

## Nanostructured materials for applications in heterogeneous catalysis†

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In this review, a brief survey is offered on the main nanotechnology synthetic approaches available to heterogeneous catalysis, and a few examples are provided of their usefulness for such applications. We start by discussing the use of colloidal, reverse micelle, and dendrimer chemistry in the production of active metal and metal oxide nanoparticles with well-defined sizes, shapes, and compositions, as a way to control the surface atomic ensembles available for selective catalysis. Next we introduce the use of sol-gel and atomic layer deposition chemistry for the production and modification of high-surface-area supports and active phases. Reference is then made to the more complex active sites that can be created or carved on such supports by using organic structure-directing agents. We follow with an examination of the ability to achieve multiple functionality in catalysis via the design of dumbbells, core@shell, and other complex nanostructures. Finally, we consider the mixed molecular-nanostructure approach that can be used to develop more demanding catalytic sites, by derivatizing the surface of solids or tethering or immobilizing homogeneous catalysts or other chemical functionalities. We conclude with a personal and critical perspective on the importance of fully exploiting the synergies between nanotechnology and surface science to optimize the search for new catalysts and catalytic processes.

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### 1. Introduction

Heterogeneous catalysis is quite prevalent in the chemical industry, and affects our everyday life in many ways. Over 90% of all chemical manufacturing is based or relies heavily on catalytic processes, and, by some estimates, catalysis contributes to approximately 35% of the world's gross domestic product (GDP).<sup>1</sup> Catalytic reactions are not only at the heart of the making of most chemicals and materials, including some of the polymers and composites found in so many modern products, but also play a central role in energy applications old and new (in oil refining, biofuel production, and fuel cells, to name a few), in pollution control (to limit the emission of noxious gases from automobiles and stationary sources, to remove CO and odors from indoor air, to clean groundwaters), in medical applications (to make pharmaceuticals, in biosensors), and in food production (by aiding with the synthesis of fertilizers and pesticides, in oil hydrogenation, in other food processing).

Historically, catalysis has been understood as a way to accelerate chemical reactions. Indeed, this was the emphasis that Berzelius provided when he introduced the term in 1835.<sup>2</sup> In many early implementations of catalysis, where the requirement was to make simple reactions such as the oxidation of sulfur dioxide to sulfuric acid, the production of ammonia from N<sub>2</sub> and H<sub>2</sub> (the Haber process), and the synthesis of methanol and its

oxidation to formaldehyde kinetically accessible, a focus on the rate of reaction was appropriate.<sup>1,3</sup> However, in more recent applications, increasingly complex reaction networks are at play, and there is a need not only to promote a given desired conversion but also to avoid any undesirable side reactions. This is required to improve reaction yields, to simplify the overall manufacturing process, eliminating expensive product separation steps, and to minimize the generation of potentially polluting byproducts.<sup>4,5</sup> Selective processes are particularly important in the manufacturing of speciality chemicals.<sup>6</sup> In pharmaceutical and agrochemical uses, for instance, enantioselectivity to produce chiral compounds is often indispensable because of the unique handedness of the biochemistry of living systems.<sup>7,8</sup>

This shift toward an emphasis on reaction selectivity in catalysis has imposed new and stringent constraints on the requirements for the promotion of the desired reactions,<sup>9</sup> and the fulfillment of those requirements requires great control on the characteristics of the solids used as catalysts. Traditionally, heterogeneous catalysts have been made by using simple synthetic routes with limited control over the morphology and nature of the solids. For instance, in cases where expensive transition metals need to be dispersed onto cheap high-surface-area oxides, to enhance the surface-to-volume ratio of the active phase and reduce the cost of the catalyst, the latter are often impregnated with selected salts of the latter and then calcined. The consequence of this approach is that the resulting small metal particles produced display a wide distribution of sizes and shapes, with their corresponding array of surface ensembles. Different surface sites typically display significantly different catalytic activities, and the performance of the overall catalyst is determined by an average of all of those. It is not easy to control selectivity with such samples, in particular when subtle effects such as stereo or enantio selectivities are considered.

Fortunately, novel nanotechnologies have been developed in recent years to synthesize complex solids with well-defined characteristics, and those have already found applications in catalysis.<sup>10,11</sup> The ability to produce samples with specific sizes or shapes, or to grow complex solid nanostructures, can be exploited to fulfill specific requirements in catalysis in terms of selectivity, as identified by molecular-level investigations on the reaction mechanisms. This synergy between the surface chemistry of catalysis and nanotechnology is still in its infancy, but has already led to many exciting developments, and promises to revolutionize chemical manufacturing. In this review, we survey the main synthetic approaches from nanotechnology being used in catalysis, including colloidal and reverse micelle chemistry, dendrimer encapsulation, sol-gel solid growth, surface-protected etching, atomic layer deposition, scaffolding using organic structure-directing agents, the making of dumbbell, core@shell, yolk@shell and related nanoarchitectures, and silylation and other surface derivatization, tethering, and immobilization procedures. Our emphasis is on identifying the driving forces for the design of particular catalysts, a concrete mechanistic knowledge on the desired reaction that defines the requirements from nanotechnology in the manufacturing of useful catalysts. It is our belief that only *via* this synergy between nanotechnology and basic mechanistic studies, aided by

surface science<sup>12–15</sup> and computational simulations,<sup>16,17</sup> that new catalytic developments can successfully flourish.<sup>18</sup>

## 2. Colloidal and reverse micelle nanoparticle synthesis: control of size

As mentioned above, many catalytic processes require the dispersion of metals as small nanoparticles onto a high-surface-area porous support. This dispersion is mainly required to optimize the amount of the surface of the expensive active phase exposed. Nevertheless, it has been learned over the years that the specific characteristics of those metal nanoparticles can also affect their catalytic performance.<sup>19</sup> With demanding reactions, which typically require severe temperature and pressure conditions, significant variations in activity have been often reported as a function of catalyst dispersion, which is often correlated with average particle size.<sup>20</sup> Mild reactions such as the hydrogenation of olefins and other unsaturated organic molecules, by contrast, have traditionally been considered structure insensitive.<sup>14</sup> However, recent surface-science experiments have suggested that even those processes may exhibit different rates and selectivities as a function of the size and structure of the metal nanoparticles in the catalyst.<sup>21–23</sup> It is only because of the averaging of the catalytic performance over nanoparticles with many sizes and shapes, as it occurs in most present catalysts, that these potential differences have been masked in past studies.

Fortunately, metal nanoparticles can now be made with quite narrow size distributions by using colloidal,<sup>24–26</sup> reverse micelle,<sup>27,28</sup> or dendrimer-based<sup>29,30</sup> chemistry. In fact, nanoparticles made this way have already been tested for catalysis in solution,<sup>26</sup> and even in electrochemical systems.<sup>31</sup> Their extension to heterogeneous catalysis, however, has only been started, and only a handful of examples are available where a careful correlation between particle size and catalytic performance has been drawn. In one case provided by Somorjai and co-workers, the hydrogenation and hydrogenolysis of pyrrole on platinum catalysts were shown to shift from almost exclusive *n*-butylamine formation to the production of significant quantities of pyrrolidine as the nanoparticle size was lowered to  $\sim 1$  nm in diameter.<sup>32</sup> Other examples from the same group include the hydrogenation of CO<sub>2</sub> over cobalt catalysts,<sup>33</sup> the hydrogenation of cyclohexene,<sup>34</sup> crotonaldehyde,<sup>35</sup> and benzene and toluene,<sup>36</sup> and the ring opening of methylcyclopentane,<sup>37</sup> all on Pt/SBA-15, and the oxidation of carbon monoxide over ruthenium supported on a silicon wafer.<sup>38</sup>

A particularly interesting size dependence of catalytic activity has been identified with gold catalysts, because bulk gold is often inert but gold nanoparticles can promote many reactions under mild conditions.<sup>39</sup> Such effects have been reported for CO oxidation, for instance,<sup>40,41</sup> where the maximum in activity seen with Au nanoparticles  $\sim 2$ –3 nm in diameter has been explained by a quantum effect related to their thickness on the surface.<sup>42</sup> A separate study showed that the catalytic activity of gold nanoparticles toward the reduction of 4-nitrophenol decreases monotonically starting with nanoparticles 8 nm in diameter.<sup>43</sup> The oxidation of ethylene glycol was also found to be optimum on carbon-supported gold

nanoparticles  $\sim 7$  nm in diameter.<sup>44</sup> Particle size effects using colloidal-made catalysts have been reported in electrocatalysis as well.<sup>45,46</sup>

### 3. Colloidal and reverse micelle nanoparticle synthesis: control of shape

Perhaps more interesting than the dependence of catalytic performance on nanoparticle size is the changes that have been identified with respect to nanoparticle shape. In fact, structure sensitivity in catalysis has typically been explained in terms of the different active sites present on the surface of the nanoparticles used as the active phase. It is known from surface-science work with single crystals<sup>15,21</sup> and with model catalysts<sup>23,47</sup> that surface reactions may display different activities and selectivities on different exposed facets, and that those can in principle be enhanced by using nanoparticles of specific shapes.<sup>48</sup> However, with supported catalysts, structure sensitivity has most often been detected by contrasting the performance of catalysts with varying average particle sizes. It is only now, with the ability to control both size and shape in nanoparticles independently by using novel colloidal synthetic procedures, that the two effects can be untangled.

