Engineering of Yolk/Core–Shell Structured Nanoreactors for Thermal Hydrogenations

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Dedicated to Professor Can Li on the occasion of his 60th birthday

Heterogeneous hydrogenation reactions are of great importance for chemical upgrading and synthesis, but still face the challenges of controlling selectivity and long-term stability. To improve the catalytic performance, many hydrogenation reactions utilize special yolk/core–shell nanoreactors (YCSNs) with unique architectures and advantageous properties. This work presents the developmental and technological challenges in the preparation of YCSNs that are potentially useful for hydrogenation reactions, and provides a summary of the properties of these materials. The work also addresses the scientific challenges in applications of these YCSNs in various gas and liquid-phase hydrogenation reactions. The catalyst structures, catalytic performance, structure–performance relationships, reaction mechanisms, and unsolved problems are discussed too. Also, a brief outlook and opportunities for future research in this field are presented. This work on the advancements in YCSNs might inspire the creation of new materials with desired structures for achieving maximal hydrogenation performances.

1. Introduction

One of the most challenging catalytic reactions is hydrogenation reactions, which are of great importance for pharmaceutical and fine chemical production.[5] Commonly, hydrogenation processes are applied to low carbon number molecules (CO, CO₂), biomass-derived compounds, nitroarenes, alkenes, alkynes and esters, for the production of valuable products. Compared to the homogeneous hydrogenation, the heterogeneous hydrogenation has the advantages of separation and controlled hydrogenation. However, there are some challenges facing heterogeneous hydrogenation reactions that need to be addressed. It is still challenging to precisely control a specific hydrogenation step in a multistep hydrogenation, making the selective hydrogenation of target groups difficult. For example, the Pt catalysts usually hydrogenate both the highly reductive alkynyl group and nitro group simultaneously, making the synthesis of 4-aminophenylacetylene by 4-nitrophenylacetylene hydrogenation difficult.[6] The difficulty in controlling selectivity is due to complex separations and subsequent costly purification processes. Furthermore, some traditional catalysts tend to be instable and could be deactivated at high temperature and/or in the solution due to the leaching of metal nanoparticles (NPs), carbon deposition, sintering or poisoning by toxic substances.[3] An ideal hydrogenation catalyst is one that exhibits not only excellent activity and selectivity, but also long-term stability and deactivation resistance. However, there are great difficulties in achieving the goal of high-performance and stable catalysts for hydrogenation reactions.

Yolk/core–shell nanoreactors (YCSNs), in which particles are encapsulated in hollow-shelled nanoreactors,[4] have recently attracted much attention because of their unique structures and extensive applicational versatility. Various materials such as zeolites, metal oxides, metal-organic frameworks (MOFs) and carbons can be designed to construct the shells with a high degree of control over thickness, shape, size and porosity.[17] YCSNs are one of the most promising catalysts proposed to solve the energy crisis and address the challenges facing hydrogenation reactions. YCSNs possess several advantages over usual catalysts such as controlling the reaction microenvironment, confinement effects, compartmentalization or accumulation of various types of elementary reactions. These characteristics would help improve the catalyst stability. Additionally, YCSNs exhibit not only tunable pore size, shell thickness, and hydrophobic/hydrophobic properties, but also controllable temperature, pH and
even light intensity of experimental conditions. These offer the further avenues and benefits of YCSNs to regulate the product selectivity. Therefore, YCSNs are expected to have great potentials in solving the problems of product selectivity and catalyst stability that exist in hydrogenation reactions. Also, YCSNs have been widely applied in the fields of biomedicine,5–8 environmental science,9 energy storage and conversion during the last three years,10,11 especially in catalysis research.12

