

Review

Multifunctional nanocatalysts for tandem reactions: A leap toward sustainability



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ABSTRACT

Design of new multifunctional nanocatalysts is a hot area of research that aims to introduce multiple types of active sites on a single nanocatalyst. Multifunctional nanocatalysts are useful to carry out a multi-step reaction requiring same or different active sites in a single pot. Such catalysts must possess the active sites at spatially distinct locations to avoid neutralization but yet remain active independently or through cooperative actions. The necessity of nanostructuring the active sites have emerged as the key point in a successful design of the catalysts. The review covers the progress in this area of research done in the last five years. It includes the classification of catalysts based on active sites and structure of active sites at the nanoscale. The review covers exhaustively with 250+ references and ample examples to present the concept succinctly. The review covers the evolution of multifunctional catalysts from the perspective of materials chemistry.

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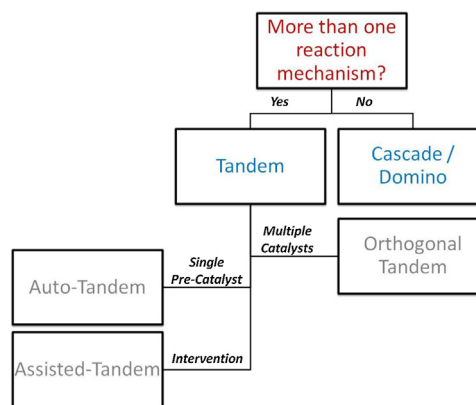
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1. Introduction

Enzymes are natural catalysts which are often held as a benchmark for manmade catalysts in terms of performance [1,2]. The ability of enzymes to catalyze several consecutive reactions under mild and same conditions in one pot is one of the most intriguing inspirations from nature [3–7]. The greatest advantage of multifunctional enzymes is their high selectivity. However, the kinetics of the reaction is often slow which is unfavorable when applied to large scale productions. The advantages are numerous. For example, in cases where the synthetic intermediate is too thermally unstable for isolation, it may be transformed into the desired products by readily entering a subsequent catalytic cycle prior to its decomposition with the aid of a multifunctional catalyst. When applied to a large industrial level reaction, multifunctional catalysts can assure process intensification [8–10]. From the chemistry point of view, coupling two or more inevitable reaction steps sequentially in one pot is crucial to maximize the output [11,12]. The economic viability of a chemical manufacturing process is improved by reducing the number of steps involving isolation and purification of synthetic intermediates and catalysts. Process becomes green, sustainable and attractive with a reduced energy consumption and waste production [13,14].

A major challenge in the field of multifunctional solid catalysts is that chemically interfering active sites must be stable under the reaction conditions of all the steps in a reaction sequence. There should not be any tendency towards deactivation in the presence of the reagents or byproducts used in the reaction sequence. Although this sounds like stringent criteria to qualify for a multifunctional catalyst, it turns out that the statement is merely a pronouncement of a practical indispensability. It often becomes necessary to understand the thermodynamics of the reactions steps that are desired to be coupled so that the multifunctionality of the catalysts can be sufficiently demonstrated [15]. This would define the experimental conditions in which the reaction steps would progress favorably towards the final products. Carrying out the reactions under such steps would not only retain the functionality of the catalysts but also guarantee with advantages such as greenness and process intensification.

There is a significant progress in the field of multifunctional nanocatalysts in the last few years [15]. Multifunctionality in this review is used in the context, where all the active sites required for a complete sequence of a multistep reaction are present on a single catalyst. Some multistep, one-pot reactions are carried out in the presence of a physical mixture of two different catalysts. The article has excluded such works as they are not truly multifunctional although they would serve the purpose. The active sites described here are in nano regime (less than 15 nm) or molecular regime consisting of few atoms of a reactive functional group. The aim of this review is to bring out more succinctly the evolution that has happened in the development of multifunctional catalysts in creating stable, isolated active sites that are capable of performing different functions in tandem catalysis. The article differs from other reviews [15] by attempting to present the development of the field from the perspective of materials. To aid the understanding, a



Scheme 1. Types of multistep, one-pot reactions. Adapted from Ref. [16].

classification based on nano architectures is introduced with sufficient examples. It is envisaged that the discussion will pave way for the further development of the novel multifunctional materials.

2. Multistep, one-pot reactions

There are different types of multistep, one pot reactions. The classification of these reactions is usually based on the mechanism of the reaction. Accordingly, there are two major types namely Domino or Cascade reactions and Tandem reactions. The classification is given in the Scheme 1. Technically, if the mechanism of each step of the reaction is same, then such multistep reactions are referred to as domino/cascade reactions. In other words, domino reactions involve a sequence of a single catalytic event. If each step of the reaction differs in mechanism, then such reactions may be classified as tandem reactions. Tandem reactions are further sub-categorized into auto-tandem and assisted-tandem. Auto-tandem reactions use a single catalyst to carry out two or more mechanistically distinct catalytic cycles. In contrast, assisted-tandem reactions require purposeful shift between one catalytic cycle and another [15–17]. The purposeful intervention is usually caused by the addition of a reagent which affects the catalytic active site for a reaction A and converts it into a suitable form to catalyze a reaction B. The temporal distinction between the first and the second step is often challenging in assisted tandem catalysis—for example Pd catalyzed bromoallylation and Sonogashira coupling (Scheme 2). [18–20] As an example of a typical tandem reaction it may be beneficial to cite the synthesis of 4-methyl-2-pentanone (MIBK) from acetone (Scheme 3). The reaction is by far the most studied process in this area due to its applications in solvent for paints, inks and lacquers. In the classical industrial process, acetone is condensed with soda as a catalyst to diacetone alcohol which is dehydrated to mesityl oxide (MO). MIBK is formed by selectively hydrogenating C=C bond in the α,β -unsaturated ketone. The process is not green and generates large amounts of wastes. The new processes based on bifunctional acid/metal catalysts [21–24] and others with multifunctional base/acid/metal catalysts [25–33] increase the selectivity of MIBK with less amount of waste. Most promising catalysts materials may

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