The control of nanoparticle shape during growth has been accomplished by using surfactants that selectively favor metal atom incorporation on facets with specific crystallographic orientations.<sup>25,49,50</sup> A number of shapes have been grown this way, including not only simple cubes, tetrahedra, octahedra, decahedra, and triangular and hexagonal plates, but also more complex tetrahexahedra, trapezohedra, trisoctahedra and hexoctahedra as well as asymmetric and branched structures such as crosses, bars, rods, prisms, wires, and stars.<sup>51,52</sup> Comparative reactivity studies have been carried out with some of these shape-controlled colloidal nanoparticles both in solution and in electrochemical systems.<sup>24,26,53,54</sup>

A few examples are also available on the use of these shape-controlled particles for the preparation of heterogeneous catalysts. In one case, supported Rh nanocubes were found to exhibit slightly higher turnover frequencies and lower activation energies for the conversion of CO with NO than Rh nanopolyhedra.<sup>55</sup> In another more recent report on the oxidation of CO using Pd/SiO<sub>2</sub> catalysts, octahedral and spherical nanoparticles, which predominantly expose (111) crystal facets, exhibited significantly better catalytic activity than palladium nanocubes, which possess (100) surfaces instead.<sup>56</sup> In a third case, cubic and nanowire-shaped silver nanoparticles were shown to be particularly selective for the epoxidation of ethylene to ethylene oxide, suggesting that the reaction takes place preferentially on the (100) termination facets of those nanoparticles.<sup>57</sup> However, it is not clear that the effects reported in these cases are large enough to be outside the margin of the experimental errors. One concern is that, with demanding or highly exothermic reactions such as oxidations, the original nanoparticle shapes may not be preserved during reaction. This is an issue that requires further exploration. Better *a priori* correlation of activity or selectivity on surface

structure for a given reaction, extracted from mechanistic studies with model systems, would also be desirable to better target the shape-selective catalysts to be made with these colloidal synthetic techniques.

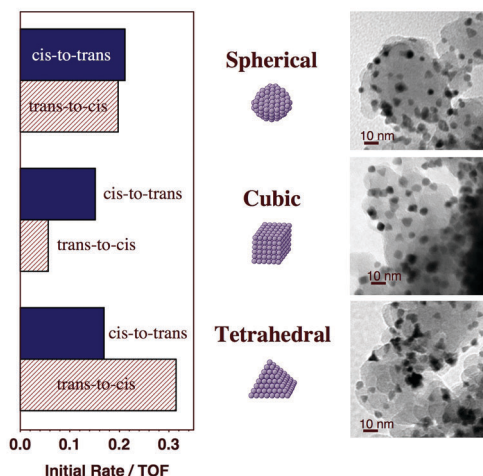
With milder reactions such as with hydrogenations of organic compounds, the problem of nanoparticle restructuring may be avoided. A few reports are already available on the identification of shape selectivity in such cases. It was shown, for instance, that catalysts made with anisotropically grown Pd nanorods, which preferentially expose (100) facets, perform a selective hydrogenation of buta-1,3-diene into butenes without further hydrogenation into butane.<sup>58</sup> An opposite selectivity toward partial hydrogenation has been seen for the case of benzene on platinum catalysts: while both cyclohexene and cyclohexane are produced on cuboctahedral nanoparticles (which expose both (111) and (100) facets), only cyclohexane is produced on cubic nanoparticles (with only (100) surfaces).<sup>59</sup> The hydrogenation of butenes to butane is also promoted more selectively relative to their *cis-trans* isomerization on Pt nanocubes, with (100) facets exposed, than on Pt nanotetrahedra, which expose (111) planes instead.<sup>60</sup> In terms of hydrogenolysis pathways, the conversion of pyrrole stops at the hydrogenation product, pyrrolidine, on Pt nanopolyhedra, but continues to *n*-butylamine on Pt nanocubes; it seems that (100) facets enhance ring-opening steps.<sup>32</sup>

In our laboratory, extensive surface-science work and quantum-mechanics calculations led to the conclusion that the *cis* isomers of olefins are more stable than their *trans* counterparts on Pt(111) facets.<sup>61–66</sup> This was an interesting observation, because it runs against the expectation from known relative thermodynamic stabilities, and because it suggested that *cis* isomers could be produced selectively on catalysts with (111) facets exposed. Our hypothesis was successfully tested by using tetrahedral colloidal Pt particles, which were dispersed on a silica support.<sup>60,67</sup> It was shown that, indeed, *trans-to-cis* isomerization runs at about twice the rate of the *cis-to-trans* conversion on such dispersed tetrahedral nanoparticles as long as mild pretreatments are used so the nanoparticle shapes are not disturbed.<sup>68</sup> If harsher pretreatments are employed, by contrast, selectivity toward *trans* formation is detected, as with most other catalysts.<sup>68</sup> The relevant data are summarized in Fig. 1. This particular example illustrates how studies with model systems can be used in a predictive manner to direct the design of new nanocatalysts.

A number of studies have also been directed to understand the effect of nanoparticle shape in catalysis promoted by metal oxides. For instance, in an early example, it was shown that exposure of (100) facets in CeO<sub>2</sub> nanoplates enhances their CO catalytic oxidation activity.<sup>69</sup> A second more detailed study of this system proved that the trend in CO oxidation activity follows the sequence rods > cubes > octahedra, which expose (110) + (100), (100), and (111) facets, respectively.<sup>70</sup> The same ordering was seen in terms of oxide reducibility and lattice oxygen mobility, suggesting that the formation of surface oxygen vacancies plays a direct role in facilitating the reaction. In another case, Co<sub>3</sub>O<sub>4</sub> nanorods with predominant (110) planes exposed, which favor the presence of Co<sup>3+</sup> sites, were

## 2-Butene Isomerization on Pt/SiO<sub>2</sub>

Initial Rate versus Particle Shape



**Fig. 1** Example of how control on catalytic selectivity can be exerted by controlling the structure of the active catalytic phase.<sup>11</sup> Left panel: initial reaction rates, in turnover frequency (TOF), for both the conversion of *cis*-2-butene to its *trans* isomer (solid blue) and the opposite *trans*-to-*cis* reaction (hatched red) on catalysts made out of spherical, cubic, and tetrahedral nanoparticles, all approximately 5 nm in diameter. Right panels: TEM images of those catalysts. It can clearly be seen that selectivity in this *cis*-*trans* isomerization reaction depends strongly on the shape of the nanoparticles used as catalysts: with tetrahedral Pt, which preferentially expose (111) facets, high selectivity is detected for the isomerization of *trans* olefins to their *cis* counterparts, whereas nanocubes, which expose (100) facets, promote the *cis*-to-*trans* conversion instead; spherical particles show no particular selectivity for either reaction. Reproduced from ref. 11 with permission, Copyright 2011 the PCCP Owner Societies.

used to show the particularly high activity of those sites for low-temperature CO oxidation.<sup>71</sup> Using a series of Co<sub>3</sub>O<sub>4</sub> nanosheets, nanobelts, and nanocubes, a structure sensitivity was also reported for the catalytic combustion of methane, with activity following the following order with respect to crystal planes: (112) > (011) >> (001).<sup>72</sup> A third example is Cu<sub>2</sub>O: it was determined from studies with Cu<sub>2</sub>O nanoparticles in the shapes of cubes, octahedra, spheres, plates, and polyhedra, that the (111) plane of the oxide is twice as active as its (100) facet at 300 K for the N-arylation of iodobenzene with imidazole.<sup>73</sup>

