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Understanding active species in catalytic transformations: From molecular catalysis to nanoparticles, leaching, "Cocktails" of catalysts and dynamic systems

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ABSTRACT

In the present review, we consider the transformations of molecular catalysts, leaching, aggregation and various interconversions of metal complexes, clusters and nanoparticles that occur during catalytic processes. The role of catalyst evolution and the mechanistic picture of "Cocktail"-type systems are considered from the perspective of the development of a new generation of efficient, selective and re-usable catalysts for synthetic applications. Rational catalyst development and the improvement of catalyst performance cannot be achieved without an understanding of the dynamic nature of catalytic systems.

Contents

1. Introduction

During recent decades, catalysis has made a paramount impact on the development of new industrial technologies and has facilitated the advancement of science in several key directions. The cost-efficient manufacturing of chemicals at a large scale is necessary to meet demands for fuels, polymers, energy, materials, agrochemicals and many other industrial products. On the other hand, demanding pharmaceutical and medical applications have motivated the development of fine organic syntheses of relatively small quantities of unique molecular architectures of the upmost level of molecular complexity [1–24].

Mechanistic studies have uncovered the intriguing nature of catalytic transformations, and at each stage, this new mechanistic knowledge has inspired the development of more efficient and

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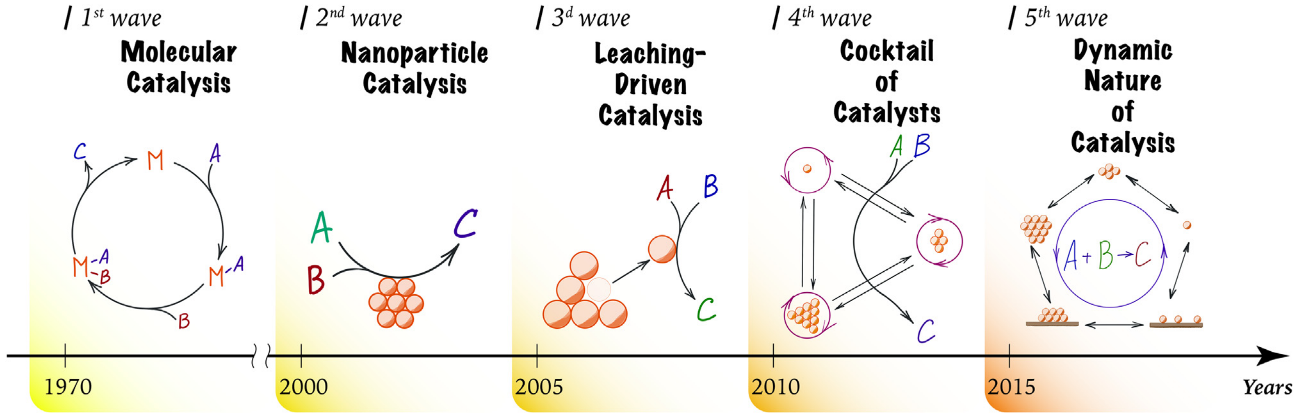

Fig. 1. "Waves" in the mechanistic studies of the nature of transition-metal-catalyzed reactions considered in the present review (the 'years' axis shows influential periods of mechanistic studies in the development of new applications in organic synthesis, rather than the year of the first mention or discovery).

selective catalytic systems. In the areas of fine organic synthesis and the production of complex organic frameworks, molecular mechanisms within the homogeneous catalysis framework have been ubiquitously explored (1st Wave, Fig. 1). The active application of nanosized catalysts and the investigation of leaching have initiated new waves in mechanistic studies and have led to a number of novel approaches in catalyst design (2nd and 3rd Waves, Fig. 1) [25–46]. An amazing increase in catalyst efficiency has rendered synthetic transformations possible at ppm and ppb levels of catalyst and has even given rise to the discussion of "homeopathic" catalytic systems [47–51]. Studies on the interconversion of various metal species during catalytic reactions, including molecular complexes, clusters and nanoparticles, have governed the development of the concept of a "Cocktail" of catalysts (4th Wave, Fig. 1) [52]. Indeed, several metal-containing species can be generated in solution, and at least one type of metal species may exhibit the desired catalytic activity. The adaptive nature of "Cocktail"-type systems is one of the key factors that facilitate catalytic reactions for a broad range of substrates [53].