There are several recent reviews that have highlighted the advances in the synthesis and application of YCSNs. A comprehensive review work on the hollow nano- and microstructures was presented by Prieto et al.,12 summarizing the synthesis strategies and applications of hollow nano- and microstructures as bio-, electro-, and photocatalysts. Other minireviews and perspectives have been focused on the specific classes of YCSNs consisting of certain materials or concerning targeted applications. Largely, the existing literature focuses on the synthesis of varied shell media or core compositions and their subsequent applications. When considering the shell-related research, for example, the use of metal-organic frameworks (MOFs) to encapsulate active nanoparticles (NPs@MOFs) has been well discussed and outlined by Li et al.13 These NPs@MOFs catalysts have been reviewed in the fields of thermo-, photo-, and electro-catalysis. Also, the noble metals confined in metal oxides or zeolites have been reviewed in terms of preparation methodologies and confinement effects.14,15 As regards synthetic developments, there is a considerable amount of research concerning solely the catalytic application of these materials. Li et al. have given some insight into high temperature clean energy-related applications and high selectivity design of core/yolk shell nanocatalysts.16 However, the special reviews focused on the hydrogenation reactions have been rarely reported. Although there are several reviews that cover other families of catalysts toward these reactions. Chen et al.16 published an overview of MOF-based catalysts and Ye et al.17 summarized the copper-based catalysts for hydrogenation of alkenes, alkynes, benzene, and carbon–oxygen bonds. To the best of our knowledge, a review covering yolk/core–shell nanoreactors for heterogeneous hydrogenation reactions has not been reported. In our previous work, Boyjoo et al. have made substantial efforts toward critical assessment and collection of synthesis techniques for porous non-silica metal oxide submicrospheres with yolk/core–shell structures.18 Tian et al. have reviewed the nanoengineering carbon spheres as nanoreactors for sustainable energy applications.19 Therefore, this work is aimed to give a focused review on the unsolved problems in yolk/core–shell nanoreactors for hydrogenation reactions.

In the current review, we will first overview the progress in the general synthetic methods for YCSNs. Then the unique properties of YCSNs in terms of improved catalytic activity, selectivity and stability will be presented. Subsequently, the state-of-the-art in the area of YCSNs will be discussed to explain how the YCSNs structures can improve the catalytic activity, selectivity and stability for specific hydrogenation reactions, such as hydrogenation of biomass, aromatics and small energy-related molecules. The heterogeneous hydrogenation discussed here is related to the thermally stable catalytic materials; the bio-, electro- and photocatalysts are not presented. Finally, an outlook of future developments in the area of YCSNs for hydrogenation reactions is presented. The schematic illustration of this review is shown in Figure 1.

2. Synthetic Strategies for YCSNs with Confined Metal NPs

Although different methods for preparing various YCSNs have been extensively developed, the synthetic strategies can be roughly divided into two categories: “inside-to-outside” and “outside-to-inside” (Figure 2). “Inside-to-outside,” that is, the inner core is first formed, followed by coating with one
or more shell layers through physical and chemical processes such as adsorption, precipitation, or self-assembly to construct the core–shell structure. Then, the yolk–shell structure can be achieved by eliminating some of the core, shell or any intermediate component to form a space between core and shell; some examples of methods used to achieve this type of structures are etching, Kirkendall diffusion, galvanic replacement, etc.[8,10,20] “Outside-to-inside” involves introducing seeds into the voids of hollow materials like zeolites, MOFs and other materials containing voids. The seeds then gradually grow until the whole void is filled. Through careful control of the seed growth, the yolk–shell structure can be achieved with specific core sizes. Making use of smaller metal particles is ideal for improving the utilization rate of metal atoms, because catalytic reactions occur on the surface of metal nanoparticles. However, the shape, structure and scale of metal NPs will change under harsh reaction conditions. Encapsulating metal NPs, therefore, is an effective choice to avoid several reasons of deactivation (sintering, leaching, coking, etc.). Meanwhile, the shell can also be functionalized to further enhance these materials with multiple functions other than physical separation and protection, in order to affect the catalytic process. When considering the catalyst design that makes the best use of the unique morphology to optimize performance, there are numerous properties that are available to control and alter to achieve the desired outcome. The size and morphology of the metal particles, the thickness and porosity of the shell, as well as the interaction between the metal particles and the supports should be considered in any synthetic strategy.