A few recent examples of the effect of nanoparticle shape within the oxide substrate in metal/oxide catalysts can be cited as well. In one, a favorable synergetic effect for the catalytic oxidation of CO over CuO/CeO<sub>2</sub> nanorods, as compared to CuO/CeO<sub>2</sub> nanoparticles, was ascribed to the exposure of high-energy, more reactive, (110) and (100) crystal planes in the former case.<sup>74</sup> In another study, the shape of the nanoparticles of ceria used to make Au/CeO<sub>2</sub> catalysts was found to affect their activity for the water-gas shift reaction, with gold on the (110) facets of ceria nanorods showing the highest activity.<sup>75</sup> This was explained in terms of the relative ease with which oxygen vacancies, which are indispensable for stabilizing metals, can form on the different planes of the oxide. In a third report, Pd/Co<sub>3</sub>O<sub>4</sub> catalysts based on nanosheets of the oxide were found to be more reactive than those made out of nanobelts or nanocubes, presumably because of stronger surface interaction between the (112) crystal planes of the Co<sub>3</sub>O<sub>4</sub> exposed in the former samples with PdO.<sup>76</sup>

## 4. Dendrimer encapsulation of metal nanoparticles

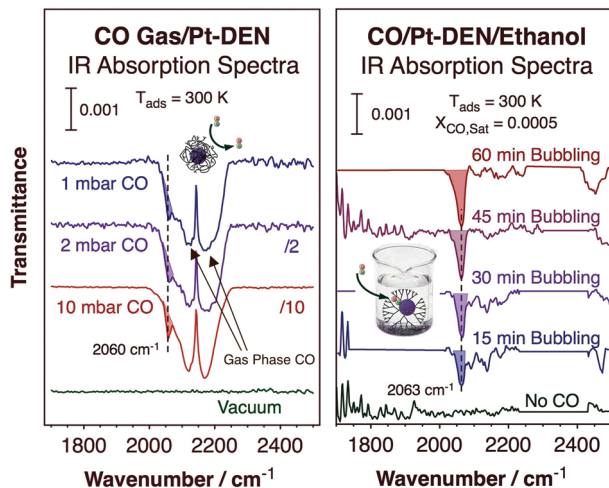
An alternative procedure for the controlled growth of metal nanoparticles is to use organic dendritic structures as scaffolds. Dendrimers are molecules with repeated motives multiplied at branched intersections. One powerful characteristic of dendrimers is that they can be synthesized in a stepwise fashion in order to control their size, which is done by repeating similar addition chemistry at each branching generation; near perfect polydispersity can be achieved even at high molecular weights this way.<sup>77</sup> Dendrimers by themselves have found multiple applications in catalysis and nanotechnology, and additional catalytic functionality, in the form of active metal centers, for instance, can be tethered at the termini of the dendritic branches as well.<sup>78,79</sup> More relevant to this review, dendrimers can also be used to grow metal nanoparticles.<sup>80</sup> This can be achieved by complexing metal ions with specific molecular centers such as the amine groups present in some dendrimers such as polyamidoamines (PAMAMs), and then reducing the composites to yield zero-valent dendrimer-encapsulated nanoparticles (DENS). Because dendrimers have a well-defined number of centers for complexation, this titration-like approach leads to the growth of nanoparticles with a fixed number of constituent atoms. That number can be varied by using dendrimers of different sizes (different generations).

Metal DENS have been used in solution for several catalytic processes.<sup>81–86</sup> Characterization experiments on the adsorption of carbon monoxide on the metal surface of untreated DENS, either by themselves or dispersed on a high-surface-area support, have indicated that in the gas phase the metal surface is usually not available for adsorption or reaction.<sup>87–89</sup> However, in a proper solvent, adsorption is possible (Fig. 2),<sup>87,89</sup> suggesting that these DENS may be used as they are for liquid-phase catalysis.<sup>90</sup> Examples are also available on the use of DENS in electrocatalysis.<sup>86,91</sup>

In heterogeneous catalysis, to make supported metal catalysts, this dendrimer synthetic route has mainly been used to create small nanoparticles, with diameters on the order of 1–2 nanometres, which are difficult to grow and make stable by colloidal chemistry.<sup>84</sup> Examples include studies on the oxidation of carbon monoxide on supported platinum<sup>92</sup> and gold,<sup>93</sup> as well as on the selective reduction (SCR) of NO<sub>x</sub> on Pt.<sup>94</sup> With hydrocarbons, studies can be found on the hydrogenation of ethylene on supported Pt and Rh catalysts<sup>95</sup> and of benzene and toluene on supported Pt,<sup>36,96,97</sup> on the hydrogenation and isomerization of butenes on supported Pt,<sup>30</sup> and on the hydrogenolysis of pyrrole on Pt.<sup>98</sup> However, the database of heterogeneous catalysis performed with samples made out of DENS is still small. In general, it is clear that the DENS-based catalyst preparation can lead to narrow size distributions, yet no obvious justification has been offered on why this expensive route should be chosen for specific applications. Perhaps more fundamental studies indicating the need of particular small nanoparticle sizes may provide compelling support for this approach.

One important issue associated with the growth of metal nanoparticles with either colloidal or dendrimer chemistry is





**Fig. 2** Contrasting behavior of dendrimer-encapsulated platinum nanoparticles (Pt-DENs), in terms of CO adsorption as probed by infrared (IR) absorption spectroscopy, between gas (left panel) and liquid (right panel) phases.<sup>89</sup> Adsorption in the gas phase is limited, reversible, and only visible, as a peak at  $2060\text{ cm}^{-1}$ , in the presence of gas-phase CO (which is responsible for the two broad features at  $\sim 2125$  and  $2175\text{ cm}^{-1}$ ); all IR peaks disappear immediately upon pumping. Spectra recorded with Pt DENs suspended in ethanol, on the other hand, show a significant amount of CO irreversibly adsorbed on the Pt surface (indicated by the peak at  $2063\text{ cm}^{-1}$ ). The data indicate that the dendrimer structure may collapse and block the surface of the metal under gas-phase conditions, but may open up and allow for metal exposure to the adsorbates if suspended in a liquid solvent. Reproduced from ref. 89 with permission, Copyright 2010 The American Chemical Society.

that, once dispersed on the high-surface-area support, the metal needs to be activated for catalysis, which means that the organic matter needs to be removed. Several procedures have been attempted for this, including oxidation–reduction cycles, ozonolysis, and UV treatments, but none of those have proven completely satisfactory. The challenge is that the surface of the nanoparticles needs to be cleaned without them losing their original size (and shape) distribution.<sup>67</sup> In one study directed at the evaluation of UV/ozone cleaning treatments, it was determined that such procedures may perturb the surface structure of the nanoparticles, significantly modifying their catalytic properties, even without altering their size or overall shape.<sup>99</sup> In another report, UV/ozone treatments were found to be effective in removing the poly(vinylpyrrolidone) (PVP) and tetradecyl tributylammonium bromide (TTAB) capping layers of platinum nanoparticles without modifying their overall shape.<sup>100</sup>

Several studies<sup>88,95,101,102</sup> have indicated that although some of the organic matter may need to be removed from the surface to activate the catalyst, keeping at least some of those fragments may help avoid particle sintering,<sup>103,104</sup> protect them from oxidation or other degenerative processes, and even modify their electronic surface properties in beneficial ways.<sup>105</sup> In fact, it has been shown that mild reduction treatments such as reductions in hydrogen atmospheres at low temperatures sometimes lead to better catalytic activity even if some of the organic matter is left behind,<sup>30,95,102</sup> perhaps because the remaining carbonaceous deposits may actually aid in the performance of the catalyst.<sup>11</sup> Of course, that behavior is likely to be highly dependent on the nature of the catalytic reaction being promoted: the beneficial role of the

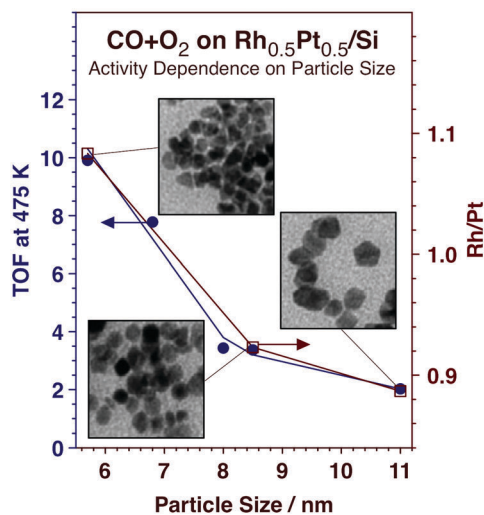
carbonaceous layer is expected in many hydrocarbon-conversion reactions, but has been shown not to work for the oxidation of carbon monoxide.<sup>106</sup>

