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INTRODUCTION TO  
NANOCATALYSIS

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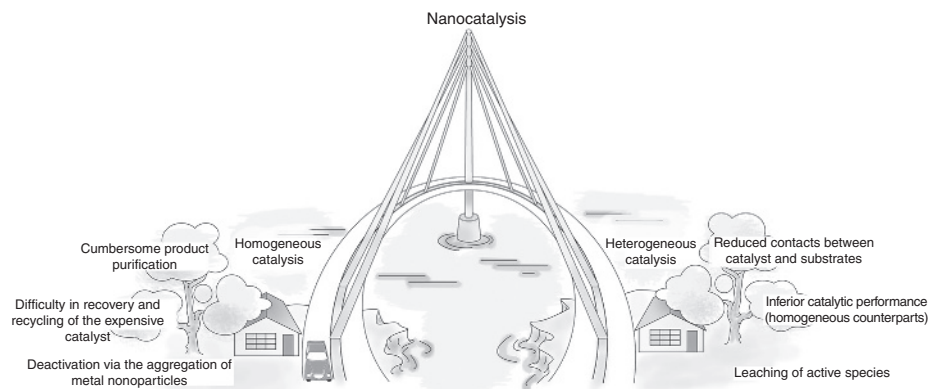
Catalysis provides sustainable and cost-effective methods to transform raw materials into valuable chemicals. Thus, catalytic processes have long become essential to solving the energy and environmental challenges that we currently face around the globe. Catalysis can be broadly divided into homogeneous and heterogeneous catalysis. Homogeneous catalysis involves catalysts and reactants in the same phase.<sup>1</sup> As homogeneous catalysts are generally soluble molecular or ionic compounds, they have more easily accessible active catalytic sites, and thus often exhibit good catalytic activity. Moreover, their structures and functional groups can easily be changed to result in chemo-, regio-, and enantioselectivity. However, despite their many advantages and being widely used in industry, homogeneous catalysts do have some disadvantages, which is mainly to do with the fact that they are difficult to separate from the final products or reaction mixtures. Furthermore, even with the use of numerous techniques, such as chromatography, distillation, or extraction, the removal of trace amounts of residual catalytic species from the reaction mixture is always challenging in the case of homogeneous catalysis. This is an important issue that requires attention, given the fact that the presence of trace amounts of catalytic moieties, especially metallic ones, is strictly regulated in the commodity chemicals and pharmaceutical products, which are often produced using catalysts. All of these issues together, therefore, pose major hurdles for homogeneous catalysts, making many of them to have only limited applications.

Some of these drawbacks of homogeneous catalysts can be overcome by supporting the homogeneous catalytic species on solid support materials and producing their corresponding solid catalysts, known as heterogeneous catalysts.<sup>2</sup> The general approach behind the synthesis of heterogeneous catalysts involves either the entrapment (immobilization) or the attachment of an active catalytic moiety on the solid support material. The former can be accomplished by letting the catalytic species to adsorb on the solid support materials, whereas the latter can be realized by tethering the catalytic groups on the support materials with covalent bonds, preferably with strong covalent bonds that can tolerate severe reaction conditions. Because of the physical attachment of the catalytic groups onto the solid support materials, heterogeneous catalysts often possess numerous advantages, such as their ease of handling, efficient recovery, enhanced stability and shelf-life, and reusability. However, because the reactants and the catalysts in heterogeneous catalysis must necessarily be in two different phases, the interaction between the reactant and the catalyst is reduced. This, in turn, can result in reduced overall catalytic activity in heterogeneous catalysts compared with their homogeneous counterparts. Possible leaching of active catalytic sites from the solid support materials, either from the cleavage of the covalent bonds between the catalytic groups and the solid support material or from the possible desorption of the catalytic groups off the solid support material, can also be an issue for some heterogeneous catalytic systems. Although the concentration of trace metals can often be much smaller in heterogeneous catalytic systems compared with that in the corresponding homogeneous catalytic systems, such possible leached trace metals in heterogeneous catalytic systems might still require separation from final products.

To overcome some of the limitations associated with both homogeneous and heterogeneous catalysts, new catalytic systems were needed that could have the advantages of both homogeneous and heterogeneous catalytic systems, allow all catalytic active sites to be accessible and effective (i.e., give good catalytic activity, selectivity, and yield), and make catalyst separation easily possible (i.e., stable catalyst, catalyst recovery, and catalyst reuse). Nanocatalysts and nanocatalysis could meet the need of such new catalyst systems (Figure 1.1).