2.1. “Inside-to-Outside” Strategy

The straightforward approach of encapsulating metal NPs in the shell is to coat the metal NPs with the desired material. Metal oxide,[21,22] silica,[21–23] and carbon[26,27] from a wide array of sources have been used to produce highly stable shells and have received considerable attention. Recently, Zhang et al. fabricated an Au-Pd@CeO2 core–shell structure through a one pot autoredox route.[28] Autoredox reaction between Ce3+ and metal precursors by virtue of the reducibility of Ce3+ in base solvent makes the self-assembly of CeO2 shell easier. The porosity of the shell, regardless of composition, is of the utmost concern as the dense coating of metal NPs will be an obstacle for transporting reactants and products in the catalytic process, greatly undermining any benefit of the catalyst. As such, mesoporous silica has been one of the most widely used materials as a shell via facile Stöber method owing to the flexibility in controlling its porosity. The preferable pore channels in the shell would be mesopores perpendicular to the surface of the metal core to improve mass transfer efficiency (Figure 3a).[29] Besides silica, porous carbon shells derived from polymers (e.g., dopamine, resorcinol-formaldehyde resin, 3-aminophenol-formaldehyde resin) has the unique characteristics of good chemical inertness, excellent thermodynamic stability and high conductivity as shells. Recently, the encapsulation of metal NPs into MOFs to form composite materials with amazing properties has attracted great interest. There are some polymers or surfactant molecules such as polyvinyl pyrrolidone and cetyltrimethylammonium bromide (CTAB) adopted for connecting NPs with MOFs to facilitate the formation of core@shell structured nanocomposites.[30] Moreover, Kuo et al. developed a sacrificial template strategy for the synthesis of nanocrystal@ZIF-8 yolk–shell nanostructures, in which Cu2O is used as an intermediate layer and can be etched simultaneously and spontaneously during the formation of ZIF-8 (Figure 3b).[31] Since MOFs are composed of metal nodes and organic ligands, it is also a method to grow MOF shells by using the metal core.
as self-sacrificial template without extra metal precursor. For example, Huang’s group successfully constructed the Pt–Ni nanowires@Ni-MOFs by using 2,5-dioxidoterephthalate as the organic ligand to in situ coordinate with the released Ni^{2+} during the dealloying process. The thickness and the composition of the MOF shell could be regulated by changing the Ni content in Pt-Ni nanowires during the in situ growth of MOF (Figure 3c). Nonetheless, MOFs coated on metal NPs are generally polycrystalline. Incorporating the preformed metal NPs in the cavities of MOF crystals is challenging because the porous MOF structure is subject to be damaged by NPs larger than the MOF cavities. A strategy that relies on the adsorption of NPs onto the continuously forming surfaces of the growing MOF crystals was proposed to resolve this issue by Huo and co-workers reporting the deposition of NPs of various size, shapes and compositions.

MOF particles have also been reported to be used as a “hard template” for yolk@shell synthesis, with a number of papers being published using ZIF-8 and ZIF-67 to produce ZnO or CoO cores, respectively. The ZIF-8 based material was coated with SiO₂ by using an extended Stöber process involving the use of CTAB to provide tunable porosity. Both methods relied on the thermal removal of the organic ligands to produce the void space. This research serves to demonstrate that MOFs are highly effective, versatile and viable for the successful and controllable synthesis of the yolk@shell structures.

Some limitation of the direct coating method is that the size of precast metal NPs cannot be too small, since the naked metal NPs dispersed in the solution are extremely unstable and will grow via the Ostwald ripening mechanism before coating can occur. Even if the size of metal particles can be reduced by subsequent etching operations, it is still difficult to control the extent of surface edges and defects caused by etching. Therefore, a method that constructs a sandwich structure by uniformly dispersing metal NPs on the core, followed by coating the protective layer was developed. Banerjee et al. demonstrated the synthesis of SiO₂@Pd@meso-SiO₂ with highly dispersed Pd₀-NPs (Figure 3d). The nanostructures containing a layer of Pt NPs that are encapsulated between a core and a shell of MIL-101 were designed by Zhao et al. However, when the core and shell are composed of heterogeneous materials with high interfacial energy due to topology conflicts, the shell seed can preferentially grow as an independent nucleus, rather than on the core. Long et al. introduced polystyrenesulfonate functioning as a molecular linker, which alters the surface charge of Pt/CoO₂ to coerce the adsorption of metal ions onto the Pt/CoO₂. This technique allows for the preparation of core@shell-structured Pt/CoO₂@MOF hybrids. SiO₂ also can also act as a
connector capable of reducing the interfacial energy. Following the etching of the SiO₂ template, voids are formed to produce structures like the Au/Fe₃O₄@void@PMO-SO₃H prepared by Zhang et al.⁴⁰ It is worth noting that the multistep deposition of materials and the subsequent removal of templates, complicates the synthetic process. There are easier ways to achieve the yolk–shell structure, as demonstrated by a prominent example showing the synthesis of uniform yolk–shell Fe₃O₄@RF@void-Au@mSiO₂ nanoparticles via the swelling-shrinkage of resorcinol-formaldehyde (RF) resin upon soaking in or removal of n-hexane, reported by Zhao’s group (Figure 3e).⁴¹