## 5. Bimetallic catalysts

Another important parameter that may be controlled by the use of colloidal or dendrimer based synthetic methodologies is the composition of nanoparticles. In the case of metals in particular, the electronic structure may be fine-tuned by mixing two or more metals, something that is commonly done in catalysis in order to promote specific pathways.<sup>107,108</sup> 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.<sup>16</sup>

Bimetallic and alloyed catalysts were already introduced in industrial applications many years ago, but, thanks to the new nanotechnology synthetic methodologies being introduced in recent times, it is now possible to prepare bimetallic nanoparticles with much better control on composition and structure, with specific distributions of the constituent elements throughout the depth profile of the nanoparticles. For example, a few reports are available on the catalytic activity of DEN-made bimetallic catalysts such as Pt–Au,<sup>109,110</sup> Pt–Cu,<sup>111</sup> Pd–Au,<sup>112</sup> and Ni–Au.<sup>113</sup> In many of these mixed systems, a synergy was identified, with the bimetallic particles showing higher catalytic activity for CO oxidation (and, in some cases, lower activation for hydrocarbon hydrogenations) than the individual metals. In principle, these structures may be used to selectively promote specific reactions.

The use of colloidal and dendrimer-based syntheses can also afford samples suited to contrast the performance of well-mixed alloys *versus* layered arrangements.<sup>84,114,115</sup> An understanding of the effect of the distribution of the different components within a given nanoparticle is not fully developed yet. On one hand, this effect may be limited by the high mobility of atoms in such small particles, which means that the initial distribution of metals within a given particle established by a given synthetic methodology may easily be lost upon thermal treatment or because of the chemisorption of reactants during catalysis; it may not be possible to retain specially tailored composition profiles in bimetallic catalysts. An elegant illustration of this phenomenon can be found in the study of the reversible segregation of Rh and Pd atoms to the surface of  $\text{Rh}_{0.5}\text{Pd}_{0.5}$  nanoparticles under alternating oxidizing and catalytic conditions during the conversion of NO with CO.<sup>116</sup> On the other hand, it is clear that bimetallic nanoparticles can display unique catalytic behavior, and that such behavior can change depending on the way they are prepared. For instance, the oxidation of carbon monoxide with  $\text{Pt}_{0.5}\text{Rh}_{0.5}$  bimetallic particles was determined to display a noticeable dependence on overall particle size, with a higher activity was seen with smaller particles, presumably because a preferential promotion of segregation of rhodium to the surface is favored in those samples (Fig. 3).<sup>117</sup> As said above, a full understanding of why activity and selectivity can be tuned *via* the control of the



**Fig. 3** Example of changes in catalyst performance with average metal nanoparticle size in bimetallic samples. In this case, rhodium–platinum nanoparticles of nominal 50:50 atomic composition were dispersed on a silicon substrate and tested for their activity toward the oxidation of carbon monoxide.<sup>117</sup> The left (blue) scale and filled (blue) circles correspond to the turnover frequencies measured at 475 K. The decrease in activity with particle size indicated by those data was explained by a change in surface composition, measured by X-ray photoelectron spectroscopy (XPS). Right –red– scale and open –red– squares). Also shown are transmission electron microscopy (TEM) images (50 nm × 50 nm in size) for selected nanoparticle sizes. It was concluded that an increase in rhodium segregation with smaller nanoparticles facilitates the dissociation of O<sub>2</sub>, the limiting step of the reaction. Adapted from ref. 117 with permission, Copyright 2012 Elsevier.

initial distribution of each of the components within the bimetallic nanoparticles in spite of the dynamical changes that can occur in those under catalytic conditions awaits further research. What is clear is that the new colloidal and dendrimer-based synthetic routes added to the arsenal of catalyst preparation offer new powerful tools to prepare better-defined bimetallic samples for those studies.

## 6. Sol–gel growth

Additional catalytic engineering may be accomplished by addressing issues associated with the high-surface-area oxide supports often used in catalysis. Typically, an amorphous and highly porous solid, most often a silica or alumina powder, is used to disperse the active catalytic phase, the metal nanoparticles discussed above, for instance. The porous oxides traditionally used in catalysis have complex and ill-defined structures. If the sole role of such materials were to act as supports for the active phase, as they were originally conceived, a lack of control on their structural details would not be an issue. However, it has been determined that in many instances the support contributes to the performance of the catalyst, either because of its own surface functionalities or because of interactions with the active phase, which may create unique sites at the interface.

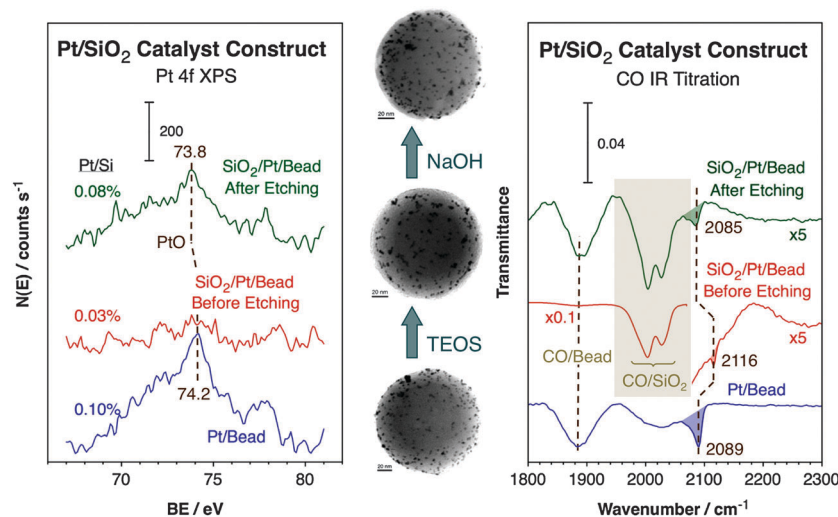
The nature of the support can be controlled during its synthesis. Alternatively, additional functionality can be added after dispersion of the catalytic active phase. Perhaps the most common synthetic approach to grow additional oxide material on an existing catalyst is sol–gel chemistry.<sup>118–120</sup> Sol–gel

processes are based on a two-step solid growth, where a molecular precursor, such as tetraethyl orthosilicate (TEOS) for silica growth, is hydrolyzed in water so the individual units first polymerize to form colloidal particles that then aggregate to form a solid gel.<sup>121</sup> Solvent removal and gel aging can be attained subsequently by heat treatments. The characteristics of the final product, in particular its porosity, may be controlled by adjusting a number of parameters during synthesis, including the pH of the solution, the stoichiometry of the reactants (in particular if mixed oxides are to be grown), the gelation temperature and time, and the choice of solvent.<sup>122</sup>

Although sol–gel chemistry has been available for some time already, it has nevertheless found some new and exciting applications in recent times in connection with catalyst preparations. In general, sol–gel synthesis can be used to make high-surface-area materials such as catalytic membranes and superacids,<sup>122</sup> and mixed oxides or solids with metal active phases intimately interlaced in the oxide network.<sup>123</sup> Sol–gel chemistry is also good to add thermal and mechanical stability, and can be used to prevent sintering in supported catalysts.

One approach for the preparation of thermally stable metal-based catalysts is by co-precipitation of the metal and the support in a one-step sol–gel process.<sup>124</sup> This technique was first reported by Reetz and Dugal to stabilize a liquid-phase Pd-based 1,5-cyclooctadiene hydrogenation catalyst.<sup>125</sup> An analogous procedure was used soon after to prepare encapsulated Pd–Au hydrogenation catalysts.<sup>126</sup> Those authors did not check on the thermal stability of their samples, but it has been later shown that, in some instances, it is possible to prevent the agglomeration of the metal particles during surfactant removal this way.<sup>127</sup> In one case, a modified sol–gel approach was designed for the preparation of low-temperature CO oxidation Au/SiO<sub>2</sub> and Au/CeO<sub>2</sub> catalysts where the metal nanoparticles were incorporated in what the authors characterized as an “open shell” of the oxide.<sup>128,129</sup> Similar procedures were later extended to the preparation of other supported catalysts, including samples made out of palladium nanoparticles dispersed in silica for the promotion of Suzuki coupling reactions,<sup>130,131</sup> of platinum on ceria for the water-shift reaction,<sup>132</sup> and of ruthenium on zirconia for ammonia decomposition.<sup>133</sup> Unfortunately, no long-term stability studies have been carried out on these catalysts to check for their stability under realistic conditions.

