites, where the aluminum ion is bonded to the calixarene ring through a single Al–O bond, show significant activity in Meerwein–Ponndorf–Verley (MPV) reductions (the activity is almost entirely suppressed if bonding involves two Al–O bonds, which creates a close site) [123].

7 Catalysis Applications, Old and New

So far we have focused on the new tools that have become available for the better design of heterogeneous catalysts at

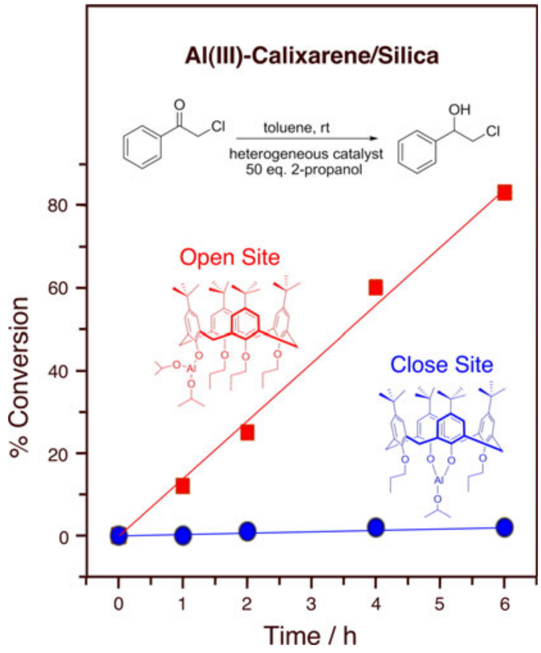

Fig. 12 Example of an anchored organometallic catalysis, the selectivity of which was tuned via changes in coordination of the ligand to the metal. In this case, a calixarene ring is used to control the activity of aluminum (III) sites toward the Meerwein–Ponndorf–Verley (MPV) reduction of ketones [123]. An aluminum catalyst anchored to silica can display high activity toward the MVP reaction in an open configuration, with one single coordination bond to the calixarene. However, that activity can be almost completely suppressed if a close site is used instead, via coordination of the individual aluminum ion to two oxygen atoms within the calixarene ring. Figure courtesy of Alexander Katz, reproduced with permission

a molecular level. There are also many new challenges ahead in the field of catalysis in terms of the chemical reactions to be promoted. For one, there is still ongoing research to improve well-established processes such as the hydrogenation, hydrocracking, and reforming of hydrocarbons, the synthesis of fuels (Fischer–Tropsch, methanation, syngas synthesis), the fixation and processing of nitrogen, and the production of commodity chemicals, to mention a few. The example in Fig. 5, which refers to the development of new hydrodesulfurization catalysts, illustrates how new molecular-level understanding of catalytic sites and catalytic reactions can be used to improve on the performance of known catalytic materials. There are also some old processes still in search of viable answers. It is still, for instance, quite difficult to promote epoxidation reactions with heterogeneous catalysts for olefins other than ethylene [124, 125]. The selective partial oxidation of hydrocarbons in general represents a challenge to which heterogeneous catalysis has much to contribute [126, 127].

Many old catalytic processes can certainly be improved, either by increasing their selectivity toward the desired reaction or by finding alternatives that require milder conditions, that is, lower pressures and/or temperatures. This is one of the reasons why there has been so much excitement about the ability of catalysts based on gold nanoparticles to promote so many oxidation reactions around room temperature [128]. In fact, gold catalysis has turned out to be quite versatile, its use extending also to hydrogenations and nucleophilic additions to pi systems. However, there is no consensus yet on how gold nanoparticles promote these chemical reactions, and that is needed to tune the many parameters that affect the catalytic behavior in a more systematic way. Gold catalysts also tend to be somewhat unstable and to sinter over time, a problem that remains unresolved [20].

There are certain practical applications for which catalysis is ideally suited. One is the harvesting, storage, and use of energy [129]. For instance, the main source of hydrogen, a promising clean fuel [130, 131], is via steam reforming, a catalytic process [132, 133]. However, this is a reaction that still needs improvement, and that produces CO_2 as a byproduct. More efficient processes for hydrogen production are highly desirable, but yet not available. Photocatalysis, for instance, has been identified as a clean and potentially cheap way to make hydrogen out of water, but no photocatalyst has been developed to date with sufficient efficiency to make this approach commercially feasible [103, 104]. The processing of biomass is another alternative for the production of renewable fuels. In this case, the main obstacle is the selective activation of the key bonds in the cellulose and lignin that constitute the bulk of those materials, to convert the raw feedstock into useful chemicals; this is a step that has proven quite challenging [134–136]. On the energy production side, fuel cells are being implemented in many applications, including for the propulsion of automobiles, but their development has been hampered by a couple of key unresolved issues, specifically the ease with which the anode, where hydrogen is consumed, is poisoned by other gases (i.e., CO), and the slow kinetics of oxygen reduction reaction (ORR) at the cathode [100, 137]. There is much active research in all these catalytic issues in terms of the manufacturing and consumption of fuels, but new unforeseen transformative advances are still possible and needed.