2.2. “Outside-to-Inside” Strategy

The metal NPs grown in the voids of hollow materials offer more control over particle size and produce narrower particle size distribution because of the adjustable size of the confined space. Wang et al. reported on the ship-in-a-bottle growth of noble metal nanostructures inside hollow mesoporous silica microspheres.⁴² In detail, small Au seeds were first introduced into the interior of the hollow microspheres. Au nanospheres with an average diameter of 18 ± 2 nm were obtained through this seed-mediated growth within the microspheres. However, Au seeds were formed both inside and outside the shell during the preparation process, resulting in the low atomic utilization ratio as Au seeds outside the shell are removed by centrifugation. Tang and co-workers fabricated a unique silica nanorattle that contained plenty of residual internal alkylamino groups, which can act as in situ reducing agent and stabilizer for the growth of a metal core only inside the hollow cavity (Figure 4a).⁴³ In this way, the final atomic utilization ratio of gold was increased to 66%. Similarly, the process of incorporating metal NPs into the cavities of MOFs or zeolites can be completed via “ship-in-a-bottle” approaches. The loading position of the metal NPs remains a substantial challenge. This is because precursors tend to be randomly deposited on the external surface of MOFs or zeolites. Considerable efforts have been made to counter this and provide targeted deposition of the metal NPs. For instance, Huang and co-workers initially synthesized C₆₀@UiO-67 by a one pot method so that C₆₀ is uniformly distributed on UiO-67 in molecular form.⁴⁴ Then Pd NPs coordinating with C₆₀ were successfully embedded into the framework, which was attributed to the induction of the metal–π interaction between Pd and C₆₀. Xu and co-workers developed a “double solvent” method to immobilized Pt NPs

![Figure 4](https://www.advancedsciencenews.com)

**Figure 4.** Representative examples of “outside-to-inside” strategy. a) Schematic illustration of the preparation of gold NPs in silica nanorattle. Reproduced with permission.⁴³ Copyright 2010, Wiley-VCH. b) Schematic representation of synthesis of Pt@MIL-101 via the double-solvents method. Reproduced with permission.⁴⁵ Copyright 2012, American Chemical Society. TEM images of c) Pt@Si-MFI and d) Pt@HZSM-5. Reproduced with permission.⁴⁶ Copyright 2018, American Chemical Society.
inside the pores of MIL-101, in which the small amount of aqueous H₃PtCl₆ solution was absorbed within the hydrophilic pores via capillary force, while the large amount of hydrophobic solvent was used for suspending MIL-101 and avoiding adsorption of NPs on the external surface (Figure 4b). Furthermore, many synthetic methods for incorporating metal NPs into zeolites have been developed. Xiao and co-workers demonstrated that the newly formed zeolite grows from the seeds of β-crystals containing Pd NPs through the seed-directed synthesis with a core–shell growth mechanism. Xu and co-workers reported a cationic polymer-assisted synthetic strategy to encapsulate Pt NPs into MFI zeolites. In this case, the cationic PDDA polymer not only interacts electrostatically with the Pt precursor and zeolite building blocks but reduces the Pt precursors. The effectiveness of this technique was exemplified by the results, finding that >90% Pt NPs are encapsulated in the zeolite matrix (Figure 4c,d).

3. The Unique Properties of YCSNs

In material science, the composition, structure, and performance of materials are closely related. Materials with unique composition or structure can often perform unexpectedly in certain areas, which is exactly the motivation for researchers to constantly explore new materials. Nowadays, the requirements for catalysts have become more stringent, such as higher mechanical strength, higher activity and selectivity, longer catalyst lifetime, stronger toxicity resistance and higher heat transfer efficiency. The design and development of YCSNs are exactly based on this purpose, while a great many particular properties of YCSNs are emerged, as illustrated in Figure 5.