## WHAT IS NANOCATALYSIS?

The seemingly magical properties of nanoparticles have been unknowingly taken advantage of and used for various applications for centuries. Early uses of nanostructured materials include the third-century Lycurgus Cup,<sup>1</sup> made of a dichroic glass of gold and silver nanoparticles, which made the cup look opaque green when lit from the outside and glowing red when lit from the inside. Similar shiny and sparkling ceramic glazes, which were used between the ninth and seventeenth centuries,<sup>2</sup> also contained various metallic nanoparticles. The qualities of “Damascus” saber blades, used from 300 BCE to 1700 CE, including their excellent strength, toughness, and resistance to shattering, as well as their ability to remain extremely sharp, all came from their construction from carbon nanotubes and cementite nanowires.<sup>3</sup> Even in the century-old Haber–Bosch process for ammonia synthesis,<sup>4</sup> iron nanoparticles were present.<sup>5</sup> It was also in the beginning of



**Figure 1.1.** Nanocatalysis can bridge the gap between homogeneous and heterogeneous catalysis, bring together the advantages of both homogeneous and heterogeneous catalysts, and overcome some of the issues associated with both homogeneous and heterogeneous catalytic systems.

the twentieth century that Ostwald performed simple experimental demonstration that indicated the considerable increase of surface area from dividing cubes and its consequences for surface-dependent catalysis. In fact, we now use, perhaps still unknowingly too, huge varieties of nanomaterials in our daily lives<sup>6</sup> as well as in industrial processes such as catalysis. As is often said, “nature makes and chemistry reshapes.”

Nanocatalysis has long become an important part of nanoscience.<sup>7</sup> Nanoparticles can substitute conventional materials and serve as active and stable heterogeneous catalysts<sup>6</sup> or as support materials for various catalytic groups.<sup>7</sup> Due to their small sizes, catalytic-active nanoparticles have higher surface area and increased exposed active sites, and thereby improved contact areas with reactants, akin to those of homogeneous catalytic systems. At the same time, nanostructured catalysts can behave as heterogeneous catalysts; thus, they can also be easily separated from the reaction mixtures. In addition to their tunable catalytic activity and selectivity, often with activities close to homogeneous catalytic systems, the stability of nanocatalysts can be improved by tailoring the chemical and physical properties of the nanomaterials by various synthetic methods. For example, nanocatalysts with better activity, stability, and selectivity can be designed and synthesized merely by controlling the sizes, shapes, and morphologies of nanomaterials.<sup>7-9</sup>

## NANOCATALYSIS: TRUTH OR HYPE?

There has been much discussion about the originality of the concept “nanocatalysis.” The question whether nanocatalysis is novel science or merely a fancy version of already known catalysis has often been posed. Several researchers have said, “Catalysis is always nano”. But, is this true? If it is true, then why is gold not active in its bulk state when it exhibits extraordinary catalytic activity when reduced to the nanoscale? Why does

bulk cobalt oxide need high temperatures to oxidize CO to CO<sub>2</sub>, while cobalt oxide can catalyze the same reaction at very low temperatures at nanoscale size? There are a huge number of such examples (with their numbers increasing every day) of materials that show unprecedented catalytic activities when reduced from the bulk into nanoscale sizes.

Thus, the statement that “catalysis is always nano” may not be correct. What we can safely say, however, is that “catalytic interactions are always in the nanoscale.” More precisely, nanocatalysis (catalysis using nanomaterials), with catalytic interactions obviously in the nanoscale range, is at least a step beyond conventional catalysis (catalysis using bulk materials).

