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Concepts in Nanocatalysis

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1.1

Introduction

Catalysis occupies an important place in chemistry, where it develops in three directions, which still present very few overlaps: heterogeneous, homogeneous and enzymatic. Thus, homogeneous and heterogeneous catalysis are well-known as being two different domains defended by two scientific communities (molecular chemistry and solid state), although both are looking for the same objective, the discovery of better catalytic performance. This difference between homogeneous and heterogeneous catalysis is mainly due to the materials used as catalysts (molecular complexes in solution versus solid particles, often grafted onto a support), as well as to the catalytic reaction conditions applied (for example liquid-phase reactions versus gas-phase ones). Considering the advantages of these two catalytic approaches, on the one hand heterogeneous catalysts are easy to recover but present some drawbacks, such as the drastic conditions they require to be efficient and the mass transport problems; on the other hand, homogeneous catalysts are known for their higher activity and selectivity, but the separation of expensive transition metal catalysts from substrates and products remains a key issue for industrial applications [1]. The first attempts to bridge the gap between these two communities date from the 1970s to the early 1980s. From one side chemists working in the molecular field, such as J.M. Basset, M. Che, B.C. Gates, Y. Iwasawa and R. Ugo, among others, initiated pioneering works on surface molecular chemistry to develop single-site catalysts, and/or reach a better understanding of conventional supported catalyst preparation through a molecular approach; from the other side, chemists of the solid state, such as G. Ertl and G. Somorjai, were interested in the molecular understanding of surface chemical catalytic processes. For the latter, the revolutionary development of surface science at the molecular level was possible thanks to the development of techniques of preparation of clean single crystal surfaces and characterization of structure and chemical composition under ultrahigh vacuum [(X-ray photoelectron spectroscopy (XPS), atomic emission spectroscopy (AES), low energy electron diffraction (LEED) etc]. Once again, although these scientists aimed at a common objective, little interaction or cross-fertilization action

has appeared during the last 20 years. One should however cite the first International Symposium on Relations between Homogeneous and Heterogeneous Catalysis, organized on Prof. Delmon's initiative in Brussels (Belgium) in 1973. Interestingly, this event appeared 17 years after the first International Congress on Catalysis (Philadelphia, 1956) and 5 years before the first International Symposium on Homogeneous Catalysis (Corpus Christi, 1978). In parallel, although colloidal metals of Group 8 were among the first catalysts employed in the hydrogenation of organic compounds, the advent of high pressure hydrogenation and the development of supported and skeletal catalysts meant that colloidal catalysis has hardly been explored for many years [2–4].

Since the end of the 1990s, and with the development of nanosciences, nanocatalysis has clearly emerged as a domain at the interface between homogeneous and heterogeneous catalysis, which offer unique solutions to answer the demanding conditions for catalyst improvement [5, 6]. The main focus is to develop well-defined catalysts, which may include both metal nanoparticles and a nanomaterial as support. These nanocatalysts should be able to display the ensuing benefits of both homogenous and heterogeneous catalysts, namely high efficiency and selectivity, stability and easy recovery/recycling. Specific reactivity can be anticipated due to the nanodimension that can afford specific properties which cannot be achieved with regular, non-nano materials (Figure 1.1).

In this approach, the environmental problems are also considered. Definitions can be given: the term 'colloids' is generally used for nanoparticles (NPs) in liquid-phase catalysis, giving rise to 'colloidal catalysis,' while 'nanoparticle' is more often attributed to NPs in the solid state, thus related to the heterogeneous catalysis domain. The terms 'nanostructured' or 'nanoscale' materials (and by extension 'nanomaterials') are any solid that has a nanometer dimension. Despite these differences in nomenclature, NPs are always implicated and 'nanocatalysts' or 'nanocatalysis' summarize well all the different cases.

In the nanoscale regime, neither quantum chemistry nor the classical laws of physics hold. In materials where strong chemical bonding is present, delocalization of electrons can be extensive, and the extent of delocalization can vary with the size

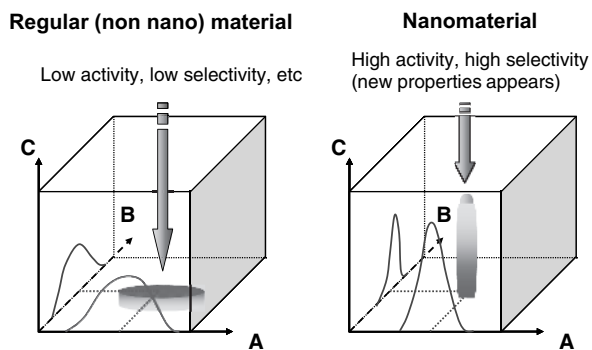


Figure 1.1 Nanoarchitecture: an avenue to superior precision. Axes are: A: composition of functional sites; B: ordering level of sites; C: functional properties of material.

of the system. This effect, coupled with structural changes, can lead to different chemical and physical properties, depending on size. As for other properties, surface reactivity of nanoscale particles is thus highly size-dependent. Of particular importance for chemistry, surface energies and surface morphologies are also size-dependent, and this can translate to enhanced intrinsic surface reactivity. Added to this are large surface areas for nanocrystalline powders and this can also affect their chemistry in substantial ways [7]. Size reduction to the nanometer scale thus leads to particular intrinsic properties (quantum size effect) for the materials that render them very promising candidates for various applications, including catalysis. Such interest is well established in heterogeneous catalysis, but colloids are currently experiencing renewed interest to get well-defined nanocatalysts to increase selectivity.

Much work in the field has focused on the elucidation of the effects of nanoparticle size on catalytic behavior. As early as 1966, Boudart asked fundamental questions about the underlying relationship between particle size and catalysis, such as how catalyst activity is affected by size in the regime between atoms and bulk, whether some minimum bulk-like lattice is required for normal catalytic behavior, and whether an intermediate ideal size exists for which catalytic activity is maximized [8]. Somorjai's group has studied this issue extensively. Although there is tremendous variation in the relationships between size and activity depending on the choice of catalyst and choice of reaction, these relationships are often broken into three primary groups: positive size-sensitivity reactions, negative size-sensitivity reactions, and size-insensitive reactions. There is also a fourth category composed of reactions for which a local minima or maxima in activity exists at a particular NP size (see Figure 1.2) [9, 10]. Positive size-sensitivity reactions are those for which turnover frequency increases with decreasing particle size. The prototypical reaction demonstrating positive size-sensitivity is methane activation. Dissociative bond cleavage via σ -bond activation as the rate-limiting step is a

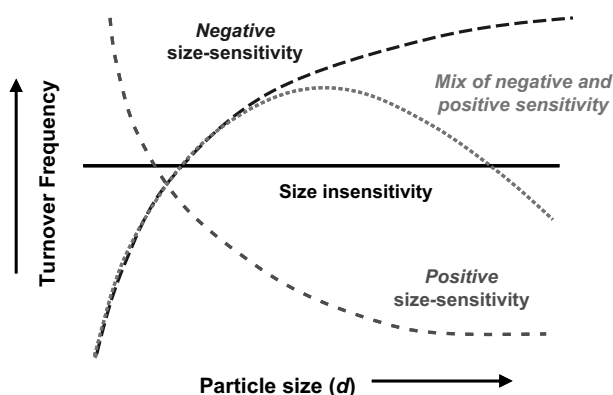


Figure 1.2 Major classes of size-sensitivity, which describe the relationships between NP size and turnover frequency for a given combination of reaction and NP catalyst. (-----) negative size-sensitivity; (- · - ·) positive size-sensitivity; (·····) Mix of negative and positive sensitivity.

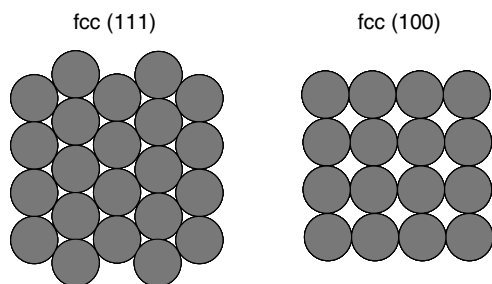


Figure 1.3 Two of the most common fcc crystal faces, (111) (left) and (100) (right).

common feature in reactions with positive size-sensitivity. Negative size-sensitivity reactions are those for which turnover frequency decreases with decreasing particle size. In this case, formation or dissociation of a π -bond is often the rate-limiting step. The prototypical reactions for this group are dissociation of CO and N₂ molecules, which each require step-edge sites and contact with multiple atoms. These sites do not always exist on very small NPs, in which step-edges approximate adatom sites. These reactions also sometimes fall into the fourth category of those with a local maximum in turnover frequency versus particle size because certain particle sizes geometrically favor the formation of these sorts of sites. The third type of reaction is the size-insensitive reaction, for which there is no significant dependence of turnover frequency on nanoparticle diameter. The prototypical size-insensitive reaction is hydrocarbon hydrogenation on transition metal catalysts, for which the rate-limiting step is complementary associative σ -bond formation. Although these effects are often referred to as structure-sensitivity effects, they are referred to as size-sensitivity effects here in order to further distinguish them from another type of structure-sensitivity, which is derived from differences in crystal face and which is discussed below.

Aside from considerations of NP size, a second major area of inquiry is that of the effect of nanoparticle shape on reaction rate, selectivity, and deactivation. This work is derived from the abundance of research done on single crystal surfaces, which has demonstrated what is known as structure sensitivity in catalysis. Experiments on a wide variety of catalysts have determined that the atomic arrangement of atoms on a surface has a significant effect on catalyst behavior. As demonstrated in Figures 1.3 and 1.4, the type of crystal face dramatically affects the coordination,

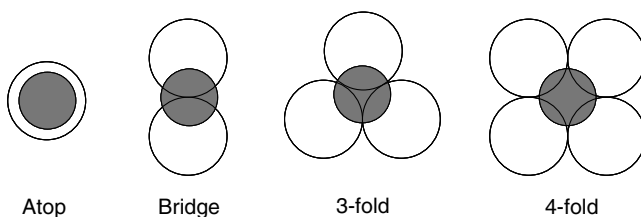


Figure 1.4 Four of the most common adsorption sites found on single crystal terraces.

number of nearest neighbors, and both two- and three-dimensional geometry of the catalytically active surface atoms. The availability of particular types of adsorption sites can have a large effect on catalysis, as it is common for adsorbates to differ in their affinity for each type of adsorption site. Consequently, the presence or absence of a particular type of site can affect not only reaction rates, but also selectivity. However, not all reactions are structure sensitive and some reactions are known to be structure sensitive only within a range of specific conditions. In the case of nanoparticle catalysts, structure-sensitivity is manifested in terms of NP shape. When little attention is given to shape, most NPs adopt roughly spherical shapes, often referred to as polyhedra or octahedra, in order to minimize surface energy.

These NPs predominately feature (111)-oriented surface atoms, which is the lowest energy crystal face. Under certain conditions, however, nanoparticle catalysts can be synthesized such that the shape, and consequently the surface atom orientation, is kinetically trapped into a nonequilibrium shape, such as a cube, triangle, platelet, or rod [11]. Nanoparticles of different shape have been shown to have different activity and selectivity [12, 13], as well as stability [14] in catalytic reactions. Shape-controlled NPs play an important role as model catalysts in furthering the large-scale effort to bridge the ‘materials gap’ between the real-world systems and scientific understanding in catalysis.

Since nanocatalysts are made of nanoparticles or/and nanomaterials, as a metal or metal oxide active phase or as a support or a combination of both, nanoparticles and nanomaterials have been the object of an ever increasing interest during recent decades. The common goal is the development of well-defined nanoparticles/nanomaterials displaying well-controlled properties to get efficient and selective nanocatalysts for numerous relevant catalytic reactions (as examples are arene hydrogenation, carbon–carbon coupling, CO oxidation. . .).

1.2

The Impact of the Intrinsic Properties of Nanomaterials on Catalysis

Involvement of interatomic interaction causes the performance of a solid, or a cluster of atoms, to vary from that of an isolated atom. Adjustment of the relative number of the under-coordinated surface atoms provides an additional freedom that allows one to tune the properties of a nanosolid with respect to that of its bulk counterpart. Hence, contribution from the under-coordinated atoms and the involvement of interatomic interaction can be the starting point of consideration to bridge the gap between an isolated atom and a bulk solid in chemical and physical performances. The impact of atomic coordination reduction (deviation of bond order, length, and angle) is tremendous. It unifies the performance of a surface, a nanosolid, and a solid in amorphous state consistently in terms of bond relaxation and its consequences on bond energy [15, 16]. The unusual behavior of a surface and a nanosolid has been consistently understood and systematically formulated as functions of atomic coordination reduction and its derivatives (size dependence) on

the atomic trapping potential, crystal binding intensity, and electron–phonon coupling. If one could establish the functional dependence of a detectable quantity, Q , on atomic separation or its derivatives, the size dependency of the quantity Q is then certain. One can hence design a nanomaterial with desired functions based on such prediction. The physical quantities of a solid can be normally categorized as follows:

- Quantities that are directly related to bond length, such as the mean lattice constant, atomic density, and binding energy. Lattice contraction in a nanosolid induces densification and surface relaxation.
- Quantities that depend on the cohesive energy per discrete atom, such as self-organization growth; thermal stability; Coulomb blockade; critical temperature for phase transitions, and evaporation in a nanosolid; and the activation energy for atomic dislocation, diffusion, and chemical reactions.
- Properties that vary with the binding energy density in the relaxed continuum region such as the Hamiltonian that determine the entire band structure and related properties such as band gap, core level energy, photoabsorption, and photoemission.
- Properties from the joint effect of the binding energy density and atomic cohesive energy such as the mechanical strength Young's modulus, surface energy, surface stress, extensibility and compressibility of a nanosolid, as well as the magnetic performance of a ferromagnetic nanosolid.

Structural miniaturization has indeed given a new freedom that allows us to tune the physical properties that are initially nonvariable for the bulk chunks by simply changing the shape and size to make use of the effect of atomic coordination reduction.

The intrinsic properties of nanomaterials and their size dependency will induce, directly or not, several effects on catalysis (Figure 1.5), that will be discussed in detail throughout this book. Some relevant examples are given below, which will be developed in more details in the following chapters.