Alternatively, the metal nanoparticles may be dispersed onto the high-surface-area support and then covered with additional material, grown by sol–gel chemistry, in order to anchor and to add thermal stability to those nanoparticles. Increased thermal and electrochemical stability has indeed been reported by using this technique, by growing silica layers *via* sol–gel chemistry, on Pt/zeolite three-way catalysts,<sup>134</sup> on Pt catalysts dispersed on carbon supports, used for methane combustion<sup>135</sup> and for cyclohexane decomposition,<sup>136</sup> and on a Pt/Fe<sub>2</sub>O<sub>3</sub> water-shift catalyst.<sup>137</sup> This approach was also demonstrated by using a model catalyst based on silica beads decorated with Pt nanoparticles: the subsequent deposition of a mesoporous silica layer, used as a selective membrane, rendered the catalyst quite resistant against poisoning in H<sub>2</sub>S containing streams.<sup>138</sup> Other oxides can be added this way as well: in one example, titania was added to a Au/SiO<sub>2</sub> catalyst to create the



**Fig. 4** Pt 4f XPS (left), TEM images (center), and CO-adsorption IR absorption spectroscopy (right) evidence for the effectiveness of our surface-protected etching procedure in re-exposing platinum nanoparticles dispersed on silica supports (silica beads in this example) after their embedding in a layer of mesoporous silica grown by sol-gel chemistry.<sup>90,251</sup> Data are shown for the naked Pt-decorated silica beads, after deposition of a 20 nm layer of mesoporous silica, and after partial surface-protected etching of the latter using NaOH. The restoration of the accessibility of the Pt nanoparticles after etching is indicated by the renewed Pt 4f XPS peak and by the reappearance of the 2085  $\text{cm}^{-1}$  peak in the IR spectra, indicative of carbon monoxide chemisorbed on the platinum surface. Adapted and enhanced from ref. 90 with permission, Copyright 2012 John Wiley and Sons.

unique interface sites believed to be responsible for low-temperature CO oxidation catalysis.<sup>139</sup>

Unfortunately, encapsulation of metal nanoparticles in a solid matrix, either during co-deposition or if encapsulation is added afterward, is known to often limit exposure of metal nanoparticles to the reactant, and consequently decrease catalytic activity.<sup>140</sup> For instance, when a sol-gel silica layer was added to CO oxidation Au/TiO<sub>2</sub> catalysts, higher stability was indicated by retention of activity to higher temperatures than when using the naked catalyst, up to 975 K, but activity below 475 K was totally suppressed.<sup>141</sup> It is also important to point out that porous solids prepared by sol-gel methods keep evolving over long periods of time, typically aging by forming additional network bonds and closing up some pores. This means that additional treatments may be required to re-gain access to the surface of the embedded metal nanoparticles. The newly sol-gel deposited layer may, for instance, be partially etched, by using NaOH or another similar agent. However, such procedure may undo the added stabilization of the new silica layer. A novel surface-protected etching procedure was developed in our laboratory to prevent this problem, where a surfactant is used to inhibit silica etching at the outside surface and to promote pore opening.<sup>142</sup> Significant thermal stability of the Pt nanoparticles was obtained without sacrificing catalytic performance, which could be reinstated after proper etching (Fig. 4).<sup>11</sup> It may even be possible to use organic growth-directing agents to define the directionality and/or shape of the pores of the newly deposited mesoporous material.<sup>143</sup>

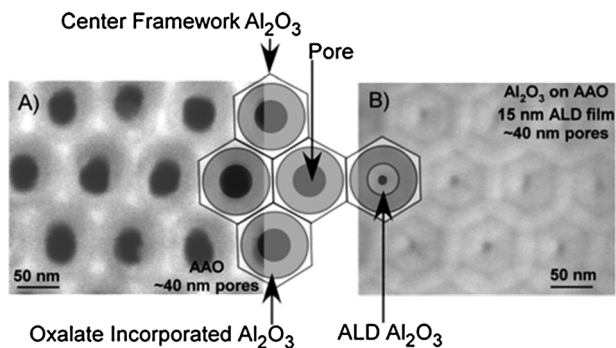
## 7. Atomic layer deposition (ALD)

Sol-gel methods are quite versatile and useful in catalysis, as discussed above, but offer limited control on the rate or extent of growth of the material being deposited. There are instances

where it is desirable to conformally deposit only a few monolayers of a given material, either because complete blocking of the active phase is to be avoided, or because extensive deposition may block the pores of the high-surface-area support, for instance. In order to deposit either metals or other materials with monolayer precision, recent interest has grown in adapting atomic layer deposition (ALD) processes to the preparation of heterogeneous catalysis.<sup>144,145</sup> ALD, which has mainly been developed in connection with the microelectronics and semiconductor industries,<sup>146,147</sup> relies on the separation of the surface chemistry used for the deposition into two self-limiting and complementary half-reactions, which are carried out in an alternating fashion.<sup>148,149</sup> This way, only sub-monolayer coverages of the desired material are deposited in each ALD cycle.

ALD can be used to make or modify the high-surface-area support used in many catalysts. The idea here is to prepare surfaces with well-defined properties that may be used for further catalyst development. However, one well known but not fully resolved issue in ALD is that it sometimes leads to the deposition of rough films, presumably because of the quality of the substrate used and/or the possible presence of nucleation sites on those where deposition is initiated. A nice example of how this effect can affect further catalytic activity is provided by a study on the growth of carbon nanotubes using iron nanoparticles dispersed on alumina as catalyst.<sup>150</sup> It was found that the catalytic activity of the Fe deposited on ALD-grown alumina was better than those seen on iron supported on sapphire or e-beam annealed surfaces, but worse than with alumina prepared by sputtering or e-beam procedures. Perhaps more importantly, it was also determined that both the Ostwald ripening of the catalysts and the porosity of the alumina support correlate with the lifetime and activity of the catalyst, with carbon nanotube growth being maximized by the low





**Fig. 5** Example of the use of atomic layer deposition (ALD) to modify the characteristics of catalyst supports at a molecular level. In this case, the diameters of the pores in a model porous alumina material made out of anodized aluminium oxide (AAO) were reduced *via* deposition of extra alumina layers.<sup>155</sup> Shown are SEM top view micrographs of the original AAO, displaying its 40 nm in diameter pores (a, left), and the same AAO after a 15 nm alumina layer grown by ALD, showing the remaining 10 nm pores (b, right). Reproduced from ref. 155 with permission, Copyright 2005 The American Chemical Society.

Ostwald ripening rates, mild subsurface diffusion rates, and high porosity obtained with the sputtered/Fe catalyst.

Another factor to consider in terms of the quality of the support of a catalyst is its crystallinity. By varying the deposition temperature and the film thickness, for instance, titania films can be deposited by ALD with different degrees of crystallinity, from amorphous to anatase and to anatase-rutile mixtures; in tests on the photocatalytic degradation of organic molecules, it was the latter that displayed the best activity.<sup>151,152</sup> Finally, the size and composition of the pores in porous solids can be modified by ALD as well. This is particularly useful when well-defined microporous or mesoporous materials are used. In catalytic membranes, for instance, pore reduction can be done in a controlled way by using ALD (Fig. 5).<sup>153–155</sup>

A second application of ALD in catalysis is as an alternative way to embed nanoparticles dispersed on the high-surface-area support, to prevent their sintering. The monolayer deposition control afforded by ALD can be used here to prevent the full coverage of the active surface, which may kill the activity of the catalyst. This application has been nicely demonstrated for the case of the decomposition of methanol on Pd/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>156</sup> The layer-by-layer addition of a protective alumina overlayer was shown to initially lead to the preservation of (in fact, to a slight increase in) the catalytic activity while preventing sintering of the Pd nanoparticles even at temperatures as high as 775 K. On the other hand, deposition of thicker layers, by using more ALD cycles, resulted in the complete inactivation of the catalyst. In another example, Pd nanoparticles were protected against coagulation by ALD-grown alumina.<sup>157</sup> It should be said that this ALD procedure is not always successful: in a case where protective silica layers were deposited on a Au/TiO<sub>2</sub> catalyst, for instance, increased thermal stability was indeed observed, but catalytic activity toward CO oxidation was also partially suppressed.<sup>158</sup> Moreover, as mentioned before, long-term stability studies are still required to test these approaches under more realistic industrial conditions.