Nanocatalysts are extremely structure-sensitive, and their catalytic activity and selectivity depend heavily on the size, shape, and composition of the nanoparticles as well as their support materials. This can be exemplified by the largely unexpected results that gold nanoparticles smaller than 5 nm are very active catalysts even at subambient temperatures, while bulk and bigger size gold is inactive.<sup>8,9</sup> The benefit of the increased surface-to-volume ratio and the benefit of accessibility to specific sites (e.g., steps, edges, and corners) of nanoparticles to catalysis are now well-known.<sup>10,11</sup> Therefore, multiple and extremely varied approaches to develop efficient nanocatalysts have been pursued. This includes the synthesis of metallic and metal oxide nanomaterials with different unique structures and shapes and their applications either as catalysts or as support materials for catalytic active species. Further research in this area or the development of nanocrystalline catalytic systems are also currently continuing. Furthermore, nanocatalytic reaction mechanisms are complex and not yet fully understood,<sup>12</sup> making nanocatalysis a very exciting science with lots of room for further investigation.

Nanocatalysis can be considered as part of “green” science as well, because nanocatalysis often allows conducting chemical transformations in an environmentally friendly manner.<sup>13</sup> This is possible, for example, by adopting magnetic nanocatalyst recovery,<sup>14</sup> by mixing ionic liquids with metal nanoparticles,<sup>15</sup> by creating electrodes with nanocatalysts with improved redox properties for energy-relevant applications, by encapsulating nanoparticles in nanoporous cavities of zeolites and molecular organic frameworks, and by controlling the shapes of metal and metal oxide nanoparticles to enhance their catalytic activities.<sup>16</sup>

The purpose of this book is to give readers a broad perspective and current information about catalytic protocols developed over the past several years involving nanomaterials as catalysts, (i.e., nanocatalysis). The 18 chapters in the book cover a huge range of fields, where a variety of nanomaterials are successfully used as catalysts. In each chapter, some discussion is made about the synthesis, characterization, and application of nanocatalysts in different chemical reactions. In addition, some typical detailed experimental procedures for the synthesis and characterization of nanocatalysts and how these nanocatalysts are employed to catalyze various important chemical reactions are presented.

The first six chapters are devoted to nanocatalysts or nanocatalysis for carbon–carbon (C–C) and carbon–heteroatom coupling reactions. While there are many C–C cross-coupling reactions, the Heck, Sonogashira, Suzuki–Miyaura, Kumada–Corriu, Negishi, Stille, Hiyama, and Fukuyama coupling reactions remain among the most broadly used in industrial applications. These C–C coupling reactions are essential

in wide ranges of synthetic chemistry. This can be evidenced by the Nobel Prize in Chemistry awarded to Heck, Negishi, and Suzuki in 2010. In Chapter 2, Asefa and coworkers have reviewed the Heck reaction catalyzed by transition metal (mainly Pd) nanoparticles. The authors have also included other metal nanoparticles, such as Ru, Ni, and trimetallic Au–Ag–Pd, which have been recently shown to catalyze the Heck reaction.

The metal-catalyzed Suzuki cross-coupling reaction of aryl, vinyl, or alkyl halide or pseudohalides with organoboron reagents is among the most efficient synthetic methods to construct C–C bonds. The Suzuki reaction has, therefore, found widespread applications in organic syntheses. In Chapter 3, Rosi and coworkers have provided a critical review regarding the use of nanocatalysts for the Suzuki coupling reaction. Many advantages, such as catalyst recovery, catalyst reusability, and wide accessibility of the catalytic groups supported on organic, inorganic, or organic–inorganic hybrid solids and liquids (biphasic catalysis), are also discussed in detail.

Another important C–C coupling protocol is the Sonogashira reaction, which is often catalyzed by palladium-based catalysts and is capable of coupling a terminal sp-hybridized carbon in an alkyne with an sp<sup>2</sup> carbon of an aryl or vinyl halide (or triflate). In Chapter 4, Chinchilla and Nájera have reviewed the development of nanocatalysts for this reaction. The authors have discussed the many different methods used to synthesize Pd nanocatalysts by immobilizing palladium nanoparticles on polymers, carbon nanostructures or inorganic materials for the Sonogashira reaction, and the applications of the materials as catalysts for the reaction. They have also included a review on the synthesis and use of non-palladium nanoparticles composed of copper, iron, ruthenium, or gold as catalysts for this reaction.

In Chapter 5, Banerjee and Scott have provided a review of the use of nanocatalysts for a variety of other types of C–C coupling reactions, namely the Hiyama reaction (involving organosilicon reactants), the Negishi reaction (involving organozinc reactants), the Stille reaction (involving organotin reactants), and the Kumada–Corriu reaction (involving organomagnesium reactants). The authors have discussed the synthesis and use of stabilized nanoparticles as catalysts for these coupling reactions. They have also discussed some newer synthetic strategies to nanocatalysts for these reactions from recent literature. Furthermore, they have presented mechanistic aspects of these coupling reactions as catalyzed by nanocatalysts, which include *in situ* conversions of precatalysts to actual zerovalent catalytic metal clusters.