1.2.1

Metallic Nanoparticles

About two-thirds of chemical elements are metals. Using the molecular orbital description, as is usual for covalently bonded atoms in molecules, the generation of a metallic material can simply be understood as the formation of an infinitely extended molecular orbital, leading to energy bands. The development of a metallic band structure requires a minimum number of electronic levels, which have to be very similar in energy so that electrons can move by only thermal activation. All the properties that we know for a bulk metal derive from the existence of such a band. The most important property of a metal is its ability to transport electrons, namely the property of conductivity. To understand what conductivity is based on, it is necessary to consider the relation between occupied and unoccupied electronic bands, as electrons can become mobile only if the energy band of which they are part is

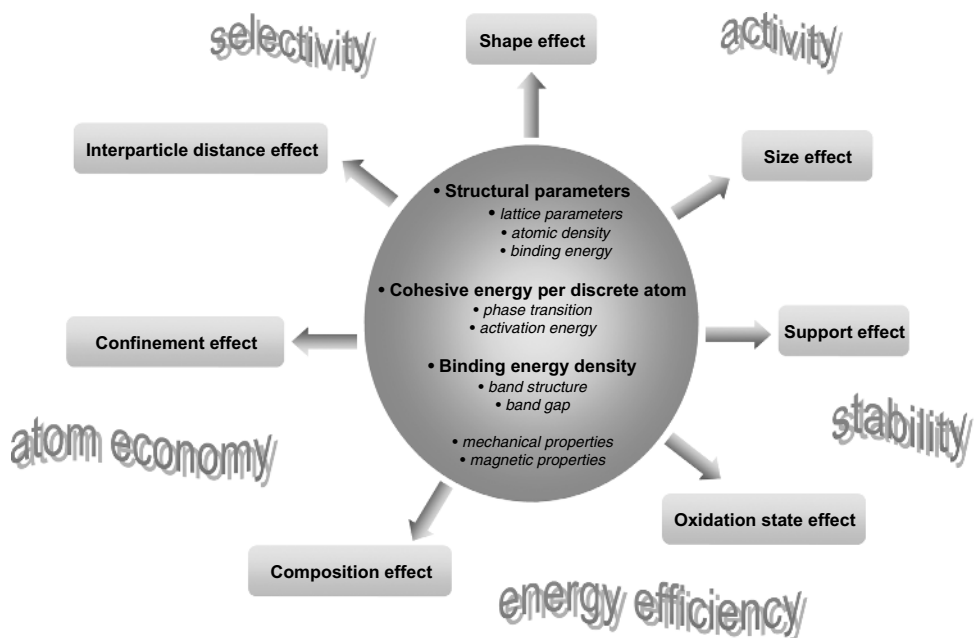


Figure 1.5 The impact of the intrinsic properties of nanomaterials on catalysis.

not fully occupied. Most of the *d*-type transition metals are characterized by only partially filled *d*-orbitals so that incompletely filled bands result in any case. d^{10} elements such as palladium, platinum or gold have nearby *s*-bands that can be used for electron transport. Another important property of metals, at least for some of them, is magnetism, for example the well-known ferromagnetism of iron, cobalt and nickel. The existence of unpaired electrons is a condition for magnetism; however, only the uniform orientation of free spins over a large area results in ferromagnetism while non-oriented free spins produce paramagnetic materials. Copper and gold are the only colored metals, the others looking 'silvery' when they have smooth surfaces. Finely dispersed metals are all dark brown or black. The silvery luster and the dark appearance are caused by the total reflection of light in the first case, and by the total absorption of light in the latter. Color is caused by the partial absorption of light by electrons in matter, resulting in the visibility of the complementary part of the light. On smooth metal surfaces, light is totally reflected by the high density of electrons and no color results; instead a mirror-like effect is observed [17].

The description of bulk materials is made by means of the laws of classical physics. A metal particle will present properties different from those of metal bulks, because of the reduction in the size (quantum size effect). Indeed, if a size range is attained where the band structure begins to disappear and discrete energy levels become dominant, quantum mechanical rules, which are well-established for describing electronic situations in molecules and atoms have to replace those of

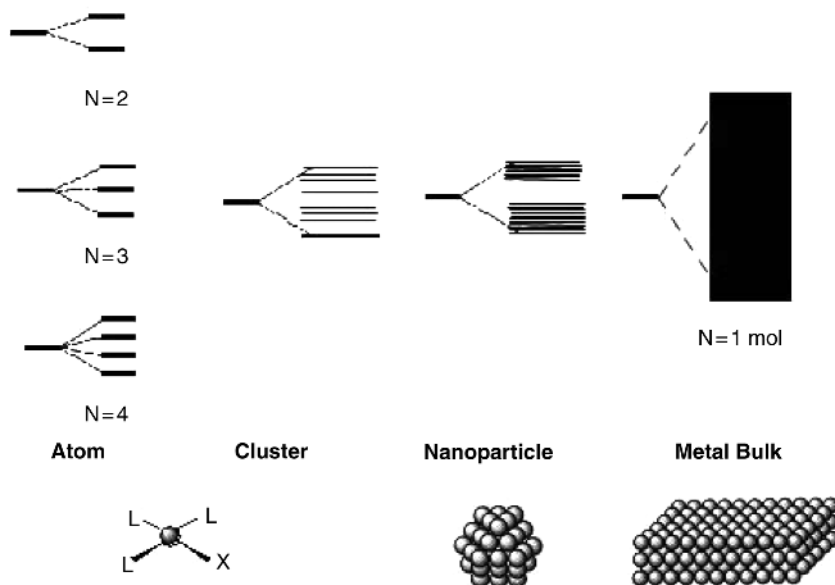


Figure 1.6 Electron levels of atom, cluster, nanoparticle and bulk metal.

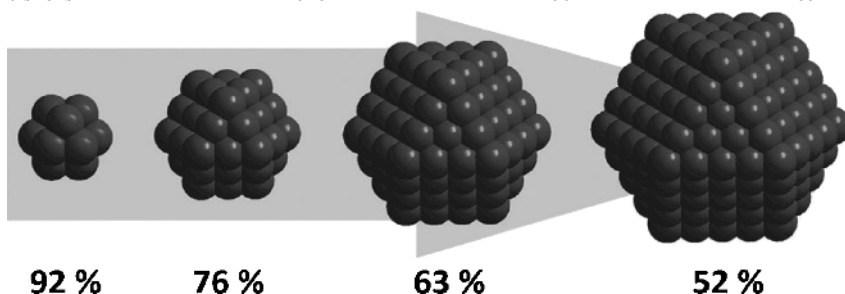
classical physics suitable for bulk materials (Figure 1.6). Nevertheless, small particles are parts of a material and not atoms nor molecules, and are thus considered as intermediate species.

Metallic NPs, also called nanoclusters, are pieces of metal at the nanometer scale, of one to a few nanometers in size. They can be noncrystalline, aggregates of crystallites or single crystallites (nanocrystals). Due to the number of bound metal atoms they contain, metallic nanoparticles display intermediate electronic energy levels in comparison with molecules and metal bulks [18]. As a result, particular physical and chemical properties are expected for metallic nanoparticles that can lead to applications in various areas such as in catalysis [19]. In this latter domain, metallic nanoparticles are generally considered as intermediate species between metal complexes and metal surfaces, and the term ‘nanocatalysts’ is now commonly used to describe them.

In heterogeneous catalysis, the use of metallic nanoparticles is well established, mainly based on their high reactivity. One of their properties is their high number of surface atoms that increases with decreasing particle size (Table 1.1), these surface atoms being the active sites for catalysis. In addition, surface atoms which are at the edges or in the corners are more active than those in planes, and their number also increases with decreasing particle size. Since the number of surface atoms present in NPs will govern their catalytic reactivity, control of the size of NPs is thus of high importance. For industrial processes, the particles are generated on supports such as alumina, silica or charcoal by impregnation from solutions of the corresponding metal salts followed by a reduction procedure giving rise to

Table 1.1 Number of surface atoms in relation with the total number of atoms in full shell clusters.

Full-shell clusters	Total number of atoms	Number of surface atoms	Surface atoms (%)
1 shell	13	12	92
2 shells	55	42	76
3 shells	147	92	63
4 shells	309	162	52
5 shells	561	252	45
6 shells	923	362	39



Decrease of surface to volume ratio for clusters of 13, 55, 147 to 309 atoms

zero-valent nanoparticles. Since the larger particles are less active than the smaller ones, only a portion of the metal particles contribute to the catalytic process [17]. To overcome this problem, other ways of synthesis have been explored like solution procedures, but in that case, the addition of a stabilizing agent (polymer, surfactant, ligand. . .) is necessary to keep the NPs stable. Besides their protecting role, and although they occupy some active sites at the surface of nanoparticles, stabilizers can tune their reactivity by influencing their morphology or/and their surface chemistry. When the nanoparticles are deposited onto a support, the organic ligands can be eliminated from the nanomaterial by washings with appropriate solvents or by calcination under air at high temperature or under plasma conditions, to obtain naked NPs.

A modern approach of colloid chemistry is presently being developed to increase the reactivity of NPs in a limited size up to 10 nm, using several types of stabilizer as well as several types of support for their heterogenization. It appears that a fundamental understanding of the surface properties of such metallic nanoparticles is needed to get more efficient and selective nanocatalysts in the future.

1.2.2

Metal Oxide Nanoparticles

The metal elements can form a large diversity of oxide compounds, which can adopt structural geometry with an electronic structure that can exhibit metallic, semiconductor, or insulator character [20]. Most of the catalysts used in industrial

applications involve an oxide as active phase, promoter, or support. At the nanoscale, these compounds can exhibit unique physical and chemical properties due to their limited size and a high density of defect sites such as edges, corners and point defects [21]. As for other materials, the process of size reduction is expected to dictate structural, transport and chemical properties, which themselves will influence the final catalytic performance. In this section we will concentrate on pure oxide nanoparticles, but one should keep in mind the important place of mixed nano-oxides, such as nanozeolites [22] or others [23–26] in catalysis.

Bulk oxides are usually robust and stable systems with well-defined crystallographic structures. However, the growing importance of surface free energy and stress with decreasing particle size must be considered, since changes in thermodynamic stability associated with size can induce modification of cell parameters and/or structural transformations [27], and in extreme cases, the NP can disappear because of interactions with its surrounding environment and of its high surface free energy [28]. To display mechanical or structural stability, a NP must have a low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures. This structural phenomenon has been detected in TiO_2 , VO_x , Al_2O_3 , or MoO_x [29–33]. Thus, in the case of alumina the stable structure for micro-sized samples is the α phase while γ appears more stable for nanostructured materials [14]. Size-induced structural distortions have been observed in NPs of Al_2O_3 [28], Fe_2O_3 [34], ZrO_2 [35] or CeO_2 [36].

The NP size is also related to the transport properties of the oxide, since, as already stated, the nanostructure produces the so-called quantum size or confinement effects, which essentially arise from the presence of discrete, molecular-like electronic states. Additional general electronic effects of quantum confinement experimentally probed on oxides are related to the energy shift of exciton levels and optical bandgap [37]. Oxide materials can present ionic or mixed ionic/electronic conductivity and it is experimentally well established that both can be influenced by the nanostructure of the solid. The number of electronic charge carriers in a metal oxide is a function of the band gap energy according to the Boltzmann statistics. The electronic conduction is referred to as n- or p-hopping-type depending on whether the principal charge carrier are, respectively, electrons or holes. In an analogous manner to hopping-type conduction, ionic conduction takes place when ions can hop from site to site within a crystal lattice as a result of thermal activation. As a result of the nanoscale derived effects, it is well known that CeO_2 exhibits an improved n-type conductivity, which may be four orders of magnitude greater than that corresponding to bulk/micro-crystalline ceria, and is ascribed to a significant enhancement of the electronic contribution [38]. The strong size-dependence observed for the electrical conductance in the context of gas-sensing devices has been recently reviewed [39–41]. Some of the most dramatic effects of the nanostructure on ionic transport in oxides are observed in the field of Li-ion batteries. An outstanding enhancement of Li-ion vacancy conductivity has been achieved using Li-infiltrated nanoporous Al_2O_3 [42].

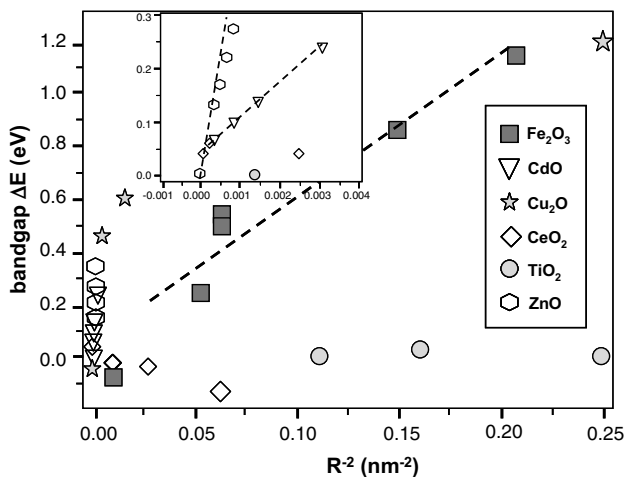


Figure 1.7 Optical band gap energy as a function of the inverse squared primary particle size for common metal oxides. (Adapted from [56]).

Structural and electronic properties obviously drive the physical and chemical properties of the solid, and this last group of properties is influenced by size in a simple classification. In their bulk state, many oxides have wide band gaps and a low reactivity [43]. A decrease in the average size of an oxide particle does in fact change the magnitude of the band gap (Figure 1.7), with strong influence on the conductivity and (photo)chemical reactivity [41, 44–46]. Surface properties of oxides nanomaterials are of central importance in catalysis. Solid–gas or solid–liquid chemical reactions can be mostly confined to the surface and/or subsurface regions of the solid. As mentioned, the two-dimensional (2D) nature of surfaces has notable structural consequences, typically a rearrangement or reconstruction of bulk geometries, and electronic consequences, such as the presence of mid-gap states, which may act as trapping centers in photocatalysis, whose behavior depend on the relative position of their energy with respect to the valence and conduction band edge position [46]. In the case of nanostructured oxides, surface properties are strongly modified with respect to 2D-infinite surfaces, producing solids with unprecedented sorption [47, 48] and acid/base characteristics [49], or metal–support interaction/epitaxy [50, 51]. Finally, the presence of under-coordinated atoms or O vacancies in an oxide NP should produce specific geometrical arrangements as well as occupied electronic states located above the valence band of the corresponding bulk material, enhancing in this way the chemical reactivity of the system [35, 45, 52–54]. This latter remark also concerns the cytotoxicity of these materials [55].