3.1. Influencing Reaction Environment

Most of the work concerning YCSNs is focused on the nanoscale confined systems. This is mainly because the confined internal environment is isolated from the external environment, which protects the reaction from external interference and gives rise to space confinement effects. This unique structural feature allows the catalytic activity to be influenced by controlling the confined microenvironment. Correspondingly, the medium in which the reaction takes place and the conditions adjacent to the active site are both to be considered. Compared to the core–shell structure, the existence of void spaces in the yolk–shell structures not only serves to expose more movable active sites for the reactants, but also provides a homogenous environment for a heterogeneous catalysis. From this perspective, the yolk–shell nanoreactors could sometimes show better catalytic performance than the core–shell nanoreactors. Moreover, the confined space increases the contact frequency between reactants and active sites through increasing local reactant concentration and retention time of intermediates, thus improving the reaction activity. Reaction is quite sensitive to the changes of the environment in confined space. For example, mass diffusion is one of the largest problems for H₂O–oil–solid triphase reaction systems. Bai et al. reported that the catalytic activity of Ru-TsDPEN confined in a nanocage can be greatly enhanced through the modification of the nanocage with amphiphilic groups that enable asymmetric transfer hydrogenation. Compared with lipophilic groups, the existence of amphiphilic groups can provide a suitable microenvironment for the substrate with different lipophilicity and enhance the diffusion rates of the reactants in the catalytic process.

The importance of the interaction and synergistic effect between the metal NPs and the supports cannot be neglected when the core–shell structure is formed. Long et al. demonstrated that the higher catalytic activity of Pt–Ni NF@CeO₂ was resulted from the intimate and strong interactions between Pt–Ni NF core and the CeO₂ shell. Such interactions alter the electronic properties of Pt NPs and limit the formation of PtOₓ species so as to produce more Pt-active sites.

3.2. Regulating Product Selectivity

Considering the existence of multiple reaction sites in the substrate or the stereoisomeric products obtained from the reaction, it is very essential to develop catalysts that can improve the selectivity toward the target products, otherwise the subsequent separation and purification processes will consume energy and lead to high costs. The confinement effect of YCSNs is essential for controlling the selectivity of the desired reactions. For example, the channels of zeolites or mesoporous shells with shape- or size-selectivity properties can be used to screen out the desired products. In addition, reactants are very sensitive to the structure and composition of the catalyst, and different products will be obtained in the case of different adsorption behaviors. Therefore, the selectivity of the reaction is optimized by adjusting these two parameters. Corma and co-workers reported that bimetallic CoNi@C maintained higher selectivity over monometallic Co@C or Ni@C in the chemoselective hydrogenation of nitroaranes. Recently, Pecchi and co-workers demonstrated that the highest selectivity toward the unsaturated alcohol in chemoselective hydrogenation of cinnamaldehyde over Co-CoO@SiO₂, 500 °C catalyst was attributed to an optimum Co/CoO surface ratio. The precise location of different active sites is especially important for tandem reactions. If all active sites are exposed at the beginning of the reaction, the reaction will proceed in parallel instead of

Figure 5. Schematic illustration of the properties of YCSNs applied in hydrogenation reactions.
in a specific sequence, resulting in wide product distribution. Given the design of multifunctional catalysts, YCSNs are a promising candidate. Yang et al. fabricated the yolk–shell NPs with a basic core (–NH₂) and acidic shell (–SO₃H) by an organosilane-assisted selective etching method tested in a one-pot deacetalization-Henry cascade reaction.[54] For cascade reactions involving hydrogenation, the loaded or encapsulated location of metal NPs plays a decisive role in the distribution of products in the case where the shell possesses acidic sites.[47]

In short, there are many differences between yolk/core–shell nanoreactors and usual catalysts. It is similar in cell in terms of operation mode, in which multicomponents work cooperatively and orderly. The local concentration and diffusion of substrates as well as retention time of intermediates could be influenced by the confined effect of nanoreactors. It is worth noting that tiny adjustment of microenvironment where reaction occurs will significantly influence the pathway of reaction. Therefore, nanoreactor is not simple nanosize reaction vessel like bench-top or microreactor. The size, shape, and microenvironment within a nanoreactor have a remarkable role in the chemical process and can achieve new stability and selectivity.