In Chapter 6, Ranu and coworkers have reviewed the research works on nanocatalysts for carbon–heteroatom bond-forming reactions. The latter include carbon–sulfur, carbon–nitrogen, carbon–oxygen, and carbon–selenium reactions, which are used extensively in various chemical, material, and industrial processes. The authors have provided some accounts of the developments in the field of nanocatalysis and also discussed both the advantages and disadvantages of many nanocatalytic processes.

The next two chapters are devoted to nanocatalysis for fine chemical synthesis. In Chapter 7, Asefa and coworkers have reviewed nanocatalysis of three important and related reactions, namely the Henry, Aldol, and Knoevenagel reactions. The authors have also included several different synthetic approaches or methods developed to various nanocatalysts for these reactions.

The concept of atom economy, that is, designing synthetic methods to maximize the incorporation of all atoms used in a reaction into final reaction products, has emerged as a major goal for chemists in recent years. The skeletal rearrangements of organic molecules (e.g., isomerizations, cycloisomerizations, and pericyclic reactions) are typical notable examples of atom economical reactions because such reactions generate no by-products. In Chapter 8, García-Álvarez and coworkers have provided an up-to-date overview of published literature on the synthesis and applications of metal and metal oxide nanoparticles that can serve as catalysts for various rearrangement reactions of organic compounds.

The subsequent four chapters are devoted to the use of nanocatalysts for oxidation and hydrogenation reactions. Oxidation of alcohols is widely recognized as a fundamental and important transformation in both laboratory and industrial chemistry because the reaction results in carbonyl compounds that can serve as versatile solvents, polymer precursors, fragrances, and intermediates for fine chemicals and pharmaceuticals. In Chapter 9, Mitsudome and Kaneda have reviewed nanocatalysts based on inorganic material- or polymer-supported active metals of Ru, Pd, and Au for alcohol oxidation reaction in the liquid phase. The chapter not only provides good understanding of nanocatalysis for alcohol oxidation reactions but also highlights the issues related in this area that still need to be addressed in the future.

Besides their size, the shape of nanocatalysts plays an important role in determining the catalytic activity, selectivity, and stability of various nanocatalysts. In Chapter 10, Shen has summarized recent progress on morphologically controlled synthesis of  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{CeO}_2$  nanomaterials. Furthermore, the authors have described how tuning the shapes of these metal oxide nanocatalysts modulates their surface atomic configurations, and thereby catalytic properties for various reactions, including oxidation. In addition, the authors have discussed how morphology-dependent nanocatalysis has enabled our fundamental understanding of the structure–reactivity relationship in heterogeneous catalysis and provided some of their thoughts for some new direction for the development of highly efficient nanocatalysts.

Like oxidation, hydrogenation is an important reaction. In Chapter 11, Narayanan has reviewed the different types of nanocatalysts developed for hydrogenation reactions of alkenes, alkynes, and aromatic compounds. The author has also presented a survey of various nanocatalysts, including metal nanoparticles in colloidal solutions and metal nanoparticles adsorbed onto different supports, for hydrogenation and related reactions.

Along similar lines, Fihri and Polshettiwar have discussed nanocatalysts for hydrogenolysis reactions in Chapter 12. The authors have divided the chapter into two sections: the first one is on the nanocatalytic hydrogenolysis of glycerol, an important category of processes for glycerol conversion into commodity chemicals; and the second one is on the hydrogenolysis of alkanes, which potentially allows the conversion of natural gas into hydrocarbons with higher carbon numbers or liquid form. In both sections, various nanocatalytic systems that use mono- and bimetallic nanomaterials as well as metal nanoparticles modified by metal oxides are discussed.