We feel that it is important to stress the need for a fundamental understanding of the properties of nanostructured oxides, particularly for sizes in which the atoms directly affected in their properties are a significant percentage of the total number of atoms present in the solid particle; this usually implies a dimension limited to

about or below 10 nm. When this fact occurs exclusively in one dimension, we are dealing with a surface or film, whereas in two dimensions, nanotubes, nanowires, and other interesting morphologies are obtained. Finally, when the three dimensions are limited to the nanoscale, nanoparticles are formed.

1.2.3

Carbon Nanoparticles

Carbon is unique in the number and the variety of its polymorphs. Figure 1.8 illustrates how the inorganic (nano)carbons can result from the extension of organic materials through large molecules [57]. These inorganic (nano)materials are very different in structure and properties, and their structural as well as surface chemistry is extremely complex.

In heterogeneous catalysis, carbon materials are unique catalyst supports, allowing the anchoring of the active phase, and can also be catalysts or catalyst poisons (carbon deposits) by themselves [58]. Although activated carbon and carbon blacks (CBs) are the most commonly used carbon supports, there is an increasing interest in the application of new carbon nanoparticles [fullerenes [59], carbon nanotubes (CNTs), carbon nanofibers (CNFs) [60], and graphene [61]] as supports for catalysis

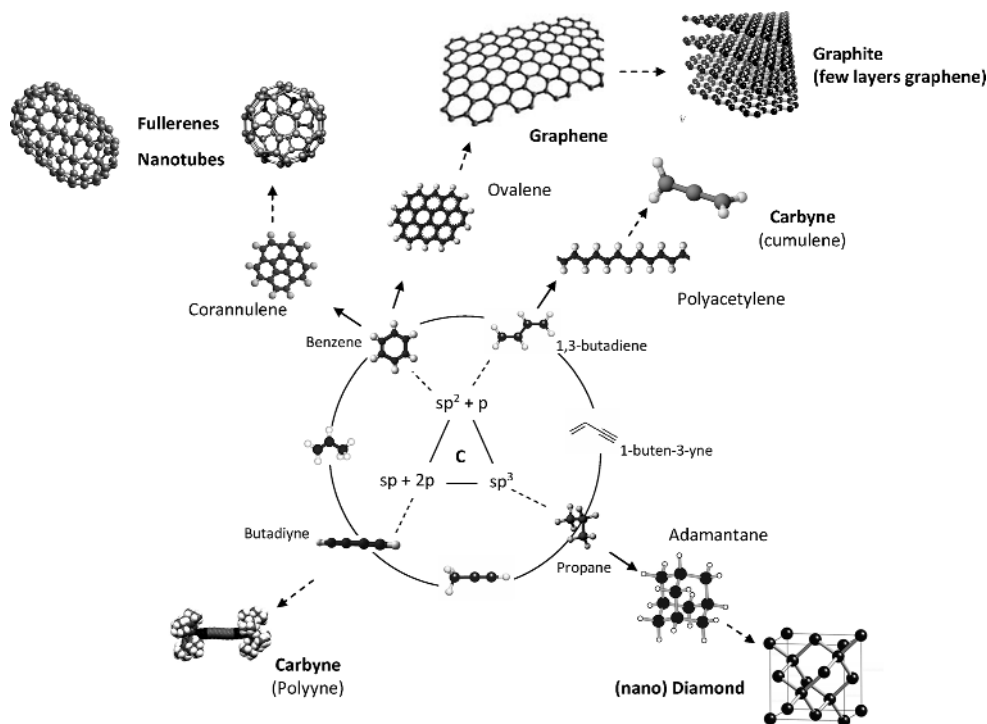


Figure 1.8 C—C bonds to form a large number of hydrocarbons and their extension to carbon families. (Adapted from [58]).

or catalysts since the nanostructure of these materials can offer a unique combination of properties. The catalytic behavior of solid carbons depends of course on their surface properties, but these surface properties are to a large extent a direct consequence of their bulk properties.

The controlled curvature or the orientation of the graphene layers in carbon nanoparticles dictated important properties. The curvature in fullerenes, CBs or CNTs is introduced by including pentagons and heptagons, together with hexagons, as starting fragments. This curvature of the graphene sheets induces strong modifications of the electronic properties; and comparison with graphite shows modification of the π -electron cloud [62]. The rolling-up of the graphene sheet to form a CNT causes a rehybridization of carbon orbital's (nonplanar sp^2) configuration, thus leading to modification of the π density in the graphene sheet, which will depend on CNT diameter. It is worth noting that the theoretically predicted electronic properties are often modified by the presence of defects such as pentagons, heptagons, vacancies or impurities [63]. Similarly, in order to account for the bonding of the carbon atoms of a fullerene molecule, the hybridization must be a modification of the sp^3 hybridization of diamond and sp^2 hybridization of graphite. It is such that the σ orbital no longer contain all of the s-orbital character and the π orbital is no longer of the purely p-orbital character, as they are in graphite. Unlike the sp^3 or sp^2 hybridizations, the fullerene hybridization is not fixed but has variable characteristics depending on the number of carbon atoms in the molecule and consequently of its diameter. The number of carbon atoms, the pyramidalization angle ($\theta - 90^\circ$), and the nature of the hybridization are related and this relationship (in this case the s character in the π -orbital) is given in Figure 1.9 [64].

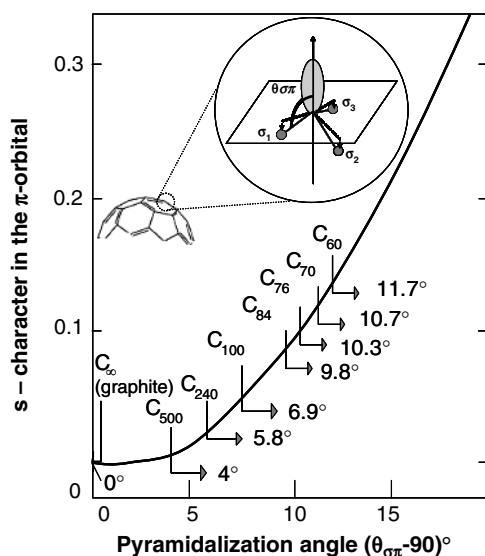


Figure 1.9 Hybridization of fullerene molecules as a function of pyramidalization angle ($\theta_{\sigma\pi} - 90^\circ$). $\theta_{\sigma\pi}$ is the common angle of the three σ bonds. (Adapted from [64]).

The rehybridization plays an important role in determining the electronic structure of the fullerene's family and it is the combination of topology and rehybridization that together account for the possible specific reactivity of all the curved sp^2 nanostructures. The influence of carbon curvature on molecular adsorption of hydrogen has been reported [65, 66]. The hydrogen adsorption energy barrier is found to strongly depend on the local curvature of the carbon network whereby the barrier is lowered with increasing curvature. Whereas in the case of C_{60} and CNTs, hydrogen chemisorption can be achieved by exposure to atomic hydrogen, the chemisorption on graphite (0001) requires hydrogen ions of low kinetic energy (~ 1 eV).

For CNTs, the presence of relatively well-defined and nanometric inner hollow cavities can also induce differences of reactivity between the convex (external) and concave (internal) surfaces. Thus, it has been experimentally proven that hematite NPs located inside the CNT inner cavity are more easily reduced (873 K) by the support than those on the outer surface (1073 K) [67]. Beside CNTs, other carbon nanostructures with the negative curvature analog of fullerenes have been proposed as materials with interesting structural and functional properties [68]. Another property of CNTs is the possibility to perform reactivity in a well-defined confined space (see Chapter 11), and to take advantage of plausible confinement effects [69, 70]. The confinement effects that influence chemical reactions can be classified into three groups: (i) shape-catalytic effects, that is, the effect of the shape of the confining material and/or the reduced dimensionality of the porous space; (ii) physical (or 'soft') effects including the influence of dispersion and electrostatic interactions with the confining material; and (iii) chemical (or 'hard') effects that involve significant electron rearrangement, including the formation and breaking of chemical bonds with the confining material [71]. The latter is usually considered to be the actual catalytic effect, and it is the one that has the most obvious influence on the reaction rates, as it alters the reaction mechanism. However, the first and second types of effect can also have a strong influence on both the rates and equilibrium yields, as has been shown in several recent theoretical calculations [72] and experimental studies [73].

By careful manipulation of various synthesis parameters, it is possible to generate filamentous carbon nanostructures in assorted conformations and also to control their crystalline order (Figure 1.10). The tunable orientation of the graphene layers can directly affect catalytic activity and selectivity, for example by specific metal catalyst crystallographic face exposure according to the support [60].

Finally, the thermal control on nanocatalysts becomes increasingly important as the size of the system diminishes. Therefore, for exothermic reactions the thermal conductivity of CNTs or graphene should play a critical role in controlling the performance of the catalyst.

Besides CNTs, graphene and fullerenes, catalytic applications of other carbon nanomaterials such as carbon nano-onions [74], or recently nanodiamonds [75, 76], and carbon nanohorns [77] have been much less studied.

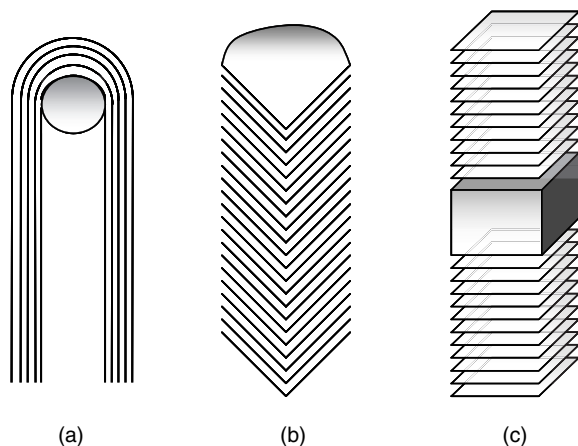


Figure 1.10 Different carbon nanostructures produced by catalytic chemical vapor deposition: (a) multiwalled carbon nanotubes; (b) fishbone-carbon nanofibers (f-CNFs); and (c) platelet-carbon nanofibers (p-CNFs).

1.3

How can Nanocatalyst Properties be Tailored?

The use of metallic/oxide NPs in catalysis is crucial as they mimic metal surface activation and catalysis at the nanoscale and thereby bring selectivity and efficiency to heterogeneous catalysis [78]. But, to be of interest, NPs should at least: (i) have a specific size (1–10 nm); (ii) have a well-defined surface composition; (iii) have reproducible syntheses and properties; and (iv) be able to be isolated and redissolved [79]. If the nanoparticle is supported, the question of precise control of its location, and thus of its spatial and chemical environment should also be addressed. Tailoring nanocatalysts properties thus necessitates being able to control these NP characteristics as well as their morphology, crystalline structure and composition (intrinsic composition and surface state).

1.3.1

Size, Shape and Surface Chemistry of Nanoparticles

Nowadays, to develop efficient catalytic systems, two important concepts are considered in nanocatalysis, namely the bottom-up strategy for the synthesis of well-controlled in size/shape NPs and the molecular approach to obtain more selective nanocatalysts. The bottom-up strategy allows the building of metallic nanoparticles from monometallic species. The control of NPs size is made possible by addition of a stabilizing agent, also called a capping agent (ligand, surfactant, polymer, dendrimer. . .). The introduction of ligands as nanoparticles stabilizers is of special interest because it focuses on the precise molecular definition of the catalytic materials. This strategy potentially allows optimization of the parameters that govern the

efficiency in catalytic reactions, including enantioselectivity [80, 81]. As for homogeneous catalysts, an appropriate choice of the protecting agent means that the surface properties of the NPs can be tuned, as it can modify the nature of active sites (morphology) and the surface chemical environment (steric and/or electronic effect). As a result, NPs are very soluble in water or classic solvents, depending on the way of preparation and the stabilizer. The surface of nanoparticles can also be modified to render them more soluble in specific media (for example ionic liquids (IL)s or $scCO_2$). They can also be handled and even characterized as molecular compounds by spectroscopic techniques [nuclear magnetic resonance (NMR), infrared (IR), ultraviolet-visible (UV-vis) spectroscopy, electrochemistry] in addition to solid-state techniques [transmission electron microscopy (TEM), wide-angle X-ray scattering (WAXS), powder-X-ray diffraction (XRD), X-ray excited photoelectron spectroscopy (XPS), extended X-ray absorption fine structure (EXAFS). . .].

Concerning the control of nanoparticle size on which the number of surface active sites will be dependent, chemists have developed several methods, and very small NPs are already produced by different procedures [82–84]. The most well-known method is the reduction of a metal salt which gives rise to nanoparticles in an aqueous phase followed by the decomposition of metal-organic precursors also called the organometallic approach, which is more appropriate for obtaining NPs in organic media [85]. Size control is attained by the use of a large variety of capping agents, which limit the growth of nanoparticles. One can cite as examples of stabilizing agents, ions, polyoxoanions, surfactants (ammonium salts), polymers (polyvinylalcohol, polyvinylpyrrolidone, block-copolymers. . .), dendrimers such as polyamidoamine (PAMAM) and ligands (thiols, phosphines, amines. . .).

Considering reactivity and selectivity, the control of the surface state of the NPs is of critical importance as it can influence the course of a reaction. Since nanocrystals in their native form are dominated by the surface species [86], the protective agents used during the synthesis of metallic nanoparticles in solution play an important role. Two points are concerned, the control of the morphology and crystal structure [87] and the control of the surface composition [88].