3.3. Improving Catalytic Stability

One of the key scientific and technical issues in the research and practice of nano-catalysis, especially metal nanoparticle catalysis, is to improve and strengthen the stability of NPs under specific reaction conditions. Metal NPs are easily agglomerated into larger particles at high temperature, which is attributed to high surface energy even if immobilized on a support. Meanwhile, both leaching of metal NPs in several recycling processes and deactivation caused by constant friction with the supports or coking will occur. Wrapping the monodisperse metal NPs in a shell, core–shell, or yolk–shell confined nanoreactor that is designed to largely prevent aggregation and leaching of metal NPs and thus maintains the high catalytic activity. Dai and co-workers observed that the morphology and size of Pd clusters encapsulated in SiO₂ shells are not noticeably changed after the high-temperature treatment and confirmed the fully recyclable character of the catalyst.[51] Kawi and co-workers synthesized a yolk-satellite-shell structured Ni-yolk@Ni@SiO₂ nanocomposite, which resisted sintering of Ni NPs and prevented the carbon deposition during the reaction.[52] Zeolites have attracted extensive interest thanks to their regular and adjustable pore structures as well as improved thermal stability.[56] In addition, it should be noted that although MOFs shells benefit from structural flexibility, large surface area, especially uniform pore structure, though the structure is inclined to collapse under high temperature.

4. Applications of YCSNs for Heterogeneous Hydrogenation Reactions

Hydrogenation reactions are essential processes in the chemical industry, giving access to a variety of valuable compounds including fine chemicals, agrochemicals, and pharmaceuticals. The unique properties of yolk/core–shell nanoreactors have been summarized above. Then the application of YCSNs in gas-phase and liquid-phase hydrogenation reactions will be discussed. Gas-phase hydrogenation reactions will mainly cover the progress in the direct hydrogenation of CO/CO₂ to methane, light olefins, liquid fuels, and alcohols. Also, the indirect conversion of CO to ethanol via methyl acetate (MA) hydrogenation or to ethylene glycol via dimethyl oxalate (DMO) hydrogenation will be summarized. The liquid-phase hydrogenation reactions will be discussed for yolk/core–shell catalysts used in the hydrogenation of alkenes, alkynes biomass, and aromatic nitro compounds.

4.1. Gas-Phase Hydrogenation of CO/CO₂

4.1.1. Direct Hydrogenation of CO/CO₂

The small C₁ molecules, for instance carbon monoxide (CO) and carbon dioxide (CO₂), can be directly hydrogenated to various types of energy products such as light olefins, gasoline, diesels, and alcohols through Fischer-Tropsch synthesis (FTS) or CO₂ modified FTS (Figure 6). Furthermore, the FTS product distributions follow the Anderson-Schulz-Flory (ASF) law, which means that it is difficult to obtain a pure target product. In order to enhance the selectivity of products, many promoters have been added to Fe, Co, Ru-based catalysts to increase the surface C/H ratio, regulate the metal crystallite size and reducibility.[57,58] Further hydrocracking or hydrorefining steps for waxes are adopted to increase the selectivity toward liquid fuels.[59] However, the highly active metal nanoparticles often suffer from aggregation, lowering the energy efficiency of multiple hydrogenation processes.

Recently, considerable efforts have been made to modify the catalyst structures. For example, selectivities of up to 80% light
olefins can be achieved over a bifunctional catalyst, namely ZnCrO$_x$/MSAPO, which breaks the limitation from ASF law, owing to two different, but complimentary and compatible active sites.$^{[60]}$ Li et al. provided an expanded ASF model to describe the product distributions over bifunctional catalytic systems.$^{[61]}$ Also, the yolk/core–shell nanoreactors have been widely applied to achieve high catalytic performance owing to the confinement effect and special reaction environment with tunable shell materials. The ASF law was modified over a silica encapsulated small-sized cobalt catalyst, which obtained 66.2% selectivity toward the diesel-range (C$_{10}$–C$_{20}$) hydrocarbons or 62.4% selectivity in the gasoline-range (C$_5$–C$_{11}$) of hydrocarbons using Co NPs of different sizes.$^{[62]}$ The progress in the development of YCSNs for hydrogenation of small energy-related molecules including CO and CO$_2$ is summarized in Table 1 and will be discussed in the following section.