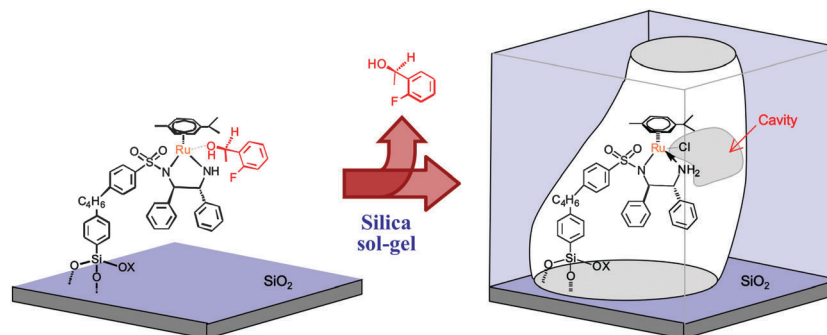
ALD can be used to deposit the active phase of a catalyst in a controlled manner as well. In one example, the ALD growth of tungsten oxide on SBA-15 mesoporous silica was shown to lead to alcohol dehydration catalysts with better dispersion and better thermal stability than those prepared by conventional impregnation methods.<sup>159</sup> In another case, an ALD method was used for the controlled preparation of bilayered vanadia/titania/silica catalysts: the improved activities seen toward both ammonia conversion<sup>160</sup> and *o*-xylene oxidation,<sup>161</sup> compared to those seen with conventional silica and titania supported samples, were ascribed to new V–O–Ti bonds. The selectivity of more complex Mo–V–Te–Nb intermixed oxide for propane ammoxidation could also be improved in another study by the selective growth of specific planes *via* ALD.<sup>162</sup> With metals, ALD has been used to control their extent of deposition, as was the case with platinum on carbon supports, where very low loadings could be accomplished: catalysts active for CO oxidation with metal loadings as low as 0.05 wt% have been made this way.<sup>163,164</sup> In general, ALD can be used to better control the nucleation and growth of metal nanoparticles on oxide supports, to lead to better dispersed samples.<sup>165,166</sup> ALD has also been used to obtain well-intermixed bimetallic catalysts.<sup>167</sup>

## 8. Use of organic structure-directing agents

Selectivity in heterogeneous catalysis may be further enhanced by developing materials with specific environments surrounding the catalytic active sites. In particular, the size and shape of the pores within the high-surface-area supports may be tailored to favor the access, adsorption, or formation of the desired molecules. Most traditional catalysts have been based on amorphous porous solids, and limited if any control is possible on the characteristics of the pores in such materials. However, the incorporation of zeolites to catalysis changed that. Zeolites are crystalline in nature, and display very specific pore structures. By choosing the appropriate materials, with pores of well-defined size and shape, it has been shown that, in some instances, the appropriate products can be selected.<sup>168</sup> Perhaps the best example of this use of zeolites is in the selective production of *para*-xylene, a feedstock in polyester production, using the 10-member-ring ZSM-5 zeolite.<sup>169</sup> Another well-known case of shape-selective catalysis involves the use of the 10-member-ring SAPO-11 zeolite to remove normal paraffins selectively from lubricating oils, leaving the branched paraffins behind.<sup>170,171</sup> A more recent system is that of the selective acylation of toluene to *para*-methylacetophenone with small-crystal-size zeolite beta.<sup>172</sup>

The first zeolites used for catalysis were taken from naturally occurring minerals, but new materials have since been developed by using modern synthetic methods. One way to design and control the growth of porous solids with specific dimensions is to use organic structure-directing agents.<sup>173</sup> The main function of these agents can be characterized as either space-filling, structure-directing, or templating.<sup>174</sup> In all cases, a solid is built around these organic agents, which are eliminated afterwards either by washing with an appropriate solvent or *via* calcination. The structural and electronic details of the organic molecules used in these syntheses define the characteristics of the pores made.





**Fig. 6** Schematic illustration of the synthetic methodology used to imprint well-defined cavities around a coordination site in an anchored ruthenium organometallic catalyst.<sup>195</sup> An *ortho*-hydroxybenzhydrol ligand is initially coordinated to a Ru complex tethered to a silica surface, and used as a templating agent for the casting of an enantioselective cavity via the deposition of additional silica by sol–gel chemistry. Figure courtesy of Zhihuan Weng and Mizuki Tada, adapted from ref. 195 with permission. Copyright 2012 John Wiley and Sons.

The significant advances made in recent years in these synthetic methods include their extension to the specific design of selective catalysts, many in connection with hydrocarbon isomerizations, alkylations, and aromatization reactions in oil processing.<sup>175</sup> Pore shape selectivity may also have a particular big impact in the production of fine chemicals,<sup>176</sup> as has already been shown in the cases of making diaminodiphenylmethane (a key intermediate in the production of polyurethanes),<sup>177</sup> the ammoximation of cyclohexanone to produce  $\epsilon$ -caprolactam (an intermediate for the production of Nylon-6),<sup>178</sup> and the carbonylation of methanol for the production of acetic acid.<sup>179</sup> It may even be possible to make and use chiral mesoporous materials<sup>180,181</sup> to promote catalytic reactions enantioselectively, although that promise has not been realized yet.

The use of organic structure-directing agents is even more critical for the production of mesoporous materials, where the inside pores are somewhere between 2 and 50 nm in diameter. This approach was introduced in catalysis in a big way with the developing of the so-called MCM-41 materials, high-surface-area aluminosilicate molecular sieves with uniform one-dimension hexagonal mesopores whose dimensions can be tailored to have diameters in a range from  $\sim 1.5$  to greater than 10 nm.<sup>182,183</sup> These solids are synthesized by using a templating mechanism, in which the liquid crystal structure of the surfactant serves as an organic template. A second popular mesoporous material is SBA-15, another silicate with well-defined hexagonal mesopores.<sup>184</sup> Newer versions of these mesoporous materials are still being developed.<sup>185</sup> All these supports have been incorporated in numerous catalytic processes at a research level, but their industrial applications have so far been limited.<sup>186,187</sup> The large pore sizes of these solids allow for the fixation of large active complexes on the walls of its pores, reduce diffusional limitations of reactants and products, and enable reactions involving bulky molecules to take place, but also provide no particular advantages in terms of shape selectivity, as zeolites do. In addition, the larger pore sizes of mesoporous materials, compared to those in zeolites, are sometimes desirable when dealing with large reactants, but make the solids intrinsically less stable.

Both zeolites and mesoporous materials exhibit some order at the atomic level, and have fairly symmetric structures. Also,

the nature of the pores is defined during the synthesis, and is fixed; to obtain a specific catalytic performance, additional functionality from metal nanoparticles or derivatization agents needs to be incorporated afterward. This may limit the ability to custom-make void spaces, to exert control over reaction selectivity, in particular if subtle effects such as those associated with stereo- and enantio-chemistry are sought. In fact, all that is required in those cases is that the environment surrounding the catalytically active site provides the structural constraints to direct reactivity, and this only needs to be achieved at a local level. Catalytic cavities with specific shapes may in principle be imprinted on a material added after dispersion of the active phase on the support, a polymer or a sol–gel silica layer, for instance, by using sacrificial organic templates.<sup>188–192</sup> Such an approach has been successfully tested recently, in one case with a Ru-based catalyst on a silica surface for the selective reduction of acetophenones.<sup>193–195</sup> By using an imprinting organic agent similar in shape as the transition state or the product of the reaction, high catalytic selectivity, even enantioselectivity, may be possible. For instance, the scheme in Fig. 6 was used to create chiral pockets around a ruthenium organometallic compound tethered to a silica surface to promote the asymmetric transfer hydrogenation of acetophenones with some enantioselectivity.<sup>194</sup> 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.