The catalytic activity of metal nanocrystals is highly dependent on the nature of their surface structure [89, 90], exposure of different crystallographic facets, together with the increased number of edges, corners and faces, being key parameters. Therefore, NPs of different shapes are highly desirable as catalysts. While the effect of metallic nanoparticles size on the catalytic activity is well documented, knowledge about the influence of metallic nanoparticle shapes has started to develop only recently [91, 92]. Thus, the efficient control of the morphology is an on-going project all over the world and very interesting works have appeared in recent years [93, 94]. Solution-phase based methods have been shown to have great capability and flexibility to produce metal nanocrystals with well-defined morphologies with crystallographic control [87]. Capping agents are chosen for their influence on the shape of the particles, and consequently on the nature of surface active sites (edges, corners, faces, kinks, terraces, defects. . .) [95–98]. Controlling precisely the kinetics of the reaction appears as a key point to control NP shape [99, 100]. This is illustrated on Figure 1.11 that depicts different Co

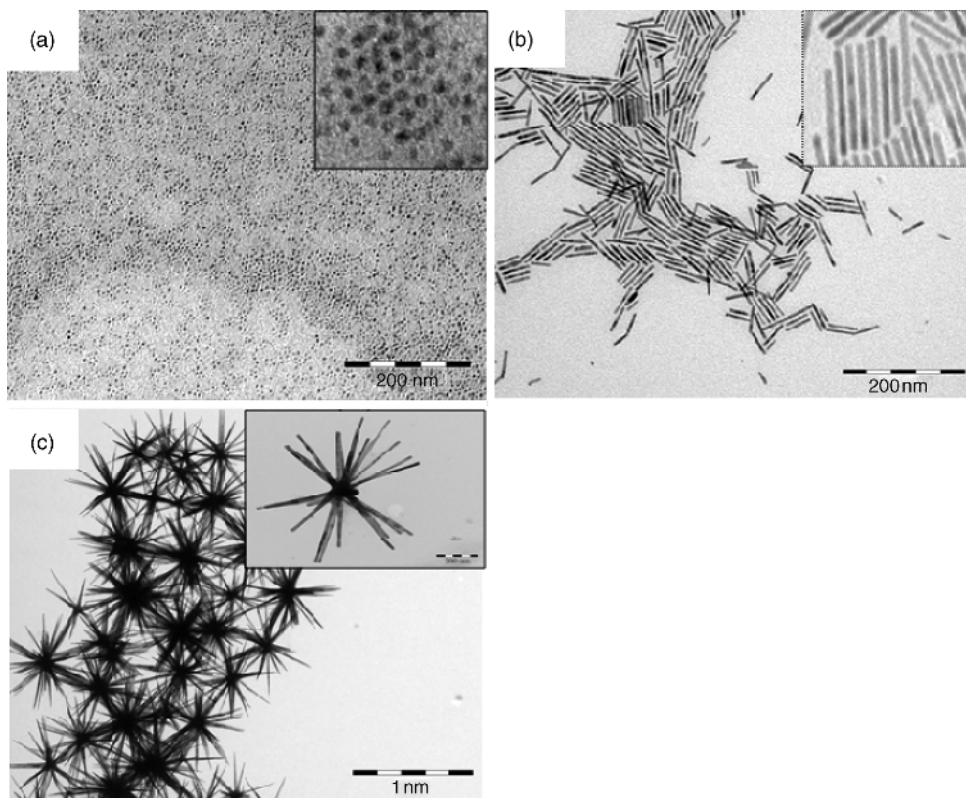


Figure 1.11 Various cobalt nano-objects synthesized from $[\text{Co}_2\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})]$ /lauric acid/hexadecyl amine mixtures by careful control of the reaction conditions, (a) spherical Co NPs (scale bar = 200 nm); (b) Co nanorods (scale bar = 200 nm); (c) Co nano-urchins (scale bar = 1 nm). With courtesy of K. Soulantica (LPCNO, France).

nano-objects synthesized from the same precursor and using the same stabilizing agents by careful adjustment of kinetic parameters.

Second, the intrinsic composition of metallic nanoparticles has also to be controlled to tune their reactivity and selectivity. For example, the synthesis of alloyed versus core-shell bimetallic systems or the synthesis of NPs with a well-controlled surface state (meaning that the influence of stabilizing agents and/or the eventual poisoning of active sites are perfectly known and directed) are key points of current interest. Bimetallic nanocrystals with core-shell, heterostructure, or intermetallic and alloyed structures are emerging as a new class of nanocatalysts. They are expected to display not only a combination of the properties associated with two distinct metals, but also new properties and capabilities due to a synergy between the two metals [101]. More importantly, bimetallic nanocrystals usually show composition-dependent surface structure and atomic segregation behavior, and therefore more interesting potential applications. Compared with monometallic

nanocrystals, preparation of bimetallic ones is much more complicated and difficult to achieve. In recent years, many research groups have made great efforts in this area, and bimetallics with controllable structures could be obtained, following different ways of synthesis [102]. For example, the preparation of uniform bimetallic Rh/Fe NPs in a phenylazomethine dendrimer, which provides improved catalytic reactivity for the hydrogenation of olefins and nitroarenes compared with monometallic RhNPs in a dendrimer cage has been reported recently [101]. Nevertheless, one of the most challenging problems is the comprehension of nucleation and growth mechanism of nanocrystals in solution, which would make the synthesis more efficient and better control the catalytic properties.

The properties of nanocrystals are also dependent on the surface chemistry. Chemical modifications of nanoparticles, such as by the use of ligands or adatoms to decorate their surface can thus provide new catalytic properties [87]. Thus, one can expect to be able to modify the chemical properties of nanoparticles by an appropriate choice of the capping agents, due to their own electronic or/and steric properties. At least, the coordination of ligands on surface atoms can block some metallic active sites and further orient catalytic reactions. Such studies are presently emerging, comparing for example the influence of a polymer and simple ligands in the dynamics and reactivity of carbon monoxide at the surface of small ruthenium NPs [103] or the influence of more sophisticated ligands as carbenes [104] or alkyl/arylphosphines [105] in the hydrogenation of aromatic derivatives. In asymmetric catalysis, the chiral capping agent used for the stabilization of metallic nanoparticles is of fundamental importance as it is expected to induce enantioselectivity. This area of nanocatalysis should be developed as only a very few examples of enantioselective nanocatalysts are known, mainly for the hydrogenation of ethyl pyruvate with cinchonidine-stabilized NPs [106]. This aspect will be treated in a specific section below.

The use of colloiddally synthesized nanoparticles for the preparation of supported catalysts offers several advantages (e.g., precise control of particle size and morphology) when compared with traditional preparation techniques. Although such NPs have already been successfully used for catalytic applications in the liquid phase, applications in heterogeneous gas-phase catalysis are still scarce [107]. This is mainly due to the fact that in heterogeneous gas-phase catalysis organic stabilizers are often considered to have a detrimental effect on catalytic activity since, due to their presence, the active centers on the NPs are partly blocked. But recent studies have been published, in which the influence of ligands on heterogeneously catalyzed reactions in the gas phase was investigated with positive impact on catalytic reactivity and selectivity.

The development of new reaction media and recovery of the nanocatalysts are also crucial aspects that are widely studied to solve environmental problems. There are presently many investigations to develop metallic nanoparticles for catalysis in green solvents [108, 109]. For example, ILs [110], in particular imidazolium-based ILs, have proven to be suitable media for the generation and stabilization of soluble metallic nanoparticles. Such metallic nanoparticles immobilized in ILs appeared as efficient green catalysts for several reactions in multiphase conditions [111]. This

aspect of nanocatalysis will be presented in Chapter 5 by M. Gomez *et al.* as well as in Chapter 6 by M. Haumann *et al.* dealing with supported IL-phase catalysis. Fluorous solvents, perfluorinated alkanes being the most representative, are also green solvents which have been used as reaction media for nanocatalysts [112]. The first work was reported by R. Crooks and co-workers who described dendrimer-encapsulated PdNPs for alkene hydrogenation in a mixture THF/perfluoro butyltetrahydrofuran with successful recycling tests up to 12 runs, with no loss of activity nor detectable leaking of the catalyst into the organic phase [113]. Other groups stabilized metallic nanoparticles with heavily fluorinated ligands or polymers to increase their solubility in fluorous solvents for catalysis [114–117]. Nevertheless, applications of fluorous solvents in nanocatalysis are practiced to a much smaller extent compared with other green solvents. In another way, some groups are developing the synthesis of metallic nanoparticles and nanomaterials soluble in supercritical fluids [118, 119]. Chapter 7 by C. Aymonier *et al.* is dedicated to this subject.

In parallel with progress in the efficiency of metallic nanoparticles, progress has also been made in their recovery and recyclability [80]. This point is of high importance as it is probable that recyclability will be the bottleneck for the industrial application of NPs in solution phase, the good dispersion of NPs within a solvent making the separation of the catalyst from the products more complicated. To solve this problem, a good strategy for easy and efficient recycling has to be applied [108]. Thus, different groups are working to obtain nanoparticles as recyclable catalysts. Most often, the experiences gained from the recycling of homogeneous catalysts is a good source of ideas, as some methods can be easily adapted to nanoparticle catalysts to get recyclable nanocatalysts, such as the use of polymers [120] or dendrimers [121]. In addition, the deposition of pre-formed NPs onto supports to get heterogeneous systems easy to recover is being explored. Traditional supports such as silica, alumina, titania, ceria or other oxides as well as carbon supports in various forms (mesostructured silica [122], alumina membranes [123], carbon nanotubes [124], . . .) are often used, but a new trend appeared in the few past years which consists in the use of magnetic supports to recover the catalyst from the catalytic media by simply applying a magnet. Indeed, magnetic separation has emerged as a robust, highly efficient and fast separation tool with many advantages compared with product/catalyst isolation by means of other chemical or physical procedures, such as liquid–liquid extraction, chromatography, distillation, filtration or centrifugation [125]. The catalyst immobilized on superparamagnetic nanomaterials can be easily separated from the products due to a strong interaction between the magnetic nanoparticles and an external applied magnetic field, and it can be easily redispersed in the absence of the magnetic field due to the absence of ‘magnetic memory.’ For example, silica-coated magnetite NPs functionalized at their surface with a pendant phosphine ligand were used as a support for the deposition of PdNPs giving rise to novel nanocatalysts active in Suzuki cross-coupling reactions and that could be reused up to ten recycles [126]. More details about the recovery of nanocatalysts will be given by D. De Vos *et al.* in Chapter 8. Today, much research work concerns the recovery of the catalysts for economical and environmental reasons.

In summary, different ways can be followed to tailor the surface properties of nanoparticles and further to optimize their catalytic performance. It appears clearly that the capping agents used for NP stabilization have to be chosen properly, as they play a key role, by influencing the growth of the particles in terms of size and crystal structure as well as in terms of surface composition. Besides development of synthetic methods to get well-defined nanocatalysts, it is also necessary to develop a toolbox of techniques for a better understanding of surface coordination chemistry at a molecular level, and even better directly under catalytic reaction conditions [127].

1.3.2

Assembling Strategies to Control Active Site Location

Well-controlled, large-scale synthesis of nanomaterials, and their nanoscale (*in situ*) characterization should enable unambiguous correlation of the structural properties, with the physical and chemical properties of the nanocatalyst. For supported nanocatalysts, the synthesis should integrate strategies to control (i) active NP structure; (ii) nano support structure; and (iii) their assembly. This also constitutes one of the major challenges in many nanotechnology applications, that is, the development of synthesis and assembly approaches for manufacturing complex and durable nanostructures. Different strategies have been investigated to reach an optimal control of active phase location in a supported nanocatalyst (Figure 1.12).

The one-pot synthesis should provide a well-defined active site in a porous structure. The metal–organic frameworks (MOFs), a synthetic, crystalline, microporous metal oxide structure linked together by organic ‘struts’, constitutes a representative example. It has been shown that, under mild conditions, MOFs successfully compete with the classical molecular sieves zeolites in selective catalysis. Their primary fields of application are fine organic synthesis and enantioselective catalysis [128]. Of course, zeolite catalysts, for which the active site (most often an acidic site) is integrated in a perfectly controlled environment, should be included in this class of catalysts. More sophisticated synthetic routes have also been developed for the one-pot preparation of PtNPs into the meso-channels of mesoporous materials such as SBA-15 [129].

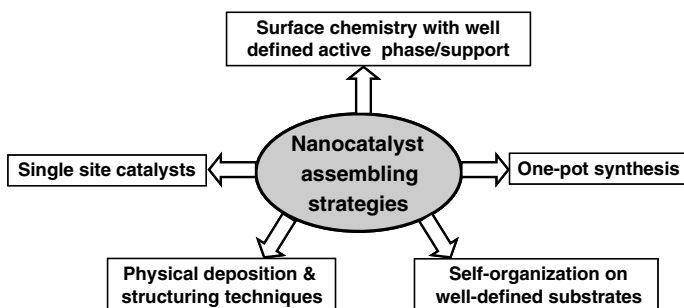


Figure 1.12 Nanocatalysts assembling strategies.

Another elegant strategy is to reduce the size of the active site to a very small number of atoms to prepare ‘single-site catalysts,’ which present an opportunity to exactly control the active site and its environment on the molecular scale. For this approach knowledge and control of the surface chemistry is an absolute prerequisite [130]. The strong structural response of such species to subtle changes in their electronic structure, and the absence of a ‘flexible’ support structure comparable to that provided by the protein structure of enzymes, limit the durability of such bio-inspired structures if they are active, or prevent their catalytic activity if they are fixed too strongly to the support. The fixation of the active species into nanostructured compartments, such as the ‘ship in the bottle’ approach in zeolites [131], constitutes an efficient way to circumvent stability issues, but introduces the problem of active site accessibility and of leaching, limiting the application of these systems to reactions performed under mild conditions. It is also worth mentioning that the rational building of single chains of a specially designed polymer that folds up in water to form an encapsulated catalytic chamber, that mimics the one used by enzymes, has recently been proposed [132]. In water, intramolecular interactions cause single chains of the polymer to adopt an enzyme-like structure (Figure 1.13): the self-assembling groups form helices, and the ruthenium ions bound to ligands become surrounded by a hydrophobic shell (black), which in turn is surrounded by hydrophilic groups (blue). These folded structures act as ruthenium catalysts for the reaction in which cyclohexanone reacts with hydrogen to form cyclohexanol.