### Table 1. Catalytic performance of representative YCSNs applied in hydrogenation of small energy-related molecules.

| Catalyst                  | Substrate | Conv. [%] | Product          | Select. [%] | Lifetime [h] | Keywords                              | Refs.  |
|---------------------------|-----------|-----------|------------------|-------------|--------------|---------------------------------------|--------|
| Mix-Cu/ZnO-zeolite        | CO        | =30.0$^{[a]}$ | C$_2$–C$_4$ paraffins | =55.0       | 60           | Synergistic effect, tandem reaction   | [136]  |
| Cu/ZnO@zeolite            |           | =55.0     |                  | =65.0       | 100          |                                       |        |
| Fe@BCNNSs                 | CO        | 8.7       | C$_2$–C$_4$      | NG          | NG$^{[c]}$   | Highly dispersed iron, high stability | [65]   |
| Fe@BCNNSs                 | CO        | 8.89      |                  | 49.2        | 1000         |                                       |        |
| FeMn                      |           | 23.0      | Light olefins    | 20.2        | 120          | Confinement effect, carbon layer      | [59]   |
| FeMn@C                    |           | 47.5      |                  | 40.6        | 200          |                                       |        |
| Fe$_2$O$_3$@SiO$_2$        | CO        | 80.6      | C$_{5+}$         | 80.0        | NG           | Modify the ASF law                    | [62]   |
| Fe$_2$O$_3$@SiO$_2$        | CO        | 98.3      | C$_{5+}$         | 39.8        | 72           | Double shell, spillover effect        | [66]   |
| Fe$_2$O$_3$@SiO$_2$@MnO$_2$| CO        | 98.1      |                  | 53.2        | 72           |                                       |        |
| Fe$_2$O$_3$@SiO$_2$-graphitic carbon | CO | 60.1 | Light olefins | 40.7 | 100 | Synergism, graphitic carbon | [68] |
| Co$_3$O$_4$@SiO$_2$        | CO        | 80.6      | C$_{5+}$         | 80.0        | NG           | Modify the ASF law                    | [62]   |
| Fe$_2$O$_3$@SiO$_2$        | CO        | 98.3      | C$_{5+}$         | 39.8        | 72           | Double shell, spillover effect        | [66]   |
| Fe$_2$O$_3$@SiO$_2$@MnO$_2$| CO        | 98.1      |                  | 53.2        | 72           |                                       |        |
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| Fe$_2$O$_3$@SiO$_2$-graphitic carbon | CO | 60.1 | Light olefins | 40.7 | 100 | Synergism, graphitic carbon | [68] |

$^a$The data are read from literature; $^b$NG, not given; $^c$BTX, benzene, toluene, and xylene.
CO Hydrogenation: Many advanced shell materials have been developed to design Fe- or Co-based YCSNs for CO hydrogenation. The porous carbon shells derived from MOFs have been used for encapsulating metal NPs. A ZIF-67@am-TiO2 precursor was prepared and then pyrolyzed under nitrogen to form the Co@C core, then the carbon shell was removed by calcination under oxygen to form well dispersed Co3O4 core with TiO2 as shell. Recently, the boron carbon nitride nanosheets (BCNNSs) were designed to encapsulate nano-iron particles (Figure 7a). The new Fe@BCNNSs catalyst could achieve and maintain ≈88.9% conversion of CO over 1000 h. The BCNNSs overcame the shortcomings of traditional carbon-based materials, which would otherwise be lost during high temperature reaction and regeneration. However, it is still challenging to optimize the selectivity of a target hydrocarbon over Fe@BCNNSs because the CH4 selectivity and CO2 yield are higher than 20%. To promote production of liquid hydrocarbons, double shells of SiO2 and MnO2 were employed to encapsulate Fe2O3 (Figure 7b), for which the selectivity of C5–C11 can be increased from 39.8% over Fe2O3@SiO2 to 53.2% over Fe2O3@SiO2@MnO2 (Table 1). The authors attributed the observed enhancement to the Mn-improved spillover effect. Note that the interlayer SiO2 can anchor Mn NPs and weaken the Fe–MnO2 interaction. Similarly, to reduce the production of CO2 that stems from water gas shift (WGS) reaction, a methyl modified Fe2O3@SiO2 (Figure 7c), namely Fe2O3@SiO2-(CH3)3 have been reported by Yu et al. The methyl modified SiO2 shell exhibits a hydrophobic environment that suppresses H2O readsorption and its further reaction with CO. As a result, the CO2 selectivity can be greatly reduced from 40% to lower than 5%, before and after methyl modification of Fe2O3@SiO2. Also, the graphitic carbon (GC) with high reducibility and hydrothermal stability was introduced to Fe@SiO2-GC catalyst to improve Fe dispersion and reducibility (Figure 7d). The GC modified core–shell structure possesses an obvious spatial restriction effect, which can increase the formation of short-chain light olefins with a selectivity of 40.7% for 100 h. In addition, microporous silicalite-1 was employed to encapsulate Co/ZSM-5 (Figure 7e). The shell of silicalite-1 not only provides an additional diffusion zone for syngas and products, but also exhibits resistance to coke formation. The selectivity of C5–C11 was as high as 74.7% while the CO2 and CH4 selectivity was decreased to 2.8% and 8.7%, respectively. Last but not at least, a fascinating core–shell MoO2@MoOx-Pla catalyst with amorphous MoOx species as shell and crystalline MoO2 as core was synthesized by radiofrequency induction thermal plasma method (Figure 7f). The shell was treated under extreme conditions to form a special phase with more active sites so that the MoO2@MoOx-Pla can efficiently and stably convert syngas to higher alcohols.