## 9. Dumbbells, core@shell, and other nanostructures

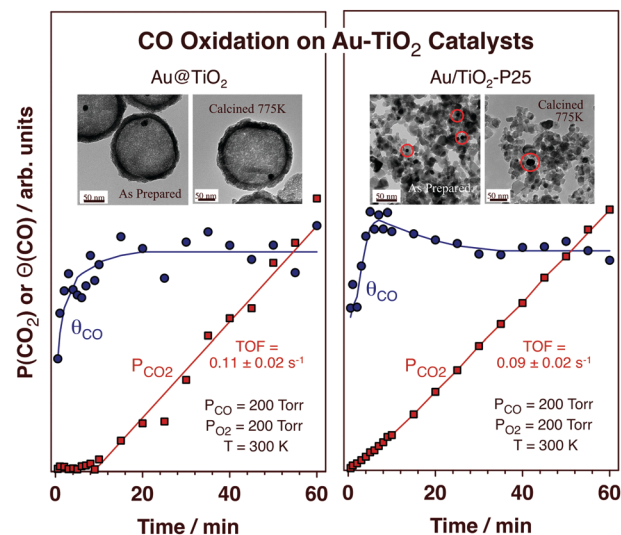
The first heterogeneous catalysts were by and large directed at the promotion of simple reactions such as ammonia synthesis and oxidation, methane formation from carbon monoxide and hydrogen, and the reduction of nitrogen oxides. However, in more recent times the demands imposed on catalysis have become much more stringent, with high selectivity requirements in conversions where many competing pathways may be available. It has been determined that, often, a single functionality in a catalyst may not be sufficient to fulfill those requirements.

Accordingly, many modern catalysts are designed with multiple, separate functionalities. An early example of this can be seen in the oil industry, where hydrocarbon reforming is typically promoted with metal particles, which act as hydrogenation-dehydrogenation agents, dispersed on an acidic support, the phase responsible for most of the isomerization, cyclization, and aromatization steps.<sup>196</sup>

By affording the assembly of different nanostructures into one single unit, nanotechnology is ideally suited to design multiple functionality catalysts. In this approach, building a catalyst may be viewed as a molecular-level version of a Tinkertoy (or Lego) set, where each individual functionality is incorporated as a separate piece and assembled together with appropriate nanotechnology chemistry. Of course, the problem can be much more complex than implied by this crude description, since not only the individual functionalities need to be preserved and kept from interfering with all others upon assembly, but they also need to be made to work together in a design where the ferrying of the reactants from one site to the next, in the right order, is possible. On the positive side, the interfaces formed by assembling two or more different materials can also display, themselves, unique and desirable catalytic properties. On the whole, this idea of assembling catalysts one functionality at a time has recently taken prominence, and offers great promise for the development of new, complex and highly selective catalytic processes.

Some nanostructures in particular have proven relatively simple to assemble to potentially address concrete issues in catalysis. One common family of nanostructures is based on the form of a dumbbell, which has been tested in several electrochemical and photochemical processes. For instance, in one case,<sup>197</sup> mono-dispersed dumbbell-like Pt-Fe<sub>3</sub>O<sub>4</sub> nanoparticles were developed for the electrocatalytic reduction of oxygen. It was shown that the advantages of using this type of assemble is that it provides a way to tune the sizes of the Pt and Fe<sub>3</sub>O<sub>4</sub> nanoparticles independently and to optimize the size and nature of the Pt-Fe<sub>3</sub>O<sub>4</sub> interface and with that the activity of the catalyst. Similar Au-Fe<sub>2</sub>O<sub>3</sub> dumbbell catalysts have also been shown to possess the unique interfacial characteristics that lead to high CO oxidation activity.<sup>198</sup> In the electrochemical reduction of H<sub>2</sub>O<sub>2</sub>, the superior performance of Au-Fe<sub>2</sub>O<sub>3</sub> dumbbell catalysts was ascribed to polarization effects from the gold to the iron oxide.

Another nanoarchitecture much exploited recently in catalysis is that based on core@shell structures.<sup>199,200</sup> Typically, a transition metal is encapsulated by an outer layer of a porous oxide, with a void space sometimes added in between in a yolk@shell or rattle-type configuration.<sup>201–205</sup> Several functionalities may be added to the core catalysts by the use of such shells, among them their protection from the outside environment, the preservation of their compositional and structural integrity, and the prevention of their aggregating or sintering into larger particles. Moreover, the porosity and chemical composition of the surfaces of the shells can also be tuned to selectively control the percolation of molecules in and out of their interior, to increase the solubility and/or biocompatibility of the overall nanostructure, and to add new physical or chemical properties.<sup>199,206,207</sup> The performance of this type of



**Fig. 7** Illustration of the performance of yolk@shell catalysts. In this example, both the coverage of CO on the gold surface and the accumulation of CO<sub>2</sub> are plotted as a function of time for experiments on the catalytic oxidation of CO with O<sub>2</sub> at room temperature in an enclosed reactor.<sup>208</sup> Data are reported for two samples: a Au@TiO<sub>2</sub> yolk@shell nanostructure (left) and a regular Au/TiO<sub>2</sub>-P25 dispersed catalyst (right). The key result from this study is that, whereas the yolk@shell nanostructure provides much more thermal stability to the catalyst, as indicated by the TEM images provided for the samples as prepared and after calcination at 775 K (the gold nanoparticles sinter in the Au/TiO<sub>2</sub>-P25 but not in the Au@TiO<sub>2</sub> catalyst), it still displays a similar catalytic activity per gold surface site as a conventional gold-on-titania material. Adapted from ref. 208 with permission. Copyright 2011 John Wiley and Sons.

catalysts is illustrated in Fig. 7 for the case of gold nanoparticles embedded inside hollow titania shells, with which additional stability of the gold nanoparticles was achieved without sacrificing specific catalytic activity for CO oxidation.<sup>208</sup> It should be noted that the shells in most of these core@shell and yolk@shell nanostructures are quite porous, making the core phase easily accessible to many (small) molecules both in gas<sup>90,208,209</sup> and liquid phases.<sup>210</sup> Crystalline<sup>211</sup> and multi-Au-nanoparticle<sup>212,213</sup> versions of this Au@TiO<sub>2</sub> nanostructures, where the shells are mostly composed of anatase, have also been shown to work well in photocatalysis.

More complex nanostructures are also possible. For instance, combinations of dumbbell and core@shell catalysts have been developed for photocatalytic applications, to both help with electron-hole pair separation following light absorption and physically separate the reduction and oxidation steps that follow.<sup>214,215</sup> Other nanoarchitectures with potential uses in catalysis include double-shelled,<sup>202,216</sup> multiply encapsulated,<sup>217</sup> and clustered<sup>218,219</sup> structures.

## 10. Surface derivatization, tethering, and immobilization

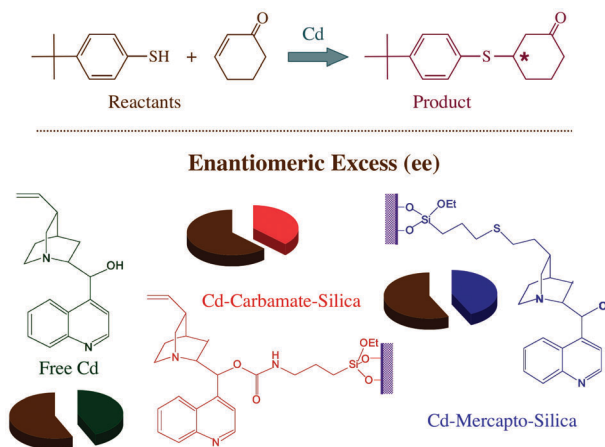
The nanotechnologies described above certainly provide new ways to develop solid materials with unique well-defined shapes and properties. These are required to tailor the catalytic

sites needed for selective catalysis. Nevertheless, it has not been possible yet to use these solid-state synthetic procedures to produce catalytic sites with the level of sophistication possible in homogeneous catalysis, where discrete molecules, typically organo-metallic complexes, are used. Such molecular control of the structural and electronic properties of the catalytic pocket is often required for the manufacturing of specific chemicals, the fine chemicals used in the pharmaceutical industry, for instance.

One option to address this shortcoming of the nanotechnology synthetic approaches discussed so far is to develop hybrid structures, where specific nanoarchitectures, made by any of the methods described in this review, are then modified at their surfaces *via* the addition of new molecular functionality. The latter step can be performed by derivitizing such surfaces with particular chemicals, or by tethering or immobilizing specific molecules, even homogeneous catalysts.<sup>220,221</sup> This way, the degree of selectivity that can be obtained with discrete molecular catalysts can be further enhanced by adding new shapes and pockets in the surrounding environment, or a second functionality provided by the surrounding solid surface. The heterogenization of molecular functions provides additional advantages, such as ease of separation of the catalyst from the reactants and products and an increase in solubility in particular solvents.