Another solution to avoid heterogeneity is to prepare solid catalysts via self-organization. In self-assembly, interactions between atoms, nanostructures, and their environment produce kinetically or thermodynamically preferred structures and patterns. Self-assembly is inherently parallel and thus is able to produce macroscopic amounts of nanostructures. Two types of spontaneous processes are important for creating nanostructures: *self-assembly* and *self-organization*.

- **Self-assembly** of nanostructures can be defined as the *spontaneous* formation of structures smaller than 10 nm (in at least one dimension) and with a *well-defined size distribution*.

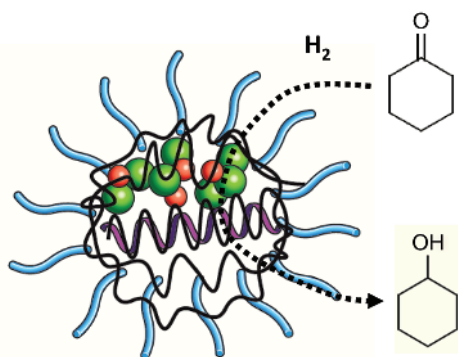


Figure 1.13 Enzyme-like polymer folding. (Adapted from [132]).

- **Self-organization** in nanoscale systems involves their natural tendency to form structures with long-range order, that is, order at the scale much larger than the size of an individual nanostructure.

In general, self-assembly is required to produce large numbers of individual nanoparticles (or nanostructures) having unique and/or tailored properties. Self-organization provides a pathway for combining nanostructures into novel materials or for establishing connections between nanostructures and the macroscopic world. Self-assembly and self-organization need not coexist in the same system, that is, self-assembled nanostructures do not always self-organize, and self-organization is not exclusive to self-assembled nanostructures. But systems that exhibit *both* self-assembly and self-organization are desirable.

Preparation of NPs by the self-organization of polymers constitutes a representative example of this approach [133]. Colloidal dispersions of polymer-protected Pd/Ag/Rh trimetallic nanoparticles were synthesized via self-organization by mixing colloidal dispersions of polymer-protected RhNPs with those of polymer-protected core-shell (Pd-core/Ag-shell) Pd/Ag bimetallic NPs. The Pd/Ag/Rh trimetallic NPs appeared to have a triple core-shell (Pd-core/Ag-interlayer/Rh-shell) [134]. A solid-phase self-organized catalyst of palladium nanoparticles was prepared from PdCl₂ with main-chain viologen polymers via complexation and reduction [135]. Convincing results on the precise spatial distribution control of metallic nanoparticles into domains of microphase-separated block copolymers have been reported [136]. The selective incorporation into a specific microphase of a block copolymer is the key issue there.

A rigorous approach to heterogeneity issues is the application of a combination of physical deposition and structuring techniques, such as physical vapor deposition (PVD), that are commonly used in nanoelectronics. This powerful and well-mastered methodology allows structuring with geometric precision and exact reproducibility at the 10-nm level. These techniques, however are extremely limited in producing large surface area materials and thus are only suitable for producing model catalysts [137]. Additionally, PVD processes are also limited in generating moderate chemical complexity.

The concept of molecular recognition through the control of surface chemistry can also be exploited to drive metallic nanoparticles on or in specific sites of the support, or to prepare bimetallic catalysts. Thus metallic nanoparticles have been selectively confined in the inner cavity of carbon nanotubes thanks to a careful choice of nanoparticle stabilizer and to the passivation of carbon nanotube surface (Figure 1.14) [124]. The specific association of metallic nanoparticles to dendrimers also represents a nice example of the surface chemistry approach [138–140].

To conclude this section, we have seen that metallic nanoparticles have been studied extensively due to their superior catalytic properties over their bulk counterparts. One of the challenging issues facing the community is to synthesize well-controlled (in size and shape) nanoparticles, and to address the issue of their precise location on a support. Although significant amounts of experimental work has

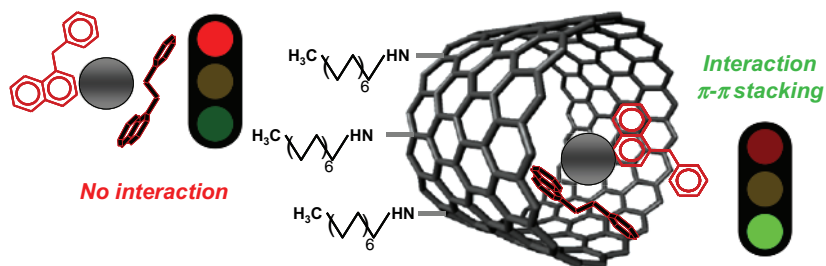


Figure 1.14 Molecular recognition: specific binding between the active phase and the support.

been devoted to these challenges, it is worth mentioning that there is an increasing need of theoretical studies to characterize and understand these complex but well-defined systems. This topic will be discussed in detail in Chapter 12 of this book.

1.4

Nanocatalysis: Applications in Chemical Industry

Nanocatalysis is a rapidly growing field, which involves the use of nanomaterials as catalysts for a variety of catalytic reactions. Heterogeneous catalysis represents one of the oldest commercial applications of nanoscience; nanoparticles of metals, semiconductors, oxides, and other compounds have been widely used for important chemical reactions. Although surface science studies have contributed significantly to our fundamental understanding of catalysis, most commercial catalysts are still produced by ‘mixing, shaking and baking’ mixtures of multicomponents; their nanoscale structures are not well controlled and the synthesis–structure–performance relationships are poorly understood. Due to their complex physico-chemical properties at the nanometer scale, even characterization of the various active sites of most commercial catalysts proves to be elusive. Key objectives of nanocatalysis research should include:

- Increased selectivity and activity, low energy consumption, and long lifetime of catalysts by controlling pore size and particle characteristics.
- Replacement of precious metal catalysts by catalysts tailored at the nanoscale and use of base metals, thus improving chemical reactivity and reducing process costs.
- Catalytic membranes by design that can remove unwanted molecules from gases or liquids by controlling the pore size and membrane characteristics.

As discussed in the previous section, this can be achieved only by precisely controlling the size, shape, spatial distribution, surface composition and electronic structure, and thermal and chemical stability of the individual nano components. In view of the numerous potential benefits (Figure 1.15a) that can accrue through their use, nanostructured catalysts have been the subject of considerable academic and industrial research attention in recent times.

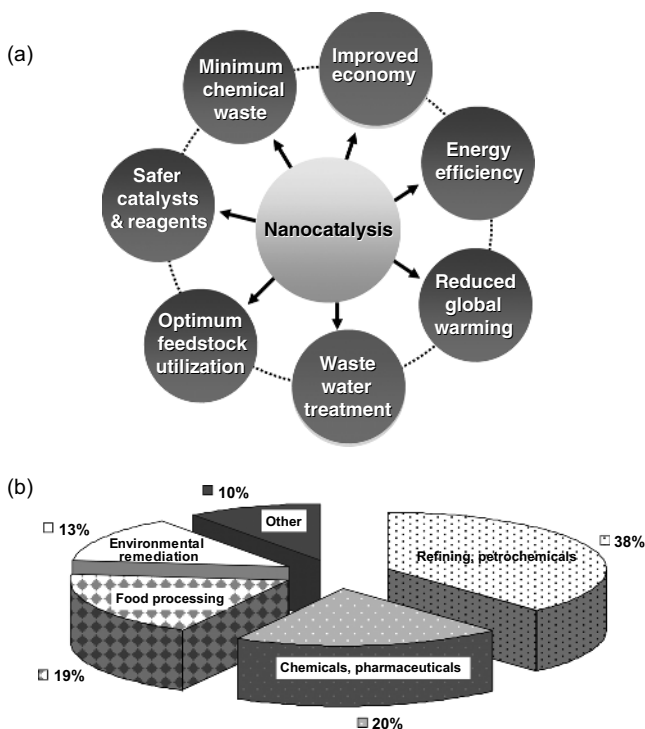


Figure 1.15 (a) Expected benefits of nanocatalysis; and (b) catalyst market by end-use.

Catalysts find application in a variety of industry segments spanning refinery, petrochemical, pharmaceuticals, chemical, food processing sectors and others. An assessment of the global catalysts' market reveals the following:

- The global market for NPs used in catalytic applications increased from US \$193.74 million in 2006 to an estimated US \$200.695 million in 2007. It is expected to reach US \$325 million by 2012, corresponding to a growth of 9.5% in the preceding five years, from 2007 onwards.
- Commercially well-established catalysts such as industrial enzymes, zeolites and transition metal catalysts, till recently, accounted for about 98% of global sales.
- However, nanocatalysts, such as transition metal oxides, gold catalysts, carbon nanotubes and others are expected to more than triple their combined market share from 2009 onwards.
- It is the smaller end-user segments whose consumption is growing the fastest.

Not surprisingly, nanocatalysis is a growing business. The list of companies that have already patented and/or commercialized technologies relating to nanocatalysts is already impressive. The dominant global players include Argonide Corporation, BASF Catalyst LLC, BASF SE, Bayer AG, Catalytic Solution, Inc., Evonik Degussa GmbH, Genencor International, Inc., Headwaters Nanokinetix, Inc.,

Hyperion Catalysis International, Johnson Matthey PLC, Mach I, Inc., Nanophase Technologies Corporation, NanoScale Corporation, NexTech Materials Ltd., Oxonica, PQ Corporation, Sachtleben Chemie GmbH, Süd-Chemie AG, Umicore NV and Zeolyst International, among others.

In this section, the exciting opportunities of nanocatalysis in selected chemical processes, as well as the challenges in developing nanostructured catalysts for industrial applications, are discussed.

1.4.1

Fuel Cells

One of the most important challenges for the ultimate commercialization of fuel cells is the preparation of active, robust, and low-cost catalysts. Recently, the number of publications related to the fundamentals of fuel cell (nano)electrocatalysts has grown significantly [141–145]. Catalysts composed of small, metallic particles, such as platinum or PtRu, supported on carbons or oxides are widely used in fuel cells.

The basic function of the catalyst layer present in a fuel cell is to provide a conductive environment for electrochemical reactions. The main processes that occur in the catalyst layer include mass transport, interfacial reactions at electrochemically active sites, proton transport in the electrolyte phase, and electron conduction in the electronic phase. The oxidation reaction occurs in the anode catalyst layer, while oxygen reduction occurs in the cathode catalyst layer. Anodic and cathodic reactions require metallic active sites to break molecular bonds of gaseous diatomic reactants. The oxidation reaction possesses a lower over-potential and higher rate than oxygen reduction; thus, oxygen reduction is a significant source of voltage loss.

Platinum catalysts suffer from several drawbacks including slow kinetics, low efficiency, high cost, and limited lifetime. Thus, current research is focused on the development of catalyst materials with low cost, high performance, high stability, and durability. In general, literature data show that Pt-based binary catalysts perform better as catalysts for oxygen reduction than pure Pt. However, the electrochemical activities of nanosized Pt-based materials are strongly influenced by their physical and chemical properties which are, in many cases, mutually dependent and determined by the synthetic conditions. So, it comes as no surprise to find that the electrocatalytic activities reported in the literature are dependent on the preparation methodology adopted. Different reports have interpreted activities as associated to various physical parameters, such as particle size, Pt enrichment of the surface, distance between Pt atoms, and occupancy of the 5d Pt band.

Since the activity of the Pt and Pt alloy catalysts increases as the reaction surface area of the catalyst increases, catalyst particles should be reduced in diameter to increase the active surface. So the catalysts are supported on a high surface area substrate. The use of carbon materials as catalyst supports for precious metals has increased rapidly in recent years, due to the continuous advancing development of fuel cells. The main requirements of suitable supports for fuel cell catalysts are:

high surface area, good electrical conductivity, suitable porosity to allow good reactant flux, and high stability in fuel cell environment. Carbon blacks are commonly used as low-temperature fuel cell catalysts. They are usually submitted to chemical activation to increase anchoring centers for metal catalysts (to increase metal loading and dispersion). The high availability and low cost make carbon blacks the most used support for fuel cell catalysts. The disadvantage of these carbons is the presence of a high amount of micropores, which can hinder the reactant flow. Moreover, these materials present low stability at temperatures higher than 373 K.

In that context, fuel cell electrocatalysis constitutes one of the best examples of the contribution that nanocatalysis can bring [141–143]. Nanoscience has stimulated extensive interest in nanostructured catalysts to significantly improve the energy density, power density and operation reliability while greatly reducing the manufacturing expense. In particular, nanostructured materials play a critical role in the catalysis of various innovative fuel cells, which not only possess high specific surface area and good conductivity for low polarization, but also provide unique nanoporous structures and functional chemical properties for highly intrinsic electroactivity and excellent utilization. In particular, the use of nanomaterials in fuel cells can significantly improve the electrocatalytic performance for high energy density and high power density, while reducing the manufacturing cost. The prominent electrocatalytic behavior of the nanomaterials mainly derives from their unique physico-chemical properties such as size, shape, pore structure/distribution, surface defects and chemical properties. The great challenges to synthesize and further use the various nanostructured catalysts are not only from chemistry but also from nanoengineering approaches.

In general, core-shell nanostructures provide an economic and effective way to prepare precious metal catalysts while remarkably reducing the usage of platinum. To enhance the mass activity of Pt, core-shell nano-alloy catalysts with a Pt shell have been developed to remarkably reduce Pt loading while enhancing the catalytic performance [141]. Recent work has shown that the activity and durability of the oxygen reduction reaction catalysts can be further enhanced by controlling the core particle composition and tailoring the shape of the Pt shell structure [146]. As far as pure Pt is concerned, it has been shown that the specific activity of the oxygen reduction reaction on Pt nanoparticles decreases with decreasing the particle size, with a maximum in mass activity for particles with a diameter of 3 nm [147]. Additionally, unique nanostructures such as nanowires and nanotubes provide high specific active surface area, superior conductivity, better mass transport and high intrinsic catalytic activity [148]. Sun *et al.* have developed a promising electrocatalyst based on starlike Pt nanowires presenting both good catalytic activity and durability (Figure 1.16) [149]. The progress in nanoscience should provide good opportunities to explore alternatives to replace Pt and other noble metal catalysts. Cr-decorated NiNPs [150] or cobalt porphyrin-templated nanostructured polyaniline and polypyrrole array nanorods [151, 152] have already shown interesting performances for hydrogen oxidation and oxygen reduction reactions, respectively.