Furthermore, in both homogeneous catalysis and heterogeneous catalysis [54], the dynamic nature of catalytic systems is currently being explored to develop a new generation of efficient, selective and recyclable catalysts. We believe that a new influential period in the mechanistic studies of catalytic systems will be closely related to the understanding of dynamic processes and catalyst evolution (5th Wave, Fig. 1).

In the present review, we summarize recent studies mentioning the behavior of a "Cocktail" of catalysts and mechanistic investigations regarding the evolution of transition metal species during catalytic cycles. To date, most of the studies dealing with the concept of a "Cocktail" of catalysts concern catalytic cross-coupling and Heck reactions [1–52]. However, several other catalytic systems, for example, C–H functionalization [55], atom-economic addition reactions [56], asymmetric synthesis [57] and several other transformations, clearly illustrate the influence of dynamic processes and interconversions of catalyst active centers. The comprehensive coverage of such a tremendously developing area is hardly possible within a single review. We focus on the studies that explicitly mention the "Cocktail"-type nature of catalytic reactions, and we also consider some other representative reactions. Detailed discussion of the studies already covered in other reviews will not be repeated here.

2. Catalyst evolution and dynamic effects in catalysis

Several useful solutions have emerged in practical applications of catalytic reactions depending on the type of catalyst precursor. For example, for palladium-catalyzed transformations, Pd^0 or Pd^{II} complexes are very often involved in the reaction after a ligand exchange or reduction steps in the catalyst activation (path a and path b; Scheme 1) [52]. Nanoparticles and clusters can be generated *in situ* from a variety of metal sources (path c; Scheme 1). Nanoparticle contamination in molecular complexes of Pd^0 and Pd^{II} may initiate different reaction mechanisms (path d and path e; Scheme 1) [58] and may substantially influence the selectivity [59]. Special preformed complexes provide a very efficient tool for the easy generation of catalytically active species through the replacement of dedicated labile ligands (path f; Scheme 1). Preformed or stabilized nanoparticles with an optimized morphology or a specific core/shell structure represent another efficient approach to entering the catalytic cycle after surface activation (path g; Scheme 1).

However, a particular type of catalyst precursor does not guarantee that only one type of catalytically active species will be involved in the product formation. Several processes (such as degradation, aggregation, dissociation, leaching, etc.) may facilitate the catalyst evolution and access to a variety of different metal-containing species.

In the present review, catalyst interconversions involving leaching, metal attachment/detachment and aggregation will be considered first (Sections 2.1 and 2.2), followed by the consideration of single-type vs. multiple-type active species in the catalytic reactions (Section 2.3). Next, catalyst dynamics induced by nanoparticle contamination (Section 2.4) and surface dynamics in heterogeneous catalysis (Section 2.5) will be considered. Finally, some examples of a catch-phrase description of dynamic processes in catalysis will be discussed (Section 2.6).

2.1. Leaching and generation of active species via metal detachment

The idea of the leaching process was discussed by Mizoroki in the early seventies (the formation of soluble metal species from palladium black, etc.), just after the first examples of palladium-catalyzed reactions had been published [60,61]. The essence of this complex phenomenon can be explained as an isolation of small fragments (single atoms or clusters) from insoluble species and their transfer to the liquid phase by a dissolution process. Thus, some amount of a catalyst loaded as a heterogeneous one could actually become homogeneous, and this change raises several arguments on the topic "What is a true catalyst?". The occurrence of leaching can be identified by measuring the metal concentration in the solution, but it does not answer the question of whether the turn-over occurs on the surface of a metal nanoparticle or in the liquid phase involving the leached metal species. To define the nat-