Another area where catalysis excels is in addressing environmental remediation issues [138]. In fact, the development of the three-way catalyst for the treatment of exhaust gases from automobiles is often cited as perhaps the greatest success for the molecular approach to developing catalysts [139]. Nevertheless, new fuel formulations and increasingly stringent restrictions in gas emissions demand further improvements, and additional processes are required for the processing of exhaust gases from other fuels, from stationary power plans, and from restaurants and other urban sources. Perhaps less discussed but equally important is the need of treatments to clean waste and ground waters [134]. The processing of indoor air, to remove odors as well as poisonous gases such as CO, is increasingly gaining relevance in a society that relies heavily on office work. Finally, catalytic synthetic processes are inherently greener than their stoichiometric counterparts, and therefore preferable when available. Arguably, it is in improving the quality of our environment, both the air and the water that we use for living, that catalysis may make the greatest impact in our lives.

Another big challenge for catalysis is in the activation and use of carbon dioxide. This would serve the dual purpose of using a cheap source for carbon and helping remove from the atmosphere one of the most prevalent greenhouse gases generated in combustion processes. One of the most important current applications of CO_2 is in the production of synthesis gas (syngas), the starting material for carbon-containing fuels. Another interesting target is methanol synthesis, which nowadays is mainly accomplished by using CO instead [140]. More generically, CO_2 could be one of the main feedstocks for the synthesis of high value chemicals [141]. Attempts to use CO_2 in these applications are limited by its particular thermodynamic stability, but that may in principle be overcome by kinetics. The challenge of converting CO_2 to other chemicals is very much alive.

Lastly, it would be highly desirable to develop heterogeneous catalytic processes for the manufacturing of fine chemicals, for pharmaceutical, agro, and other (adhesives, additives, antioxidants, corrosion inhibitors, cutting fluids, dyes, lubricants, pigments) applications. Many speciality chemicals are currently made by stoichiometric reactions or by using homogeneous catalysts, but greener heterogeneous catalytic processes are always preferred, because those catalysts are easier to handle and reuse. However, speciality chemical syntheses require a great deal of selectivity, in many instances even enantioselectivity (particularly important in pharmacological applications), and that is not easy to achieve with solid catalysts. As discussed above, even with the new developments in nanotechnology, there is a limit to the level of sophistication that can be engineered in the active sites of solid catalysts. The answer may lay on a hybrid approach where greater level of molecularity can be added to the initial sites of appropriate solid catalysts via the anchoring or tethering of discrete moieties, as introduced above. In fact, in addition to leading to greener chemistry, the anchoring/tethering approach can also help avoid solubility problems, and offers more flexibility in terms of adding multiple, possibly incompatible, functionalities in one-pot processes. The development of mixed organic–inorganic, molecular-solid catalysts has acquired high prominence recently, but this research area is still quite open.

8 General Outlook

In this perspective, we have identified a number of issues yet to be addressed or fully developed in terms of heterogeneous catalysis. The overall driving force for new advances in this field is that we now have the tools for a molecular approach to catalyst design. Surface-science techniques and computer calculations can now be used to obtain a detailed understanding of the mechanism of catalytic processes and to identify the requirements for more selective processes. New synthetic techniques, associated with nanotechnology and with the addition of discrete molecularity to solids, can then be employed to build catalysts with the desired characteristics.

The ability to exert greater control on the nature of the active sites in catalysts affords the use of properties that were not accessible in the past. Here we have discussed the role that the size and shape of nanoparticles of catalytic active phases may play in defining reaction selectivity. We have also identified the different ways in which the manufacturing of better-defined supports can enhance catalytic performance, by defining the environment around the active site or by adding new functionality on the surface of the solid itself or at the interface between the two components. We have indicated that multiple functionality can be assembled by tuning the electronic properties of a given phase, by using bimetallics or alloys, or by adding several active phases or promoters, inhibitors, or modifiers to the same catalyst. Finally, molecular features can also be incorporated via the anchoring or tethering of those onto the surface of the support.

These new tools, together with a greater understanding of the underlying chemistry to be promoted, can be applied to a vast variety of chemicals problems. There is still a need to improve on the performance of many old catalytic processes, for the production and processing of basic feedstocks and commodity chemicals, for instance. New processes are also desirable to tackle issues associated with the management of energy and with environmental problems. Perhaps more challenging is the need to substitute the stoichiometric synthesis and homogeneous catalysis used nowadays for the manufacturing of fine chemicals, which require highly selective processes, with easier-to-use and more environmentally friendly heterogeneous alternatives. Catalysis is an old and well-established field of chemistry, but in many respects it is still in its adolescence and it is undergoing a renaissance; the future of molecularly-focused heterogeneous catalysis is bright.

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