The replacement of carbon black by carbon nanostructures has led to significant changes in the catalytic layer of fuel cells. The arrangement of carbon nanoparticles

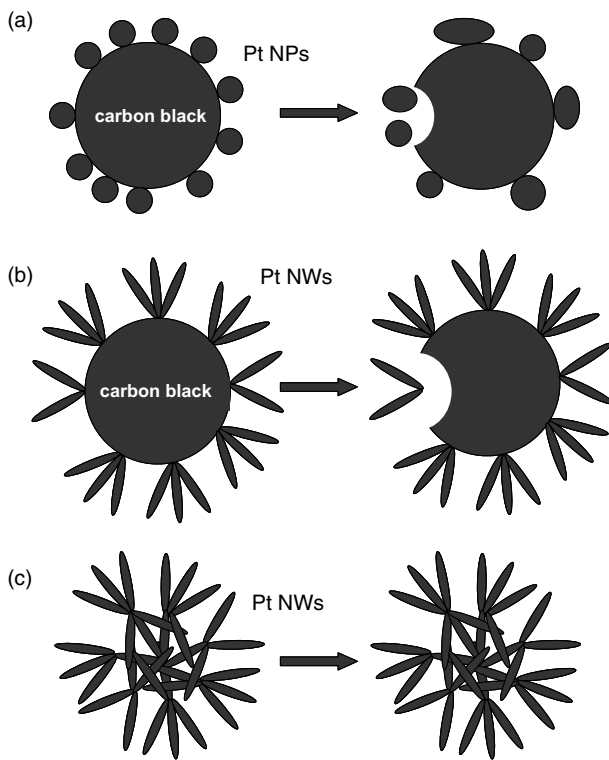


Figure 1.16 Scheme of morphology changes that occur for Pt during accelerated electrochemical cycling. (a) Pt nanoparticles on carbon; (b) Pt nanowires (NWs) on carbon; (c) unsupported Pt NWs. (Adapted from [149]).

at the anode and cathode differs significantly, which prevents the formation of small or closed pores (aggregates) in the catalytic layer of fuel cells. The high surface area and high number of mesopores in ordered mesoporous carbons and carbon gels allow high diffusivity and good reactant flux. Thus, catalysts supported on these materials show higher catalytic activity than the same catalysts supported on carbon black. Among new carbon-based materials, nanotubes are the most investigated catalyst support for low-temperature fuel cells [145]. The highly crystalline structure of CNTs provides high conductivity, surface area and porosity, resulting in exceptional diffusivity. Moreover, CNTs and CNFs have a positive effect on catalyst structure, yielding higher catalytic activity and stability than carbon black [153]. Few studies have been conducted on carbon nanohorns, nanocoils and fibers as Pt catalyst supports. Graphene could be a promising alternative for CNTs and other carbon-based supports due to its superior electronic and chemical properties [154]. If the graphene nanosheets can be fabricated onto a 3D network or vertical array structure, the surface area can be dramatically increased over that of 2D graphene. Mixtures of graphene and CNTs as support have already shown interesting synergistic effects [155].

In brief, the nanostructured catalysts for fuel cell applications currently have been fueled up and some have been used in practical devices. However, many more efforts are needed to investigate the mass production methods, and the interaction of these nanostructured materials with practical electrodes such as MEA and/or large-scale fuel cells for optimization and performance evaluations. Finally, and as for conventional nanocatalysis, for electro-nanocatalysis, computational approaches for theoretical modeling of nanomaterials such as carbon nanotubes and metallic nanoparticles through molecular dynamic techniques are needed for a better understanding of these complex systems under operating conditions. These issues will be discussed in more detail in Chapter 4, Section 4.2.1.2.

1.4.2

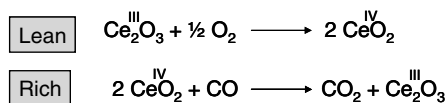
Nanostructured Exhaust Catalysts

Catalytic abatement of toxic automotive exhaust represents one of the major applications of heterogeneous catalysts all over the world. Nowadays, more than 95% of vehicles produced in the world (more than 700 million automobiles) are equipped with a catalytic converter, which, for gasoline-fueled engines, is almost exclusively based on the so-called three-way catalyst (TWC). TWCs are capable of simultaneously and efficiently converting CO, hydrocarbon and NO_x into CO₂, H₂O and N₂, provided that the air-to-fuel ratio is constantly kept at the stoichiometry, that is, under conditions where the amount of oxidants is equal to that of reducing agents. Catalytic converters comprise a high surface area mixed oxide monolith (often incorporating oxides such as CeO₂, ZrO₂, and Al₂O₃) with noble metal catalysts dispersed into the monolith. The noble metals most often include Rh, Pt, and Pd, which are used to perform seven basic reactions listed in Table 1.2. The main use of these metals is in automobile catalytic converters, where over 60% of the procured metals are used. Two of the most important reactions in the catalytic converter are the oxidation of CO by O₂ to produce CO₂ and the oxidation of CO by NO to produce CO₂ and N₂. Rhodium, in particular, is recognized as critical to efficient reduction of NO. Besides the noble metals (Pd and Pt to promote oxidation reaction and Rh to promote NO_x reduction), the current TWCs contain CeO₂-ZrO₂ mixed oxide promoters as the so-called oxygen storage/release component. The oxygen storage capacity is the ability of CeO₂-containing oxides to adsorb and release

Table 1.2 The seven basic reactions used in the catalytic converter. Several of these reactions, including all of the hydrocarbon (HC) reactions, are selective or have variable stoichiometry.

Oxidation	$2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2$
	$\text{HC} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
Reduction/three-way	$2 \text{CO} + 2 \text{NO} \rightarrow 2 \text{CO}_2 + \text{N}_2$
	$\text{HC} + \text{NO} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2$
	$2 \text{H}_2 + 2 \text{NO} \rightarrow 2 \text{H}_2\text{O} + \text{N}_2$
Water Gas Shift	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
Steam Reforming	$\text{HC} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

oxygen under, respectively, fuel-lean and fuel-rich conditions, according to the reactions:



Ce₂O₃ captures excess oxygen that would escape the tailpipe and saves it for CO oxidation when in short supply. The act of O₂ storage enhances NO reduction. The oxygen storage/release is a crucial property of the TWCs since it helps to cope with the air-to-fuel oscillations and maintains a stoichiometric composition of the exhaust at the noble metal catalyst, necessary to attain the highest exhaust conversions.

Since the advent of the TWCs, in the early 1980s, there has been a progressive tightening of the environmental legislation aimed at minimizing the amount of harmful pollutants emitted during the vehicle use. Besides the quite restrictive limits on the emissions (>97% compared with uncontrolled emissions), new materials with enhanced thermal stability and high durability are also being developed. This is due to the fact that TWCs feature the so-called light-off type of conversion *vs.* temperature behavior, where the conversion steadily increases from 0 to 100%. The light-off temperature, conventionally taken as corresponding to 50% of conversion, is typically 513–623 K. This means that to achieve the improvement of efficiency as required by the EU and US legislation, the catalyst heating time, that is, time to reach light-off temperature, must be decreased to 10–20 s. A cost-effective solution is to mount a secondary converter directly on the exhaust manifold. This, however, exposes the catalysts to extremely harsh conditions, where temperatures as high as 1373 K are reached.

Thus, today the development of new and efficient catalytic converters constitutes a real challenge for the chemists, because the use of nanostructured materials is needed both for the oxide support/promoters and the metallic particles [156, 157]. Additionally, due to the technological importance of this catalyst, much effort has been devoted to the study by sophisticated *in situ* surface science tools [X-ray absorption near edge structure (XANES), environmental TEM, high-energy-resolution fluorescence-detected, resonant inelastic X-ray scattering, time-resolved fluorescence X-ray absorption spectroscopy (XAS)] of the nanoscale compositional and structural evolution of these systems [158–161]. The development of specific high-temperature reactors for *in situ* XAS measurements should permit the study of commercial three-way catalysts under realistic gas composition and temporal conditions [162]. The in-depth and *in situ* characterization of these nanocatalysts permits the identification of the active sites, analyzes the genesis of the catalyst, ascertains its dynamic structure, and can be used to evaluate synthetic strategies. Representative examples of the input of nanomaterials in understanding and designing active sites at the surface of these catalytic materials are given below.

The importance of ceria originates from its remarkable redox and oxygen storage capability. It can undergo repeatable Ce^{IV}/Ce^{III} redox cycles depending on the

conditions in the exhaust stream. Using organic molecules to precisely control CeO₂ crystal growth, Adschiri *et al.* have prepared 10 nm, 61 m² g⁻¹ CeO₂ nanocubes [163]. These authors have demonstrated the extra-low-temperature oxygen storage capacity of these CeO₂ nanocrystals with cubic (100) facets. A considerable oxygen storage capacity occurs at 423 K without active species loading. This temperature is 250 K lower than that of irregularly shaped cerium oxide (10 nm, 100 m² g⁻¹). This result indicates that cubic (100) facets of cerium oxide have the characteristics to be a superior low-temperature catalyst.

In fact, the actual importance of oxygen uptake/release is determined by not only the oxygen storage capability but also the rates of the redox cycles. However, while the rate of cerium oxidation is very fast, reduction of ceria is generally sluggish. It has been proposed that the reduction of ceria is controlled by the nature of the oxygen vacancies, since oxygen diffusion, the rate-controlling step, depends on the type, size, and concentration of oxygen vacancies [164]. For example, Esch *et al.* showed that small size surface oxygen vacancies on CeO₂ (111) were immobile at room temperature, but linear clusters of these vacancies formed at higher temperatures [165]. This indicates that any processing condition that favors the formation of more desired oxygen vacancies will result in enhanced reducibility.

Two ceria nanorod samples with different types and distributions of oxygen vacancies were synthesized by Li *et al.* [162]. Two types of oxygen vacancies, small neutral Ce^{III}-oxygen vacancy associates and larger size clusters of these defects, were discovered in ceria nanorods from XRD and XPS analyses. The larger size oxygen vacancy clusters (i.e., dimers, trimers, or larger) result from interaction between the small neutral Ce^{III}-oxygen vacancy associates. The synthesis method was crucial to determine their distribution. These results show direct evidence of promoting the reducibility and activity of ceria nanorods with a high concentration of larger size oxygen vacancy clusters.

An inherent problem for nanocatalysts is their well-documented lack of stability under realistic technical conditions. Supported and unsupported metallic nanoparticles show rapid growth under reactive conditions, especially if the reaction temperature is very high as for automobile-exhaust control, where reaction temperatures are typically in excess of 873 K, and thermal stability of the catalyst becomes a crucial issue. Organic capping agents, which are widely used in colloidal chemistry to stabilize NPs under mild conditions, decompose at temperatures above 573 K, leaving the uncapped NPs unprotected against sintering and deactivation. Vesper *et al.* prepared bimetallic PtRh-BHA nanocomposites (BHA: barium hexa-aluminate, a high temperature-stabilized alumina with a crystallization temperature around 1473 K) in a straightforward and efficient one-pot synthesis, which results in PtRhNPs with a narrow size distribution around 4 nm, homogeneously dispersed throughout the BHA support [166]. They discover that supported PtRhNPs with sufficiently high Rh content survive extended calcination at temperatures up to 1123 K without significant sintering [167]. The extreme thermal stability of these particles depends critically on the Pt/Rh ratio, with higher Rh contents leading to increased thermal stability. Phase separation is observed when the PtRhNPs

start to sinter: Pt bleeds out from PtRhNPs and the Rh content in the remaining nanoparticle increases accordingly. This 'distillation' of the low-melting-point Pt from the PtRhNP results in a sacrificial self-stabilization of the bimetallic NPs.

Finally, it is worth noting that this type of catalytic reactor also raises the critical issue of nanoparticle possible (eco)toxicity. For example, palladium nanoparticles are recognized as components of airborne automotive pollution produced by abrasion of catalyst materials in the car exhaust system [168, 169]. The possible (eco)toxicity of cerium oxide nanoparticles, which are also used in emission control systems in automobile engines as a diesel fuel-borne catalyst to reduce particulate matter emissions, could also be envisaged [170].

1.4.3

Gas Sensors

Gas sensors, also called gas detectors, can be used to detect combustible, flammable and toxic gases, and oxygen depletion. A gas sensor is a device that detects the presence of various gases within an area, usually as part of a safety system. Such equipment can be used to detect a gas leak for example. The gas detector will thus interface with a control system so a process can be automatically shut down, or it will sound an alarm to operators in the area where the leak is occurring, giving them the opportunity to leave the area. The development of devices to be used as gas detectors is thus of high importance because there are many gases that can be harmful to organic life, such as humans or animals.

Gas detectors are of two main types: portable devices and fixed gas detectors. Portable devices are often used to monitor the atmosphere around personnel and are worn on clothing or on a belt/harness. The fixed gas detectors are often used for detection of one or more gas types. Fixed type detectors are generally mounted near the process area of a plant or control room. Generally, they are installed on fixed type mild steel structures and a cable connects the detectors to a system for continuous monitoring and where a tripping interlock can be activated for an emergency situation.

Concerning the mode of control, gas detectors can be classified according to the operation mechanism (semiconductors, oxidation, catalytic, infrared, etc.). Several types of system have thus been developed to act as gas sensors able to detect target species. Among them, electrochemical or chemical sensors are well-known.

Electrochemical gas sensors [171] are like fuel cells, but instead of being designed to produce power, they are designed to produce an electric current. Thus, electrochemical gas sensors measure the concentration of a target gas by oxidizing or reducing the target gas at an electrode and measuring the resulting current, this latter being thus precisely related to the amount of the target gas. Commercial devices based on this principle are currently used in industries or laboratories to detect carbon monoxide in the atmosphere for example. Carbon monoxide is oxidized at one electrode to carbon dioxide while oxygen is consumed at the other electrode. For carbon monoxide detection, the electrochemical cell has advantages

over other technologies in that it has a highly accurate and linear output to carbon monoxide concentration, requires minimal power as it is operated at room temperature, and has a long lifetime (typically commercial available cells now have lifetimes of five years or greater). Until recently, the cost of these cells and concerns about their long term reliability had limited uptake of this technology in the marketplace, although these concerns are now largely overcome. This technology is now the dominant technology in USA and Europe for CO detection.

