Nanocatalysis has emerged as a field at the interface between homogeneous and heterogeneous catalysis and offers unique solutions to the demanding requirements for catalyst improvement. Heterogeneous catalysis represents one of the oldest commercial applications of nanoscience and nanoparticles of metals, semiconductors, oxides, and other compounds have been widely used for important chemical reactions. The main focus of this field is the development of well-defined catalysts, which may include both metal nanoparticles and a nanomaterial as the support. These nanocatalysts should display the benefits of both homogeneous and heterogeneous catalysts, such as high efficiency and selectivity, stability and easy recovery/recycling.

The concept of nanocatalysis is outlined in this book and, in particular, it provides a comprehensive overview of the science of colloidal nanoparticles. A broad range of topics, from the fundamentals to applications in catalysis, are covered, without excluding micelles, nanoparticles in ionic liquids, dendrimers, nanotubes, and nanowires, as well as modeling, and the characterization of nanocatalysts, making it an indispensable reference for both researchers at universities and professionals in industry.

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Edited by
Philippe Serp and
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Nanomaterials in Catalysis
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With a Foreword by Gabor A. Somorjai and Bruno Chaudret
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Foreword

Catalysis has been the leading science and technology in the 60s, associated with the raise of the use of oil. Refineries and petrochemistry have then known their golden age. The rarefaction of energy sources and the need for a more rational use of the available energy provides a new opportunity for catalysis to play a leading role in society. If catalysis is traditionally divided into three main fields: heterogeneous, homogeneous and enzymatic, the present tendency is the convergence of these fields towards a molecular approach.

Thus, heterogeneous catalysis that usually is carried out at the solid-gas interface and is perhaps the technologically most utilized form as it provides high turnovers to yield products and low deactivation, which provides their long life. Homogeneous catalysis is usually carried out on transition metal ions surrounded by ligands and dissolved in organic solvents. These catalysts show very high selectivity and they play a major role in the pharmaceutical industry. Enzyme catalysts, of which there are about 3000 in the human body, usually operating in water solution under physiological conditions at room temperature and neutral pH. Catalysis is life! It accounts for most of the processes on this planet, whether operating under planetary conditions of near room temperature or making products with high selectivity by the chemical technologies. Revolution in the synthesis of nanomaterials that provides the opportunity to produce catalysts with controlled size and shape has led to the discovery that the catalytic selectivity and turnover correlates with the size and shape of nanoparticles. This observation, along with characterization techniques, allow us to carry out molecular or atomic scale studies of catalyst particles under reaction conditions and provides revolutionary developments in the field of catalysis science, which is named “nanocatalysis”. The result is a rapidly increasing interest for the molecular aspect of catalysis aiming at a new understanding of how catalysts work on molecular and atomic scales. The challenge for the future will be to develop technologies that are very (totally?) selective while little energy demanding and respecting the environment. This process in our contemporary world is commonly called “green chemistry” and can rely on nanocatalysis.

This book entitled Nanomaterials in Catalysis by K. Phillippot and P. Serp is a very timely exposure of the new science and technologies of nanocatalysis. Following an excellent introduction of the concepts in nanocatalysis, the fabrication of nanocatalysts in various media is discussed in several important papers ranging from
nanoparticles in aqueous phase, nanoclusters and colloids as catalysts precursors, nanoparticles in ionic liquid and supercritical fluids, dendrimers that serve as excellent polymeric supports for nanoparticles and finally nanocatalysts recovery, which addresses the problem of deactivation and regeneration. A section is dedicated to nanoparticle supports like carbon nanotubes and nano oxides which are discussed. The last chapter reviews modeling of nanocatalysts to show the foundation of theoretical treatment of nanocatalysis and nanomaterials that are used as catalysts.

This is a timely book and it will be a very useful addition to those interested in the field of catalysis and its most important extension by the use of nanomaterials to carry out heterogeneous, homogeneous and enzyme catalysis. Studies of nanocatalysts and characterization of these nanomaterial systems lead to an atomic and molecular level understanding of how catalyst materials work. The book describes the frontiers of catalysis on a broad front, and we believe it adds to our knowledge and perhaps rapid evolution of the field of catalysis for the near future.

Berkeley and Toulouse
October 2012

G. A. Somorjai
B. Chaudret
Preface

Process catalysts, for petroleum products, chemicals, pharmaceuticals, synthetic rubber and plastics, among others, represent a $13 billion-per-year business worldwide, and as such play a vital role in the economy. Thus, the importance of catalysis in the chemical industry is reflected by the following points:

–>95% of all products (volume) and >70% of all products (processes) are synthesized by means of catalysis,

–>80% of the added value in chemical industry is based on catalysis,

–~20% of the world economy depends directly or indirectly on catalysis.

Catalysts can be classified into two main groups: heterogeneous catalysts (solid-state catalysts) and homogeneous catalysts (transition metal complexes). Of increasing importance are the biocatalysts, enzymes that are protein molecules of colloidal size, which can be classified somewhere between molecular homogeneous catalysts and macroscopic heterogeneous catalysts. There are also intermediate forms, such as homogeneous catalysts attached to solids, also known as immobilized catalysts.

The suitability of these catalysts for an industrial process is governed mainly by the following properties:

–recovery (heterogeneous catalysts ≫ homogeneous catalysts),
–activity (heterogeneous catalysts < homogeneous catalysts),
–selectivity (heterogeneous catalysts ≪ homogeneous catalysts),
–stability (heterogeneous catalysts > homogeneous catalysts).