The subsequent two chapters are devoted to the topic of nanomaterial-based photocatalysis. Photocatalysts increase the rate of a reaction when specifically activated by either ultraviolet (UV) or visible electromagnetic radiation. Using UV or visible



light as a source of energy, especially sunlight, to promote photocatalytic reactions is of great importance to making catalytic protocols sustainable in terms of the environment and the economy. In Chapter 13, Mishra and Khushalani have summarized different types of nanomaterials used in photocatalysis, by paying particular attention to metal oxide-based photocatalytic materials and methods employed for their synthesis and their application as photocatalyst for the degradation of organic pollutants using visible light.

Water splitting is a reaction that can provide hydrogen from water; thus, it can serve as a potential energy source and solution to energy and environmental problems our world faces. Photocatalytic water splitting using nanomaterials as catalysts is extensively reviewed by Zong, Lu, and Wang in Chapter 14. The authors have started with a brief introduction of water-splitting reactions activated by nanocatalysts. They have also given an overview of semiconductor nanocatalysts by classifying them according to the type of light they can absorb or their absorption properties as well as elemental compositions. At the end of the chapter, they have discussed important criteria for the design and development of efficient and stable semiconductor nanocatalysts for water splitting and other related photochemical processes.

The next two chapters are devoted to the use of nanocatalysis to produce non-conventional sources of energy. Environmental concerns, process efficiency, and safety remain to be important issues in the development of catalysts, and these issues are stimulating the development and innovation of catalysts for sustainable H<sub>2</sub> production. Hydrogen can actually be produced from renewable sources. In Chapter 15, He and Wang have reviewed the latest research advances related to H<sub>2</sub> production from biomass and biomass-derived feedstock. They have also discussed the existing challenges behind conversion of both types of feedstock. They have included the use of synchrotron-based X-ray absorption spectroscopy as the characterization method for determination of the properties of nanocatalytic materials considered for renewable H<sub>2</sub> production.

Along similar lines, in Chapter 16, Budarin, Shuttleworth, Lanigan, and Clark have provided a critical overview of biofuel production using nanocatalysts. The authors have discussed that nanocatalysis has been increasingly used or considered in biofuel production, for greener processing of various chemical raw materials, and for affording higher yields of desired products of various chemical processes. This, in turn, results in more economically favorable and cost-competitive processes compared with conventional chemical processes.

Owing to their large surface area, physical robustness, high resistance to organic solvents, and high thermal stability, nanomaterials are also attractive as support materials for immobilizing enzymes. Consequently, a variety of future applications are envisaged for nanomaterial-based biocatalysts in the medical, industrial, pharmaceutical, and environmental areas, including biosensor development, bioremediation, and food production. In Chapter 17, Lee and coworkers discussed nanomaterial-based biocatalysts and biocatalysis. The authors have also given an overview of the state-of-the-art technologies in practice and discussed this rapidly developing field that focuses on nanomaterial-based biocatalyst systems. Because nanomaterial-based biocatalysts have greater stability and higher shelf-lives, these materials enable traditional enzymes to find applications as catalysts in conventional chemical synthesis, where relatively harsh reaction conditions are often employed.

The last two chapters focus on the use of nanocatalysts in the chemical industry. In Chapter 18, Ghosh and coworkers have critically reviewed the role of nanocatalysis in the chemical industry. Using several case studies, they have explained how nanocatalysts have already been successfully used for several important chemical processes in industry.

In the final chapter, Chapter 19, Kalidindi and Jagirdar have discussed nanocatalysts in the context of activation of small molecules and their conversion to useful chemicals. The authors have discussed three nanocatalytic processes, namely CO oxidation on Au/metal oxide catalysts, direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub>, and methanol synthesis from CO and CO<sub>2</sub>. These three reactions have great industrial and environmental importance.

In its entirety, this book provides fundamental understanding of nanocatalysis and a wealth of information on synthesis, characterization and applications of nanocatalysts. The book also provides an important and critical overview on how nanocatalysis can serve as a platform from which a virtually unlimited number of crucial chemical process issues can be resolved. The obvious applications of nanocatalysts will be in fine chemical synthesis, where refined nanocatalysts allow the production of desired products in higher yields. Another notable example where nanocatalysts have potential application is in energy (hydrogen) production from water, or a renewable source of energy with sunlight. Nanocatalysis can also play significant role in resolving the energy and environmental challenges that we as a global society now face. Thus, nanocatalysis can help us take gigantic steps forward for the betterment of humankind through the use of tiny nanoscale particles.<sup>17</sup>

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