The anchoring of molecular catalysts to solid supports has been explored for several decades already, but the results from that research have been mixed.<sup>222</sup> Indeed, there have been some interesting development in this field, and even the identification of promising leads, but final incorporation in industrial processes of heterogenized catalysts based on the tethering of known homogeneous catalysts has rarely been achieved. In one case, an iridium-based catalyst was immobilized on silica gel *via* modular covalent-bond chemistry in order to promote the enantioselective hydrogenation of a hindered *N*-arylimine used for the production of (*S*)-metolachlor.<sup>223,224</sup> The best heterogeneous catalyst made this way exhibited excellent performance in terms of enantioselectivity, turnover frequencies, and turnover numbers, among the best among immobilized catalysts, but the activity was still below that seen with the free Ir complex, and the solid catalyst deactivated faster as well. Another example is that of the tethering of olefin-metathesis catalysts to solid surfaces, a problem for which several strategies have been tested but where the activity of the homogeneous catalysts has not yet been matched.<sup>225</sup> The reasons for this mismatch in performance between the homogeneous and anchored catalysts is not yet fully understood, but may have to do with several factors, including the rigidity added by the anchoring and the confined environment of the pores where the catalyst resides, the liability of the ligands used for anchoring, which may lead to leaching of the catalyst out of the support, and the intrinsic activity of the solid, which may interfere with the finely-tuned electronic properties of the original catalytic center.

Surface derivatizations can also be used to modify the catalytic performance of the solid itself, by adding molecular functionalities to it, typically acid or basic sites.<sup>220</sup> The tethering of specific moieties to surfaces, to oxides in particular, has been greatly facilitated by the development of the so-called "click"



**Fig. 8** Enantiomeric excesses (ee), expressed as fractions of unity in the indicated pie charts, of the product from addition of *p*-tert-butylbenzenethiol to 2-cyclohexene-1-one catalyzed by cinchonidine (Cd).<sup>228</sup> Data are contrasted for three cases, in reactions using free Cd in solution (left) and for two versions of Cd tethered to aerosil silica surfaces by using a 3-triethoxysilylpropyl linker, with a carbamate link through the alcohol moiety of Cd (center) and *via* a mercapto linkage at the vinyl position (right). Comparable enantioselectivities were obtained with the solution *versus* tethered catalysts, especially between the free Cd and the anchored mercapto species, but only after several interferences from the support and the silyl moiety of the linker were minimized.

chemistry, by which the desired molecules are attached to the surface *via* the intermediate use of a linking molecule. This modular approach offers much flexibility, allowing for the independent control of the surface sites, length and properties of the linker, and nature of the terminal functionality.<sup>220,225,226</sup> One example from our laboratory, where cinchonidine molecules were tethered to silica supports to impart enantioselectivity to catalytic reactions involving tertiary amines, illustrates the power of this approach, but also offers a cautionary tale on its potential pitfalls.<sup>227,228</sup> Ultimately, similar activity and enantioselectivity could be achieved for the addition of *p*-tert-butylbenzenethiol to 2-cyclohexene-1-one with surface-cinchonidine-derivatized catalysts *versus* free cinchonidine (Fig. 8), but only after addressing a number of complications introduced by the silica support, which included the non-selective catalytic activity of the acidic surface of the solid itself, the activity of the OH species generated by hydrolysis of some of the Si-alkoxy groups in the trialkoxy moieties used to bind the linkers to oxide surfaces, and the bonding of the molecule to be tethered directly to the surface.<sup>228</sup>

More than one type of functionality can be added to the surface this way, even antagonistic functions that cannot coexist in solution,<sup>229–231</sup> but preparing catalysts where those functions are correlated by way of their physical proximity is a challenge.<sup>232–234</sup> A related approach to the molecular design of catalytic sites on surfaces is the tethering of complex organic structures as frameworks for the addition of an active phase such as a metal ion or a small nanoparticle. Calixarenes and other cavitands, crown ethers, and thiol-based self-assembling hydrocarbon chains have proven particularly useful for this application, to mimic sites similar to those seen in enzymes, for instance,<sup>235,236</sup> or by encapsulating nanoparticles in well-defined

structures.<sup>237–239</sup> However, only a few studies have been carried out to date in this direction, and virtually no applications for catalysis are known yet.

## 11. Final remarks

As stated in the introduction, the field of catalysis has a long and illustrious history already. Nevertheless, it is our belief that it still has much more new to contribute. In fact, with the incorporation of the new nanotechnologies briefly discussed in this review, heterogeneous catalysis has the potential to undergo a renaissance and to address many modern industrial processes not previously accessible to it. For one, it may be able to offer new creative solutions to issues associated with the harvesting, storage, and use of energy.<sup>240</sup> This may include ways to make biofuels<sup>241</sup> or hydrogen,<sup>242</sup> which could potentially be produced photocatalytically, by harvesting sun light,<sup>215</sup> and also to improve on the performance of fuel cells.<sup>243</sup> In terms of environmental remediation issues, further advances on the catalytic converters already developed to treat exhaust gases in automobiles are needed to address byproducts from diesel engines and stationary sources, and additional processes are desirable to treat indoor air and wastewaters.<sup>244</sup> It would be particularly interesting if catalysts could be found to efficiently convert carbon dioxide to other chemicals, both to remove such green gas from the atmosphere and to use the carbon as a starting material for energy storage.<sup>245</sup>

The expansion of the range of applications of catalysis to industrial processes relies on our ability to develop new effective and selective catalysts. One interesting development in modern times has been the discovery of the activity and versatility of gold as catalyst when used in nanosize form. Such gold-based materials have proven promising in many low-temperature oxidations<sup>39</sup> and bond-forming reactions,<sup>246</sup> but problems with stability need to be solved before they become useful in practical applications. Selective catalysts are also still required for the manufacturing of many fine chemicals.<sup>247,248</sup> The selective partial oxidation of hydrocarbons, for instance, is still an unresolved and quite general challenge.<sup>249,250</sup> Moreover, almost all modern pharmaceuticals rely on chiral compounds, so the addition of enantioselectivity to heterogeneous catalysts could offer a new approach to the production of high-value chemicals.<sup>224</sup> High selectivity in catalysis requires great control over the design and manufacturing of the active sites in catalysts. This may now be possible to an extent not available before the recent growth experienced by the nanotechnology field.

In some respects, the field of nanotechnology is ahead of that of heterogeneous catalysis in this quest. Many synthetic protocols have already been developed for the making of complex nanostructures with well-defined characteristics. Some of those approaches have been introduced above. Although they still display some limitations, and although no solids with active sites as complex and selective as those available in homogeneous catalysis can be made yet, there are still many types of solids that can be made now that were not accessible before. It is to the credit of the nanotechnology community that they have been able to make so much progress in developing their new synthetic methods in such a short period of time.

A word of caution is warranted at this point in our discussion. Having access to so many new types of nanoscaled solids offers the temptation to proceed with their indiscriminate test in catalysis. In fact, some of this is already going on: many synthetic groups develop new preparation techniques to make novel solids first, and search for possible applications afterward. Such a sequence of events may lead to an endless search with little reward, as the parameter space for the development of catalysts is vast and complex. Motivation may be obvious in some cases, as discussed above in terms of ways to increase catalyst stability or to carve specific catalytic sites in solid supports, but it is not as clear in others, such as when specific particle shapes are developed.

Here we advocate for a more targeted approach instead, where the knowledge obtained from mechanistic studies in catalysis is generated first and then used to direct the design of new catalysts. Surface-science and quantum-mechanics calculations can be first employed to determine the requirements for the catalytic sites of specific processes, and that information can then be input into the design and synthesis of the corresponding nanomaterials. A few examples of this synergy between surface-science and nanotechnology have been provided above already, including the mechanistic studies that led to the development of shape-selective catalysts for olefin *cis-trans* isomerization reactions that combined several UHV-based surface-sensitive techniques such as temperature programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS),<sup>60,61,68</sup> a correlation study between particle size and shape and alcohol activation that used scanning tunneling microscopy (STM) and X-ray absorption spectroscopy (XAS),<sup>48</sup> the characterization of the removal of organic matter from colloidal- and dendrimer-based synthetic methods to grow metal nanoparticles using infrared,<sup>30</sup> sum-frequency generation (SFG),<sup>100</sup> and X-ray photoelectron spectroscopy (XPS),<sup>30,100,106</sup> and the titration of metal sites in dendrimer-based,<sup>88,89</sup> mesoporous-protected,<sup>142,251</sup> and core-shell and yolk-shell<sup>208,209,252</sup> catalysts using carbon monoxide and infrared spectroscopy.<sup>90</sup> Nevertheless, the examples available to date on this are still quite limited. We emphasize that only by taking full advantage of the synergy between the surface-science and catalysis and nanotechnology communities it will be possible to efficiently adapt the advances made by the latter into useful applications for the former.

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