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Edited by
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Preface

Catalysis is a central concept in chemistry, playing, for instance, a key role in biological and industrial processes. For a century, catalysis has been divided into homogeneous and heterogeneous reactions, and scientific communities have crystallized around each aspect. The advent of nanosciences has now clearly promoted the bottom-up strategy over the top-down one, making this traditional frontier obsolete. Thus, the molecular approach is presently most useful for the definition of selective and efficient heterogeneous catalysts that can be removed from reaction media and re-used. Nanocrystals of size one to only a few nanometers present the best catalytic efficiency, yet their support is most important for the synergistic activation of substrates, as best illustrated by Haruta's famous catalysis of CO oxidation by O₂ at 200 K by oxide-supported gold nanoparticles (NP).

Therefore, this book is timely in gathering together the best experts in catalysis, coming originally from both homogeneous and heterogeneous catalysis communities, who have imagined a large number of synthetic approaches to catalytically active transition-metal NPs and their derivatives. All of them now focus on aspects that promote selectivity and efficiency for a broad variety of molecular-activation processes with goals ranging from organic synthesis to hydrocarbon reforming and environmental problems.

Thus the first part of the book (Chapters 1 to 9) deals with NP catalysis, emphasizing the key role of NP supports; the second part (Chapters 10 to 12) concerns specific metals (namely Pd, Ru, Ir and Au), and the last part (Chapters 13 to 18) focuses on specific substrates of particular interest for organic chemistry, hydrocarbon reforming and environmental aspects. Among the metals, Pd and Au are the most effective catalysts. Palladium is the most efficient catalyst for carbon-carbon bond formation thus, besides Chapter 10 that is devoted to PdNPs, their catalytic properties also spread over the first part of the book. Gold is the most efficient NP catalyst for a variety of aerobic (thus low-cost) oxidation reactions, and AuNP catalysis is covered in four chapters at the end of the second part and beginning of the third part. Each chapter is introduced in more detail in Chapter 1.

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We strongly believe that this book will greatly catalyze research in this key field in the forthcoming years for the benefit of our Society. Have a nice read!

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1

Transition-metal Nanoparticles in Catalysis: From Historical Background to the State-of-the Art

Didier Astruc

1.1

Introduction

The nanosciences have recently evolved as a major research direction of our modern Society resulting from an ongoing effort to miniaturize at the nanoscale processes that currently use microsystems. Towards this end, it is well admitted that the bottom-up approach should now replace the classic top-down one, a strategic move that is common to several areas of nanosciences including optoelectronics, sensing, medicine and catalysis. The latter discipline certainly is the key one for the development of starting chemicals, fine chemicals and drugs from raw materials. During the twentieth century, chemists have made considerable achievements in heterogeneous catalysis [1], whereas homogeneous catalysis [2] progressed after the second world war (hydroformylation) and especially since the early 1970s (hydrogenation). Heterogeneous catalysis, that benefits from easy removal of catalyst materials and possible use of high temperatures, suffered for a long time from lack of selectivity and understanding of the mechanistic aspects that are indispensable for parameter improvements. Homogeneous catalysis is very efficient and selective, and is used in a few industrial processes, but it suffers from the impossibility of removal of the catalyst from the reaction media and its limited thermal stability. *Green catalysis* aspects now obviously require that environmentally friendly (for instance phosphine-free) catalysts be designed for easy removal from the reaction media and recycling many times with very high efficiency. These demanding conditions bring a new research impetus for catalyst development at the interface between homogeneous and heterogeneous catalysis, gathering the sophisticated fulfilment of all the constraints that were far from being fully taken into account by the pioneers and even the specialists in each catalytic discipline in the former decades. Yet the considerable knowledge gained from the past research in homogeneous, heterogeneous, supported and biphasic catalysis, including also studies in non-classical conditions (solvent-free, aqueous, use of ionic liquids, fluorine chemistry, microemulsions, micelles, reverse micelles, vesicles, surfactants, aerogels,

polymers or dendrimers), should now help establish the desired optimized catalytic systems.

In this context, the use of transition-metal nanoparticles (NPs) in catalysis [3] is crucial as they mimic metal surface activation and catalysis at the nanoscale and thereby bring selectivity and efficiency to heterogeneous catalysis. Transition-metal NPs are clusters containing from a few tens to several thousand metal atoms, stabilized by ligands, surfactants, polymers or dendrimers protecting their surfaces. Their sizes vary between the order of one nanometer to several tens or hundreds of nanometers, but the most active in catalysis are only one or a few nanometers in diameter, i.e. they contain a few tens to a few hundred atoms only [4]. This approach is also relevant to homogeneous catalysis, because there is a full continuum between small metal clusters and large metal clusters, the latter being also called colloids, sols or NPs. NPs are also well soluble in classic solvents (unlike metal chips in heterogeneous catalysis) and can often be handled and even characterized as molecular compounds by spectroscopic techniques that are well known to molecular chemists, such as ^1H and multinuclear NMR, infrared and UV-vis spectroscopy and cyclic voltammetry. Molecular mechanisms involving the NP surfaces in catalytic reactions are much more difficult to elucidate, however, than those of monometallic catalysts, and the size and shape of the NP catalysts are key aspects of the catalytic steps. NPs themselves can also be used as catalysts in homogeneous systems or alternatively they can be heterogenized by fixation onto a heterogeneous support such as silica, alumina, other oxides or carbon, for instance carbon nanotubes. Thus, the field of NP catalysis involves both the homogeneous and heterogeneous catalysis communities, and these catalysts are sometimes therefore called “semi-heterogeneous” [3, 5]. This field has attracted a considerable amount of attention recently, as demonstrated by the burgeoning number of publications in all kinds of catalytic reactions, because NP catalysts are selective, efficient, and recyclable and thus meet the modern requirements for *green catalysts*. Applications are already numerous, and the use of these catalysts in industry will obviously considerably expand in the coming years. Table 1.1 shows the impressive number of catalytic reactions that have been achieved using transition-metal NPs under rather mild conditions.