By far, and mainly because of the recovery aspect, the most applied catalysts at an industrial level are the heterogeneous ones. Indeed, approximately 80% of all catalytic processes involve heterogeneous catalysts against 15% homogeneous catalysts and 5% biocatalysts. The homogeneous systems are currently limited to reactions for which i) heterogeneous catalysts are not stable with a dissolution of the active phase (methanol carbonylation, hydroformylation), ii) the catalyst can be lost (polymerization), or iii) heterogeneous catalysts are inefficient (asymmetric catalysis).

In the past century, catalysis became the basis of large-scale processes in bulk chemistry and petrochemistry. In the XXI century, shifting demands, energy and
new environmental challenges require new catalytic solutions. The two major issues are related to the depletion of raw materials and to the environment/health.

On one hand the depletion of raw materials drives researches:

– on catalysis for energy aiming at: i) improvements in the catalytic processes across the chemical and petroleum industries that will increase resource and energy utilization efficiencies; ii) cost-effective, environmentally sound utilization of energy resources such as coal and biomass; iii) efficient photocatalysts for water splitting and electrocatalysts for fuel cells, and iv) hydrogen storage and carbon dioxide capture and sequestration could benefit from new abilities to catalyze solid-state reactions.

– on new catalytic systems which: i) show high selectivity (atom economy), ii) are able to transform biomass in various chemicals, and iii) are based on cheap and abundant metals.

In parallel, the growing concern over environmental issues and the successful implementation of legislation drives researches in catalysis on two ways to improve the quality of our environment by:

– cleaning up emissions from current processes (catalytic converters, VOC, ozone, pesticides, dioxin . . ., indoor air quality, water pollution, organic particulate), and

– developing alternative cleaner catalytic processes (safer reagents, limited by-products, reduced mass and energy inputs . . ).

Although incremental improvements to catalytic processes will result in a better control of desired chemical transformations, in order to fully realize the needed advancements real breakthroughs must also be achieved:

• in photocatalysis to successfully and economically use solar energy to convert water into oxygen and hydrogen;
• in interfacial electrocatalysis to realize, at a realistically low cost, the efficiency potentially attainable by fuel cells;
• in the gasification and conversion of coal/biomass into transportation fuels;
• in the catalytic conversion of biomass to more useful products;
• in the development of catalysts that operate in aqueous media to fully enable the promise of “green chemistry”; and
• in the construction of multi-component (nanoscale) catalysts.

In such a challenging context, it is obvious that any new branches of catalysis science should be considered as a potential spur to reach the objectives. A promising approach consists in bridging the gap between homogeneous and heterogeneous catalysis, in order to combine the advantages of each ones. The first efforts date from the 70’s with the first International Symposium on Relations between Homogeneous and Heterogeneous Catalysis in 1973. In the middle of the 90’s, catalysis joined the nanosciences and nanotechnologies wave, which significantly contributed to reinforce the connections between molecular and solid state catalysis communities.
At that time, we both started our scientific carrier, during a period in which the prefix nano was poorly used (Figure 1). One of us (Karine) as a PhD student and after as a postdoc at Rhodia worked on the homogeneous rhodium catalyzed hydrosamination reaction and the synthesis of carbonates with tin-supported catalysts, respectively, before integrating the Centre National de la Recherche Scientifique where she develops ligand-functionalized colloidal nanoparticles for application in catalysis. The other (Philippe) as a PhD and then a post-doc student, investigated the potential of chemical vapor deposition methods to prepare supported catalysts or carbon nanomaterials, and is now the team leader of a group that develops new catalytic systems for both homogeneous and supported catalysis. We are both very excited by the catalysis with nanomaterials, due to our double scientific background that allows to conciliate the molecular and solid state point of view, and to work on the bridge in between homogeneous and heterogeneous catalysis.

Thus, the terms “nanocatalyst” and “nanocatalysis” have appeared some years ago as a continuation of the development of nanotechnologies. Today, few books are dedicated to the subject,[1–4] and a recent article [5] raises this interesting question: “Nanocatalysis: Mature science revisited or something really new?” In the present book, the concepts of nanocatalysis are defined, to give to the reader a comprehensive overview of what is a nanocatalyst, and to rationalize the advantages of nanocatalysts related to their activity, selectivity and stability. Thus, each chapter will provide a critical overview of a specific domain of nanocatalysis through the most relevant examples of the literature.

In that sense, this book is the first one that introduces concepts and main achievements, and covers the main aspects of nanocatalysis in general, considering both the active phase, and the support as well as their modeling and characterization.
Since this is a multi-authored book, significant differences in style from chapter to chapter are inevitable, but we have tried to avoid overlaps as much as possible. We thank all the authors for their efforts to meet deadlines, and to follow the format defined for the book. We would also like to acknowledge the assistance of Anne Brennfueher and Lesley Belfit at Wiley-VCH, whose advice has been most helpful at the various stages of preparation of the manuscript. Finally, we hope that the book will be useful to fellow scientists and practitioners and will stimulate further research and discussion on the development of nanomaterials for catalysis.

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1
Concepts in Nanocatalysis
Karine Philippot and Philippe Serp

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 (molec-
ular 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 pres-
ent 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 communi-

ties 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 sur-
fases 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 sci-
entists 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](image-url)  
**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.
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 $\pi$-bond is often the rate-limiting step. The prototypical reactions for this group are dissociation of CO and $N_2$ 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 $\sigma$-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,
number of nearest neighbors, and both two- and three-dimensional geometry of
the catalytically active surface atoms. The availability of particular types of adsorp-
tion 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 low-
est energy crystal face. Under certain conditions, however, nanoparticle catalysts
can be synthesized such that the shape, and consequently the surface atom orienta-
tion, 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 dif-
ferent 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 arene hydro-
genation, 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 clus-
ter of atoms, to vary from that of an isolated atom. Adjustment of the relative num-
ber 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
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
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