The detection of various species in gas mixtures, in order to evaluate the impact of these species on the quality of a product or on the environment (toxic gases, offensive odors, volatile organic compounds (VOCs) and other air pollutants) in low concentrations is a challenging subject (Figure 1.17). A practical approach can be achieved by using ‘chemical sensors.’

A chemical sensor consists of a system, including a sensitive layer (the receptor) and a device (the transducer) that transforms the atomic scale interaction between the gas and the material of the sensitive layer into a mechanical or electrical response. When the sensed molecules are physically or chemically adsorbed on the

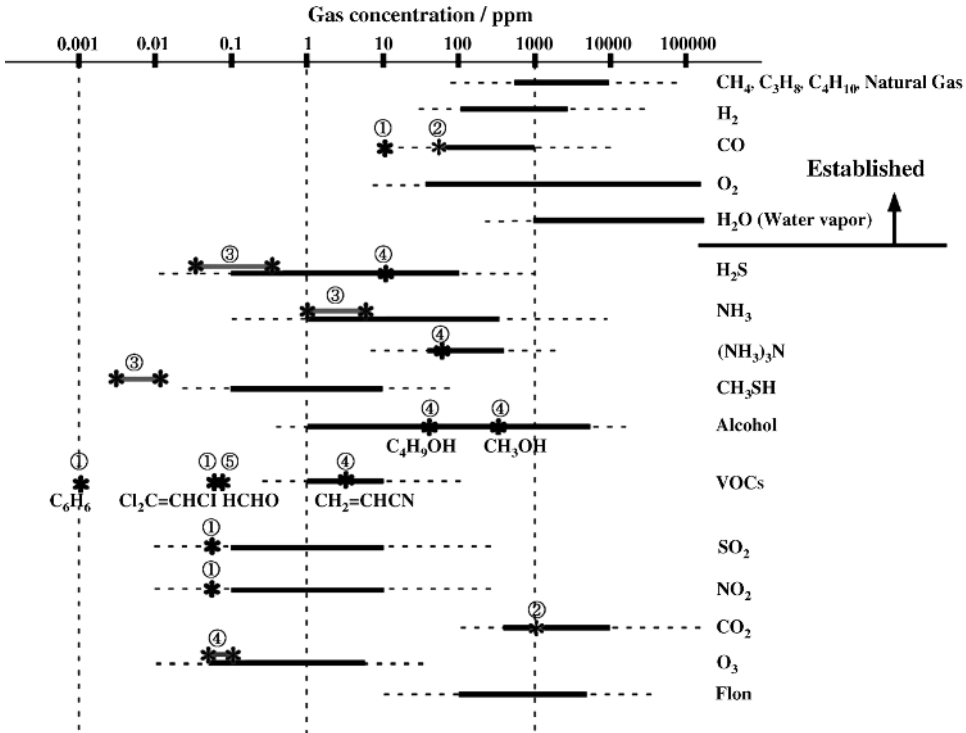


Figure 1.17 Concentration levels of typical gas components concerned. Star marks indicate the standards of the gases legislated in Japan by (1) Environmental Standard, (2) Ordinance on Health Standards in the Office, (3) Offensive Odor Control Law, (4) Working Environment Measurement Law, and (5) Ordinance by Ministry of Health, Labor and Welfare. (Reproduced with permission from [188]. Copyright © (2005) Elsevier).

sensitive layer, chemical reactions like combustion often happen. These phenomena occur at the molecular or atomic level as for a nanocatalyst. The interaction between molecules of the fluid (gas or liquid) phase induces a variation in the physical properties of the sensitive layer, such as electron density, optical properties, mass or temperature [172]. The most common sensors systems contain a solid material as sensitive layer deposited on an electronic device, and deal with the changes in the electronic charge density and charge carrier mobility when a gas interacts with the solid surface. Thus, the mode of detection of a target gas is based on the variation of the electrical properties of the sensitive layer, such as resistance or capacitance, which is detected by the device. In the research of chemical sensors, one of the main problems is the high number of parameters that interfere during the measurement:

- the *lack of specificity* for a given chemical species;
- the *cross-sensitivity*, meaning that the signal of one target species can change if this is in a mixture of species;
- the *temperature dependence*, as adsorption and chemical reactions are widely influenced by the temperature;
- the *'memory effect' of the sensor*, meaning modification of the signal with use and thus the need for recalibration;
- *drift problems* after long-term use, in other words, *stability problems*.

Gas-sensors based on semiconducting materials have become of great interest. Metal oxides are widely employed as sensitive elements in gas sensors [173] and commercial devices produced by classical ceramic processes have been available for a long time. SnO₂ sensors are the best-understood prototype of oxide-based gas sensors [174]. Nevertheless, highly specific and sensitive SnO₂ sensors are not yet available [175].

If such devices are able to detect low concentrations of flammable or toxic gases at a ppm level, their lack of selectivity and long term stability remains their major drawback, and improving the cross sensitivities between gases such as CO, hydrocarbons, and NO₂ is still a major issue. Enhancement of sensor performance can be achieved through (i) an accurate control of the morphology in the nanometer range of the composition and of the surface state of the sensing materials [176, 177]; (ii) the integration of the sensor components on micro-machined silicon platforms [178]; (iii) the optimization of the working temperature of the sensitive layer [179], the operating mode, and the signal processing [180]; and (iv) the use of filters exhibiting selective gas retention or conversion properties [181]. The use of filters combining catalyst-loaded mesoporous materials represents a very attractive way to improve the selectivity of a sensor toward a target gas and to overcome the classical problem of saturation exhibited by passive filtering membranes [182, 183]. The filtering efficiency of such a material, in terms of selectivity, reproducibility, and long term stability, nevertheless demands requirements of crucial importance regarding composition and morphology. As for any nanocatalyst, these requirements include the homogeneous dispersion and high surface area of the active sites on the

support, the homogeneous distribution of size-controllable pore channels in the support, and the immobilization of the active sites inside the pore channels to prevent any migration and coalescence into the host structure.

Besides tin oxide based nanomaterials, other nanomaterials such as zinc oxide nanostructures [184, 185] metal nanoparticle-functionalized oxide nanostructures [186] or carbon nanotubes decorated with metallic nanoparticles [187, 188] to cite a few examples, are also used as sensitive layers. Because of the small size of nanotubes, nanowires, or NPs, a few gas molecules are sufficient to change the electrical properties of the sensing elements. This allows the detection of a very low concentration of chemical species.

Whatever the nature of the nanomaterials used, the on-going research on gas sensors is mainly directed toward the increase in sensitivity and selectivity of the devices. This is performed through the development of novel sensitive layers and catalytic filters made of well-controlled nanomaterials in terms of structure and composition, to lead to efficient and reproducible devices able to detect very low quantities of target molecules in mixtures of species like in urban environments. Numerous works concern for example the shape control of the NPs acting as detecting layer or the integration of nanoparticles of a doping metal for synergy effect. Another current trend of research concerns the assembly of several individual sensors having adequate detection properties, to get multiple systems able to detect simultaneously several gases for example.

Although gas sensors are well-established in some application fields (like combustible gas monitoring, oxygen sensing for combustion exhaust control and humidity sensing for amenity or living space), there are a variety of newly emerging markets (CO₂ monitoring, air quality, odors and humidity are in increasing demand for various purposes; Figure 1.18), which will be substantiated when gas sensors are sufficiently developed [189]. The main commercial applications are nowadays environment monitoring and food quality analysis. Materials design is an important point in innovating gas sensors but attempts to make the sensor devices more intelligent and more quantitative are also important for the further advancement of gas sensor technology.

1.4.4

Photocatalysis

Photoinduced processes are studied in several industrial-oriented applications. Despite the difference in character and use, all photoinduced processes are based on the excitation of a semi-conductor by a light energy higher than the band gap thus inducing the formation of energy-rich electron-hole pairs. All photoinduced chemical processes have in common the so-called 'initial' steps, which include the absorption of light, diffusion, and trapping of charge and fate (recombination or phase transfer to the gas/liquid media) of charge carriers. By photocatalysis, it is commonly understood to be any chemical process catalyzed by a solid where the external energy source is an electromagnetic field with wavenumber in the UV-vis range. Photocatalysis is mainly involved in three areas namely organic synthesis,

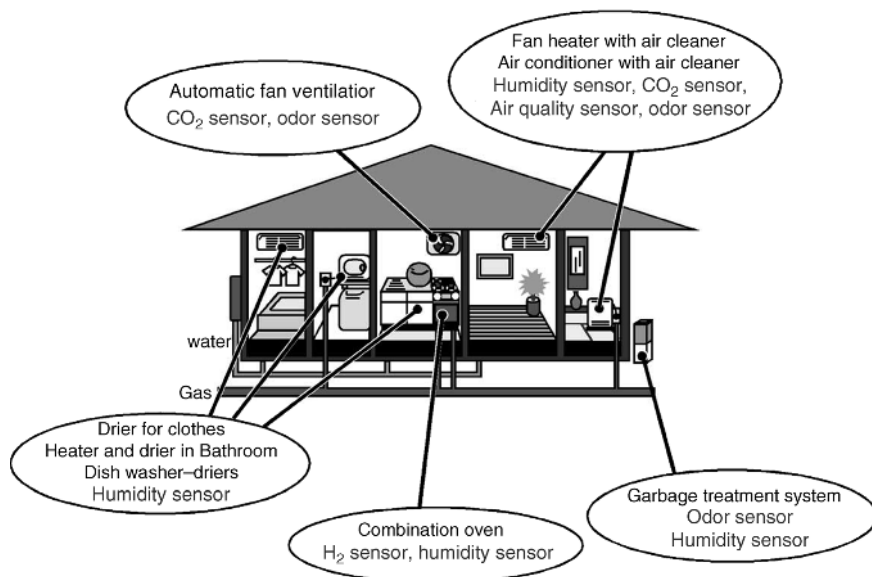


Figure 1.18 Various kinds of gas sensors equipped at various sites in a house (Reproduced with permission from [188]. Copyright © (2005) Elsevier).

degradation of pollutants (in both gas and liquid phases) and special reactions like H₂O reduction or N₂ fixation [190].

Photocatalysts are most of the time solid oxide semiconductors, among which TiO₂ in its anatase form is by far the most known and investigated photocatalyst, due to its chemical stability, nontoxicity and well positioned valence and conduction bands. Besides the research concerning metal oxide materials, recent progress has expanded the chemical nature of photoactive systems by including (oxy)sulfides and (oxy)nitrides, doped-zeolites, and molecular entities embodied in zeolites or other composite materials.

The interest of metal oxide nanomaterials either as active phases, unsupported/ supported nanoparticles or as supports for metallic nanoparticles, in photocatalysis is discussed by V. Hulea *et al.* in Chapter 10, Section 10.3.2 devoted to nano-oxides. In particular, the influence of nanomaterials characteristics (size, morphology) on their photocatalytic behavior is described. For instance, the major effect of morphology and crystal structure on the photocatalytic activity has been reported for TiO₂ and ZnO, two materials usually used in photocatalytic reactions.

Photocatalysts resulting from the combination of metallic nanoparticles and metal oxides are the subject of intensive work because of the benefits induced by such association in terms of activity and selectivity. The deposition of transition metals co-catalysts (Pt, Rh, Au, Cu and Ag) on TiO₂ catalyst usually improves the photocatalytic activity, which strongly depends on the extent, nature and the work function of the metals [191]. Several strategies have been followed to improve the photocatalytic activity by tailoring size and shape of titania and metal

nanostructures. For instance, the photoactivity of TiO_2 has been drastically enhanced with the decreasing size of gold NPs loading even at very low metal content (0.01 wt%).

Carbon materials have some beneficial effects on the photocatalytic activity of TiO_2 [192, 193]. Different preparation methods have been used to introduce carbon into the TiO_2 and activated carbon system such as: mixing TiO_2 with activated carbon, precipitating TiO_2 onto the surface of activated carbon, polymerizing a carbon source with a titanium precursor, inclusion of carbon nanotubes into an inorganic film of TiO_2 by a sol-gel method, or preparation of titania composite materials based on multiwalled carbon nanotubes (MWCNTs) by an impregnation method, and so on. MWCNTs are incorporated to optimize the surface and catalytic properties of TiO_2 since the composites containing carbon nanotubes are believed to exhibit cooperative or synergetic effects between the metal oxide and carbon phase. For example, MWCNT- TiO_2 composite catalysts prepared by a modified sol-gel method gave rise to synergetic effects on the photocatalytic degradation of phenol (Figure 1.19). The increase of MWCNT/ TiO_2 ratio from 1 to 20% favored the enhancement of the synergetic effect on phenol disappearance [194]. The results were explained in terms of the intimate contact between the MWCNT and TiO_2 phases, suggesting that a strong interphase interaction may be triggered between these two phases and MWCNTs might behave as photosensitizer in the composite catalysts.