The stabilization of NPs during their synthesis can be electrostatic, steric, electrosteric (combination of steric and electrostatic, see Fig. 1.1) or by ligands [4, 5, 8, 11]. The NP synthesis can also occasionally be carried out from metals by atomic metal vaporization or from metal(0) complexes [11]. In view of the catalyst recycling, NP catalysts are often immobilized or grafted onto inorganic or organic polymer supports [4, 5, 8, 11]. The mechanism of transition-metal NP self-assembly has recently been subjected to detailed studies by Finke’s group with a proposal of a four-step nucleation mechanism including two autocatalytic steps [11k]. Such mechanistic studies are of fundamental interest for NP catalysis overall.

There are many reviews on the multiple NP synthetic modes [4–11], and here we will not systematically detail this aspect *per se*. We concentrate our attention on catalysis, from the pioneering studies to the present state of the art.

Table 1.1 Reactions catalyzed by transition-metal nanoparticles.

Reaction	References (see also general Refs. 3–11)
Hydrogenation	
Simple olefins and dienes	2, 6b, 10d–i, 12, 14d,f,j,k,l, 16, 17a,b,d, 23, 26, 31l,o–q, 32, 33, 35a,i, 36a, 40a, 41, 43d, 44b,h, 46a–d, 58, 61
Alkynes	14c, 37b, 39, 40b, 62, 63
CO ₂	10, 82
Arene ring	12a, 29, 33k,m, 34, 37b, 65–70
Arene rings of dibenzo-18-crown-6-ether	64
Acrolein	12b, 78
Methylacrylate	16
Allylic alcohols	14d, 17b
<i>N</i> -isopropylacrylamide	17b
Ethylpyruvate	30a, 63
Citral	32c,d,e
Styrene	18i
<i>Trans</i> -stilbene	32h,f
Opening of epoxides	14a
Dehydrolinalol	14b
Citronellal	59b
9-Decen-1-ol	35n
Various olefins including functional ones	9f,g; 14e, 22b,d, 32h, 33k,m
Polar olefins	22b
Nitroaromatics	9a, 59c, 60, 61
Ketones, benzonitrile	14h, 33l, 35d,i
Cinnamaldehyde	47, 59a
Asymmetric hydrogenation	29
Heck C–C coupling (ArX + olefin → arylolefin)	7, 8b, 14f, 17f, 18i, 22, 24a, 31a–n, 32n, 33e–g,i,j, 35g,n, 40b, 43a–f, 44a–k, 53, 71, 72, 73
Suzuki C–C coupling (ArX + Ar'B(OH) ₂ → Ar–Ar')	13a,b, 14i, 17i–k, 21, 22, 23, 24a, 25, 26, 27, 31m,n, 33e,h,i 34b, 35b,o, 43c, 44c–e,l, 54, 72f, 74a, 76
Sonogashira C–C coupling (ArX + alkyne → arylalkyne)	28c, 43g,h,i
Stille C–C coupling (ArX + Bu ₃ SnR → Ar–R)	33h
Negishi C–C coupling (ArCl+RZnX → Ar–R)	44m
Kumada C–C coupling (ArCl+RMgX(Ar–R)	44j,k
Dehydrohalogenation of aryl halides	44i,n
Amination of aryl halides and sulfonates (ArX + RNHR' → Ar·N(R)R')	44k–o, 74b, 77
Hydrosilylation	9h, 49a
Coupling of silanes	28a,b
Hydroxycarbonylation of olefins	75

Table 1.1 Continued

Reaction	References (see also general Refs. 3–11)
[3 + 2] Cycloaddition	55
McMurry coupling	56, 57
Oxidation	
CO	8a, 9d,e, 11j, 17, 34, 36a,b,e, 37c,d, 45, 51b, 80
Dihydrogen	46e
Aromatic amines	33g, 46f
Alkyl amines	9d
1-Phenylethanol	38
CH ₃ OH and alcohol electro-oxidation	47
Cyclooctane	49b
Cyclohexane	46g
Ethene and propene epoxidation	50
Glucose	52, 46h
Diol, Glycerol, ethylene glycol	46c,e, 81
Oxalate	46h
Amination	24b, 43j
Carbonylation	
Aryl halides	24b
Methanol	53a
Allylic alkylation	30f, 31, 35c, 57
Mannich	57
Pauson-Khand	11h, 35c
Hydroconversion of hydrocarbons	40a
Combustion: alkanes, arenes, alcohols	32e, 35j, 79
Methanol reforming	36c, 39h

1.2

Historical Background

Soluble AuNPs appeared about two thousand years ago and were used as pigments for esthetic and curative purposes. On the materials side, their use to make ruby glass and for coloring ceramics was known in these ancient times, as exemplified by the famous Lycurgus cup (dated 4th century AD, British Museum) [8a]. Modern syntheses of NPs are often inspired by the 150-year old method of Faraday who demonstrated the formation of red solutions of AuNPs by reduction of tetrachloroaurate [AuCl₄]⁻ using phosphorus as the reducing agent [8a,b]. This strategy has been popularized again by Schiffrin's group in 1993 [8a,c], using NaBH₄ reduction of a metal precursor such as HAuCl₄ in a biphasic organic solvent–water system in the presence of the phase-transfer reagent [N(C₈H₁₇)₄]Br followed by the addition of a thiol that stabilizes the NPs as a thiolate ligand [8a,c]. Likewise,