



Review

Design of highly stable and selective core/yolk–shell nanocatalysts—A review

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ABSTRACT

In recent decades, increasing interests have been put on improving the stability and selectivity of nanocatalysts for clean energy production due to the decrease of fossil fuels. Despite the prominent feature of high catalytic activity, nanocatalysts are prone to sintering. Structural design of nanocatalysts to form core/yolk shell structure has been proven to be the most effective method to enhance their catalytic stability. In this review, design strategies for core/yolk shell nanocatalysts to attain high stability in energy related applications at high temperatures such as hydrocarbon reforming reactions for syngas production and high temperature fuel cells such as SOFC and MCFC are summarized and exemplified with the advancements made in the recent three years. In addition, measures taken to obtain outstanding selectivity for F-T synthesis and C=C bond hydrogenation reactions are also presented. Further, excellent shape and size selectivity design examples are also introduced. Finally, unsolved problems and challenges for core/yolk shell nanocatalysts design are proposed as the final part of this review.

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1. Introduction

With the continuous consumption of fossil fuels, alternative energy sources and processes for clean energy production has attracted increasing attention. Almost all these energy production processes are related to catalysis. Continuous endeavors have been made to explore new catalysts especially nanocatalysts with excellent activity, stability and selectivity for clean energy production.

It is well known that catalytic activity will be remarkably increased when the size of catalysts is decreased to nano scale as a result of the greatly increased active sites such as edge and corner atoms [1,2]. Whereas, stability issues of nanomaterials for high temperature reactions such as prone to sintering caused by their high surface energy have to be addressed before they can be employed as catalysts [3]. In addition, selectivity, the rate of a reaction along a particular pathway divided by the sum of rates along all reaction pathways, is one of the most important among the three factors making a good catalyst in addition to activity and stability. The ultimate goal for clean energy production is to achieve 100% selectivity for the desired product for a multipathway reaction while maintaining their activity and stability [4]. To achieve this goal and to efficiently improve the progress for clean energy production, understanding the design principles and the underlining science is important.

Sintering of active metal usually happens when catalysts endure harsh conditions such as high temperature either during catalyst preparation process or under reaction conditions. High temperature (700 °C) is thermodynamically or kinetically required for reactions such as reforming reactions for synthesis gas (syngas) production to achieve economically viable conversions of reactants. In addition, high temperature calcination treatment is normally needed for most catalysts to remove the surfactants which facilitate the synthesis of nanocatalysts but may block their active sites. During these high temperature processes, bonds between atoms and bonds between crystallite and the underlying surface will be broken, leading to the migration and growth of atoms and crystallites [5]. These migrations will result in the increase of particle size, deformation of the shape as well as change of composition and finally catalyst deactivation.

Various methods have been investigated to solve the above problems of nanocatalysts. These methods include: First, embedding nanoparticles inside controlled cavities [6] or channels of the pre-synthesized mesoporous materials such as SBA [7,8] and MCM [9] families, one dimensional metal oxide nanotubes [10] or carbon nanotubes [11,12] as well as within the pores of graphitic spheres [13] and metal organic frame works (MOF) [14]; Second, developing materials with stronger interaction between nanoparticles and support such as perovskite [15,16], spinel [17], hydroxalcite (HT) [18] and layered double hydroxide (LDH) [19] as well as bimetallic alloy nanoparticles supported catalysts [20–22]; Third, constructing core/yolk shell nanostructures by coating the presynthesized nanoparticles with another layer [23–34] or layers of shells [35–38], by one pot synthetic methods [39,40] and by surface-protected etching method [41].

Most of these methods described here have been reviewed by Fornasiero's group [6] and Veszteg's group [5] especially for the first two methods. The references provided above are the progresses made in the recent three years by other groups. As discussed in other studies, the first two methods cannot completely prohibit

the migration and sintering of nanoparticles [42,43]. This illustrates that these two methods cannot effectively eliminate the Ostwald ripening of nanoparticles, resulting in their growth [44]. Therefore, in this review, we will focus on the third method i.e. core/yolk shell nanostructures as active and stable catalysts.

Core/yolk shell nanocatalysts also have been continuously reviewed by different research groups, reflecting the continuing growth of interests in this topic [45–49]. However, most of them are from the materials synthesis aspect [45–48] or focused on either one type of material for instance noble metal based [39] or one type of reaction such as liquid phase reaction [49]. Even though catalytic applications were also summarized, the design principles for these core/yolk shell nanostructures to these applications are not illuminated in detail.

Core/yolk shell nanostructures have been extensively studied and applied in various areas such as catalysts [42] and energy storage materials [50], owing to their flexibility to be functionally designed catering to the specific needs. Take catalysts as an example, the structure of core shell catalysts determines their catalytic performance, as shown in Fig. 1, (1) Active sites can be designed at either the core/shell part or even at the molecules functionalized to the shell surface or at all of these places. For active sites located in the core part and embedded within the shell, the high temperature stability will be enhanced. (2) Shell porosity, the pore size and shell thickness can be finely tuned to attain size selectivity and shape selectivity. (3) Materials of both the core and shell part can be tailored to acquire the best synergetic effect [51]. In addition, multifunctionality such as amphiphilic property [52], acid-base bifunctionality [53] and temperature responsive catalytic property [54] also can be obtained. (4) Core/yolk shell nanostructures can also be combined with other nanostructures such as 1d carbon nanotubes [55] and high surface area oxides [56] to further improve their catalytic performances.

In this review, the synthesis methods and procedures for core/yolk shell nanostructures will not be covered. Instead, based on the design perspectives described above, we report the progresses in designing core/yolk shell catalysts mostly in the recent three years as follows: Firstly, design principles to achieve sinter-resistant property for high temperature energy-related applications such as synthesis gas production reactions and high temperature fuel cells; Although CO oxidation operates at relative low temperatures, it is quite sensitive to the active metal particle size. Therefore, sinter-resistant core shell catalysts including both metal and metal oxides for CO oxidation reaction will also be included. Secondly, methods used to get high catalytic selectivity for reactions such as F-T synthesis reaction and selective hydrogenation reactions for the C–C triple bonds as well as the design examples for size and shape selectivity. For selective hydrogenation reaction, since metals such as Pd exhibits outstanding high selectivity, most of the core shell catalysts will be focused on metals. Finally, the unsolved problems of core/yolk shell nanocatalysts are discussed and the potential future research directions are identified.

2. Design principles of sintering resistant property for high temperature clean energy-related applications

To prohibit high temperature sintering, active sites either metal or metal oxide have to be located at the core or embedded

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