The future of energy supply depends on innovative breakthroughs regarding the design of cheap, sustainable, and efficient systems for the conversion and the storage of renewable energy sources, such as solar energy. In that context, the production of hydrogen through sunlight-driven water splitting appears to be a promising and appealing solution (see also Chapter 4, Section 4.3.3.1). This solution, inspired by the biological process photosynthesis, has attracted the interest of numerous bioinorganic chemists in the past years. Designing original synthetic molecular systems to achieve a similar function is presently the base of a large field of research called ‘artificial photosynthesis.’ Recent developments regarding the

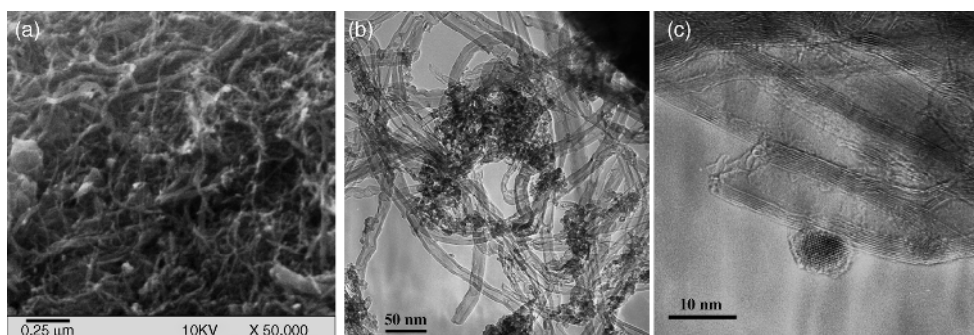


Figure 1.19 SEM micrograph (a) and TEM images (b, c) of MWCNT- TiO_2 composite material (20% CNT w/w).

design, characterization, and evaluation of cobalt-based molecular catalysts and their combination with photosensitizers to generate light-driven systems for H₂ or O₂ evolution were reported in 2011 by Artero *et al.* [195]. In their review, the authors showed how cobalt-based molecular catalysts can be immobilized onto conducting materials so as to form electrodes or photoelectrodes to be integrated in a photoelectrochemical cell for light-driven hydrogen generation from water. They also mention that besides the development of multi-component photocatalytic systems based on a molecular complex, a renewed interest regarding solid metal oxide/hydroxide materials and nanomaterials as promising water oxidation catalysts and their further implementation into light-driven systems appeared very recently. To cite a few examples cobalt oxide materials, such as cobalt nanoclusters in the mesopores of silica associated with [Ru(bipy)₃]²⁺ photosensitizer [196], Co₃O₄ nanoparticles loaded onto Ni foam supports have been reported as anode material for water electrolysis [197] as well as a hybrid material consisting of Co₃O₄ nanocrystals grown on reduced graphene oxide as a high-efficient bi-functional catalyst for the oxygen reduction reaction and oxygen evolution reaction [198]. In the latter, the unusual catalytic activity arises from synergetic chemical coupling effects between Co₃O₄ and graphene. As another example, one may cite the work of F. Odobel *et al.* who obtained an absorbed-photon to current conversion efficiency of 45% (the highest value reported for a sandwich dye-sensitized solar cell based on a nanostructured metal oxide) using a peryleneimide sensitizer and a covalently linked peryleneimide-naphthalenediimide dyad chemisorbed on nanoporous nickel oxide electrodes [199]. Concerning photocatalytic systems containing metallic nanoparticles, gold and platinum NPs have appeared as attractive platforms for the photocatalytic production of hydrogen gas. Photocatalysis of H₂ has been mainly achieved by alcohol re-forming on the surface of Au and Pt NPs supported on semiconductor materials such as titania. But the major drawback to this type of H₂ photocatalysis is that the photons must have an energy greater than the band gap of the semiconductor material in order to produce a charge-separated state that is able to sustain the reaction: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$. Thus, some groups tried to find attractive alternatives to the titania-supported particles for the photocatalytic production of H₂, by developing photosynthetic complexes based on the covalent attachment of a known active photosystem, such as ferredoxin oxidoreductase to Au and PtNPs, as shown by H. Golbeck *et al.* [200]. The challenge is to transfer the electron from the photosystem to the NP surface within 100-ms time frame. In the same way, a highly efficient photocatalytic system for hydrogen evolution has been reported by S. Fukuzumi *et al.* based on a dihydronicotinamide coenzyme (NADH) as a sacrificial agent in an aqueous solution. Their photocatalytic system has been built by using water-soluble platinum nanoclusters functionalized with methyl viologen-alkanethiol and a simple electron-donor dyad (9-mesityl-10-methylacridinium ion) [201]. In summary, despite significant efforts, developing oxygen electrode catalysts with high activity at low cost remains a great challenge in the field of sunlight-driven water splitting reaction for the production of hydrogen. It is interesting to note that immobilization of molecular catalysts on nanostructured electrode surfaces or the linkage of various active photosystems to metallic

nanoparticles might result in increased stability and/or increased activity. Finally, various nanomaterials presently know a renewed interest in this field of research.

To conclude this section, nanocatalysts appear of high interest in photocatalytic processes, as shown by the numerous works using them in the degradation of pollutants or the renewed attention they presently receive for water splitting reactions. As for other catalytic processes, the precise control of their characteristics (size, shape, surface area, composition, etc.) is a key point.

1.4.5

Enantioselective Catalysis

Enantioselective catalysis is an increasingly important method of providing enantiomeric compounds for the pharmaceutical and agrochemical industries. To date, heterogeneous catalysts have failed to match the industrial impact achieved by homogeneous systems. One successful approach to the creation of heterogeneous enantioselective catalysts has involved the modification of conventional metal particle catalysts by the adsorption of chiral molecules, as reviewed recently by C.J. Baddeley *et al.* [202].

The best known metal-based heterogeneous enantioselective catalytic reactions are the hydrogenation of activated C=C bonds [203] (mainly using palladium catalysts modified with cinchona alkaloids), α -ketoesters, [204, 205] (mainly using Pt catalysts modified with cinchona alkaloids and related modifiers) and β -ketoesters [206] (mainly using Raney Ni systems modified with tartaric acid). The reagents (e.g., methyl pyruvate or methylacetoacetate) are close to planar and it is widely believed that: (i) the surface catalyzed reaction involves the dissociation of H₂ into H(ads); (ii) the adsorbed atomic hydrogen attack the pro-chiral reagent from beneath the molecular adsorbate; and (iii) the direction of attack results in the formation of the chiral center with the C—OH bond being oriented away from the surface. The chirality of the ultimate product is therefore thought to be determined by the adsorption geometry of the pro-chiral reagent, thanks to the adsorption of a chiral molecule. The cinchonidine is the most known chiral inductor employed to achieve methylpyruvate hydrogenation. Due to its large size, the cinchonidine could act as an enzyme by encapsulating the reactant. Numerous studies on Pt/cinchonidine systems, in particular from A. Baiker *et al.*, report that the inductor interacts with the reactant molecules through H-bonding thus stabilizing a pro-chiral adsorption geometry of the reactant to the detriment of the other configuration [204]. Nevertheless, there is still a debate concerning the detailed structure of such an adsorption complex. It appears that theoretical calculations [density functional theory (DFT)] could be very helpful to rationalize the role of any supra-molecular docking structure between a substrate and a chiral inductor modified-nanoparticle in inducing chirality, as recently published by A. Baiker *et al.* [207]. Recently, a highly active and enantioselective heterogeneous asymmetric catalyst was fabricated by confining Pt nanoparticles that are modified with cinchonidine within the channels of carbon nanotubes [208]. A high turnover frequency (TOF)

and enantioselectivity are achieved when using this catalyst for the asymmetric hydrogenation of α -ketoesters.

Tartaric acid or aminoacids (alanine and glutamic acid) are other modifiers, which are mainly used with Ni catalytic systems, but their mode of action is less understood. Intensive research on the metal-based heterogeneous enantioselective catalytic hydrogenation reactions continues to get more efficient, more stable or more 'green' nanocatalysts [209–211].

The C—C coupling reactions in their enantioselective version are another type of reaction in which nanocatalysts are evaluated, mainly using Pd nanoclusters stabilized with ligands that are common in homogeneous catalysis. To cite a few examples, interesting results were obtained with chiral xylofuranoside diphosphites-modified Pd NPs in allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene with dimethyl malonate [212]. These particles displayed a high selectivity, the reaction mainly proceeding with one enantiomer of the substrate, hence demonstrating a very high degree of kinetic resolution. For comparison, the same reaction catalyzed by a corresponding molecular species accommodating the same diphosphite ligand and in conditions of dilution where the rates of both catalysts matched proceeded at similar rates with both enantiomers. When changing the ligands and/or the substrates, these systems were found to be dependent both upon the ligands and the substrates in a much more dramatic way than corresponding molecular systems [213]. As another example, H. Fujihara *et al.* reported small PdNPs (1.2–1.7 nm) stabilized with various chiral mono- and bisphosphine (binap, segphos and diop derivatives) ligands as active nanocatalysts in Suzuki–Miyaura cross-coupling reactions at room temperature. Depending on the ligand, the results in terms of yield and enantioselectivity varied with *ee* up to 58% [214, 215]. More recently, they described FePd magnetic nanoparticles modified with chiral binap ligand as a recoverable catalyst for the same asymmetric coupling reaction [216]. This work was the first example of an asymmetric catalytic reaction using chiral magnetic FePdNPs. The interest comes from the easy separation of the catalyst from the reaction mixture by simple application of a magnetic field while keeping the catalytic properties.

To summarize, interesting results in enantioselective catalysis have been obtained by using chirally modified metal surfaces. However, and in contrast to the chiral homogeneous catalysts, the main problem faced in exploiting such systems is the multitude of possible active sites that make them more complicated and most of the time less successful catalysts. The use of chiral modifiers able to interact with the metal surface and/or the prochiral substrate through hydrogen bonding interactions appeared as an attractive way which allowed in some extent to control chirality and further to optimize enantioselectivity. Numerous researchers all over the world tend to find the right catalytic systems to increase the enantioselectivity in a given reaction, by taking inspiration from homogeneous systems that varies the metallic nanoparticles and the chiral inductor, but most of the time, the results obtained are not satisfactory as they are not general. Clearly, the development of convenient nanocatalysts for enantioselective catalysis remains a challenge and a better understanding of the chirality in nanocatalysis could help to succeed in this

task. To cite a recent example, R. Jin *et al.* demonstrated that the use of NMR spectroscopy is very useful to probe the chirality of well-defined gold nanoclusters [217]. They could differentiate chiral nanoclusters from nonchiral ones by characterizing carefully the stabilizing ligands. These encouraging results show that a precise characterization of the nanocatalysts at a molecular level could give precious information on their potential in enantioselective catalysis.

1.5

Conclusions and Perspectives

The field of catalysis science is often criticized as being *ad hoc* and empirical. In that respect, the impact of nanoscience on catalysis, which has been already discussed by scientists from the heterogeneous catalysis community [218, 219], is obvious. Creative use of the modern methods of nanomaterial synthesis coupled with a deep understanding of fundamental molecular surface chemistry and advances in characterization methods has yielded significant progress in some of the most important and challenging problems in the field. This knowledge principally contributes to the development of model catalysts, which can however operate under mild conditions, but also to the design of more robust supported new catalysts.

Thus, since the pioneering work in the field already mentioned in the introduction of this chapter, impressive progress has been realized. We will give below some representative examples, which have been published in top international academic journals. As far as the characterization techniques are concerned, it is now possible: (i) to perform *in situ* studies of chemistry and structure of catalysts in reactive environments [220] [3]; (ii) to get atom-resolved TEM imaging of dynamic shape changes in NPs [221, 222] [4, 5], and to visualize by HRTEM *cis/trans*-isomerization of molecules [223]; (iii) to use the metallic tip of a scanning tunneling microscope as a hydrogenation catalyst [224, 225], or to use the same tip to create a chemical bond between CO molecules and an iron atom to form Fe(CO) and then Fe(CO)₂ [226]; and (iv) to reveal the existence of catalytic regular oscillatory patterns at the nanoscale, by combining field ion microscopy with video techniques and chemical probing [227]. The use of physical techniques such as atomic layer deposition has also made significant progress, allowing the preparation of stable subnanometer platinum clusters deposited in alumina membranes [228].

The huge potential of nanochemistry has also encouraged the development of new or improved synthetic pathways to produce high performance catalytic nanomaterials. Significant progress has been made in controlling monometallic nanoparticle size and shape [229–231], particularly for gold nanocatalysis [232–234]. New strategies to improve nanoparticle stability have been developed [235–237]. The substitution of noble metals by inexpensive nano counterparts has shown promising results, particularly in the field of electrocatalysis [238, 239]. The composition of the nanocatalyst should also be taken into account, and many examples have shown that bimetallic nanocatalysis can bring significant advantages, provided a good

tuning of the structure is achieved [240–243]. For these particles one should keep in mind that restructuring and metal segregation may occur under catalytic conditions [244]. New opportunities for improved performance arise when the multifunctionality inherent in catalytic processes, including molecular transport of reactants and products, is rethought in the light of architectures designed and fabricated from the appropriate nanoscale building blocks (nanoparticle/nanosupport), including the use of ‘nothing’ (void space) and deliberate disorder as design components [245]. The precise design of the nanosupport and the controlled localization of the active phase allows catalyst with specific properties to develop [246, 247].

In parallel, the extraordinary progress in DFT calculations for surface processes has created the possibility of computer-based catalyst design [248, 249]. Computational chemistry has been developed to the point that it can be used to greatly assist experimentalists to screen synthesis routes, to measure properties of materials that are difficult to perform under normal conditions, or to understand various mechanisms. However, nanocatalyst studies are relatively scarce [250]. The reason lies in the difficulty of accurately describing such complex systems, which exhibit a nanoscale metallic core with partially mobile organic molecules on its surface, not so easy to characterize experimentally. More investigation in this area is clearly needed. These ongoing progresses should rapidly enabling catalyst researchers in academia and industry to achieve the goal of catalysis by design.

For the next generation of catalysts, it should clearly have a reduced environmental impact. This will require entirely new catalysts: catalysts for new processes, more active and more selective catalysts and preferably catalysts that are made from earth-abundant elements. This represents a formidable challenge and it will demand an ability to design new catalytic materials well beyond our present capabilities. The ultimate goal is to have enough knowledge of the factors determining catalytic activity to be able to tailor catalysts atom-by-atom.

Beside the obvious scientific impact of nanoscience and nanotechnology on catalysis, we would like to stress the fact that nanoscience and nanotechnology have also been a tremendous lever for two communities, the coordination chemists of homogeneous catalysis and the solid-state chemists of heterogeneous catalysis, to meet and collaborate efficiently on common objectives. This is perhaps the more important contribution that nanoscience and nanotechnology have brought today to catalysis.

Finally, and to be complete, we should also stress that this new discipline combines well-known as well as new areas and concepts of both heterogeneous and homogeneous catalysis, such as:

- description of the chemical bond from both molecular and solid-state point of view
- surface science molecular analysis
- surface coverage, surface restructuring, nonequilibrium self-organizational behavior
- coordination and organometallic chemistry
- nanochemistry, supramolecular chemistry, self-organization
- nanomaterials (eco)toxicity.

just to cite some of them. Nowadays, few scientists have a general background in all of these areas. It is thus important to open new academic programs in order to form the catalysis community of tomorrow.

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