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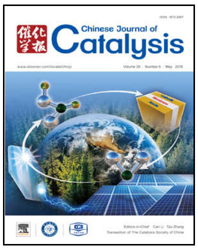

Review

Single-atom catalysis: Bridging the homo- and heterogeneous catalysis

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ABSTRACT

Single-atom catalysis, the catalysis by single-atom catalysts (SACs), has attracted considerable attention in recent years as a new frontier in the heterogeneous catalysis field. SACs have the advantages of both homogeneous catalysts (isolated active sites) and heterogeneous catalysts (stable and easy to separate), and are thus predicted to be able to bridge the homo- and heterogeneous catalysis. This prediction was first experimentally demonstrated in 2016. In this mini-review, we summarize the few homogeneous catalysis progresses reported recently where SACs have exhibited promising application: a) Rh/ZnO and Rh/CoO SAC have been used successfully in hydroformylation of olefin of which the activity are comparable to the homogeneous Wilkinson's catalyst; b) a Pt/Al_2O_3 SAC has shown excellent performance in hydrosilylation reaction; and c) *M*-N-C SACs (*M* = Fe, Co etc.) have been applied in the activation of C–H bonds. All of these examples suggest that fabrication of suitable SACs could provide a new avenue for the heterogenization of homogeneous catalysts. These pioneering works shed new light on the recognition of single-atom catalysis in bridging the homo- and heterogeneous catalysis.

1. Introduction

The concept of catalysis appeared less than 200 years ago. However, the phenomenon of catalysis has been known and utilized for thousands of years, although not so for its theory and characteristics. Catalysis has now played a central role in the modern chemical industry and in modern society. More than 85% of today's chemical products are produced by catalytic processes; and industrial catalysis contributes, both directly and indirectly through processes and products, to about 25% of the gross domestic product in developed countries [1].

Catalysis can be generally divided into two types according to the relationships between the phases of catalysts and reactants, i.e., homogeneous catalysis and heterogeneous catalysis, in addition to a rather special biocatalysis somewhere between the two [2]. In homogeneous catalysis, catalysts are in the same phase as the reactants, and often the products as well, which benefits the sufficient contact of the catalyst and reactant, thus resulting in high catalytic efficiency. Many homogeneous catalysts are composed of a (transition-) metal atom, or a cluster containing a few atoms, stabilized by appropriate ligands. The active sites can therefore be used effectively and are easy to identify. In addition, the catalyst properties as well as catalytic performance can be rationally tuned by changing the ligand. Accordingly, homogeneous catalysts generally possess not only high activity but also extremely high, and usually tunable, se-

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lectivity. However, the major issue of separating homogeneous catalysts from the raw materials and the products has severely limited their industrial application. Thus, in spite of the significant promise offered by homogeneous catalysts, few have been commercialized [3].

Heterogeneous catalysis, on the contrary, nominally covers all the cases in which catalysts and reactants are in different phases. However, in most cases, heterogeneous catalysis refers to a solid catalyst catalyzing a gas-gas or gas-liquid reaction. Although heterogeneous catalysts are usually less active and/or selective compared with homogeneous catalysts, they are quite stable and easy to separate from the reaction system. Therefore, most industrial catalysis is so far based on heterogeneous catalysis processes [4]. The comparison of the advantages and disadvantages of homo- and heterogeneous catalysts are listed in Table 1 [5]. To utilize the advantages of both homo- and heterogeneous catalysts, heterogenization of homogeneous catalysts has been attempted since the late 1960s, generally by attaching the homogeneous catalyst to an insoluble support via various physical or chemical interactions—so-called homogeneous catalyst heterogenization [6]. This process is very attractive and has been extensively studied. However, decades of study have proven that it is extremely difficult for various reasons [7]. Nevertheless, newly emergent single-atom catalysis may provide an alternative for the heterogenization of homogeneous catalysts and may bridge homo- and heterogeneous catalysis.

The term “single-atom catalysis” was first proposed in 2011 in a seminal work by Prof Zhang Tao and coworkers [8]. This concept has been gradually accepted by the catalysis community in recent years and has become a new frontier in the catalysis field [9–15]. Single-atom catalysis means catalysis by a “single-atom catalyst” (SAC), which refers to the catalyst that contains only isolated single atoms dispersed on a support [16]. The most important structural feature of SACs is their isolated, individual atoms dispersed on the support, which not only maximizes the metal’s atomic efficiency but also provides more uniform, well-defined active sites compared with common heterogeneous catalysts that consist of various kinds of active sites [17]. This renders SACs more active and selective than common heterogeneous nanocatalysts for numerous reactions and makes them behave like homogeneous catalysts in terms of both local structure and catalytic performance. The properties of SACs compared with both homo- and heterogeneous catalysts are also listed in Table 1. In short, SACs are heterogeneous catalysts and are thus quite stable and easy to separate; meanwhile, they possess isolated active sites similar to those of homogeneous catalysts, which provide them with the advantages of both homo- and heterogeneous catalysts. Thus, when the concept of “single-atom catalysis” was first proposed, researchers already foresaw and predicted that single-atom catalysis could provide a bridge between homo- and heterogeneous catalysis. However, it has not been demonstrated experimentally in the years following its introduction [9]. Only from 2016 has this prediction been experimentally verified gradually in a few progresses traditionally catalyzed by commercial homogeneous catalysis which will be highlighted in the following.

2. Applications of SACs in traditional homogeneous catalysis progresses

2.1. Hydroformylation

Hydroformylation of olefin is one of the most important homogeneously catalyzed industrial processes in industry [18]. It is a widespread strategy to produce aldehydes with olefins and syngas as feedstock, with more than 10 million tons produced globally on an annual basis. The desired aldehydes are value-added fine chemicals that are used as important organic intermediates for the synthesis of pharmaceuticals, agrochemicals, flavorings, and food additives and for the manufacture of plasticizers, coatings, adhesives, paints, and lubricant additives [19]. Nowadays, industrial hydroformylation is achieved mainly through three processes: the classic Co high-pressure process, the low-pressure process with phosphine-ligand-modified Rh complexes, and the aqueous biphasic hydroformylation process that is catalyzed by water-soluble Rh complexes [20]. The Rh-based heterogeneous catalysts for hydroformylation have been studied for more than 20 years but are still far from industrial application, primarily due to their much lower activity and selectivity compared with their homogeneous counterparts.

To verify our prediction that single-atom catalysis may bridge homo- and heterogeneous catalysis [9], we first investigated the application of SACs in the hydroformylation reaction [21]. After screening a number of catalyst formulas, we found that a ZnO nanowire-supported single-atom Rh heterogeneous

Table 1
Comparison of properties of homo- and heterogeneous catalysts.

Property	Homogeneous catalysts	SACs	Heterogeneous catalysts
Catalyst recovery	difficult and expensive	easy and cheap	easy and cheap
Thermal stability	poor	good	good
Selectivity	excellent/good	excellent/good/poor	good/poor
Catalytic performance tunability	good	poor	poor
Active sites	isolated atoms or clusters, often with ligand	isolated atoms, often with neighboring atoms from support	multiple active sites
Uniformity of active sites	uniform	relatively uniform	non-uniform
Metal electronic state	depends on ligand, commonly positive	depends on support, commonly positive	commonly metallic
Atomic efficiency	high	high	relatively low

Some entries taken from Ref. [5] with permission from UNESCO–Encyclopedia of Life Support Systems (EOLSS).