Besides the development of shell materials, the whole core–shell structure has been enriched and investigated for CO hydrogenation. For example, the core–shell Fe3O4@MnO2 catalyst was combined with a hollow HZSM-5 zeolite to form a bifunctional Fe3O4@MnO2-Hol HZSM-5 catalyst (Figure 8). The hollow HZSM-5 has two effects on the FTS process. First, a microreactor environment is created for converting the olefins intermediates to aromatics, which results in the enhancement of the selectivity toward aromatics. The second effect is to promote mass transport and suppress carbon deposition, and

![Figure 7. Progress in the shell design for YCSNs applied in CO hydrogenation. a) Fe@BCNNSs catalyst with boron carbon nitride nanosheets as shell. Reproduced with permission. Copyright 2017, American Chemical Society. b) Fe2O3@SiO2@MnO2 catalyst with both SiO2 and MnO2 as double shells that were drawn according to literature. c) Fe2O3@SiO2-(CH3)3 catalyst with methyl-modified SiO2 as shell that were drawn according to literature. d) Fe@SiO2-GC with graphitic carbon (GC) modified SiO2 as shell. Reproduced with permission. Copyright 2018, Elsevier. e) Co/ZSM-5@Silicalite-1. Reproduced with permission. Copyright 2018, Elsevier. f) MoO2@MoOx-Pla catalyst with amorphous species MoOx as shell that were drawn according to literature. Adapted with permission. Copyright 2019, Elsevier.](https://www.small-journal.com/)

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thus increase the catalyst stability. Recently, a green route with consecutive freezing and vacuum drying process was developed for the preparation of hierarchical ZSM-5.\[72\] Similarly, a bifunctional Cu/ZnO/\(\gamma\)-Al\(_2\)O\(_3\) nanoreactor was reported for highly selective conversion of syngas to dimethyl ether while a core-shell Cu-MOR@SiO\(_2\) nanoreactor was designed for conversion of syngas and dimethyl ether to ethanol.\[73,74\] This demonstrates the effectiveness of the synergistic effects achieved by proper modification of the core–shell structure. SiO\(_2\) has been used to modify an Al\(_2\)O\(_3@\)Al-supported cobalt catalyst to increase heat transfer and reduce metal–support interaction, as well as improve cobalt reduction. As a result, the methane selectivity decreased while the C\(_5^+\) selectivity increased over the Co/SAl\(_2\)O\(_3@\)Al catalyst.\[75\] Furthermore, the overall structural evolution of Fe@C catalysts during the FTS reaction has been investigated by Lyu et al.\[76\] The authors pointed out that the carbon shell was unstable and could be lost during high temperature reaction, resulting in exposing more active sites for the reaction, but favoring carbon deposition and leading to deactivation. The information about evolution of the specific surface area, pore size and Fe phase were also explored by the authors. More attention should be paid to the structural changes during reaction, which could in turn prompt catalyst design and preparation.

**CO\(_2\) Hydrogenation:** When compared to CO hydrogenation, CO\(_2\) hydrogenation is more challenging and needs more effective catalysts due to the inertness of CO\(_2\). Thus, CO\(_2\) molecules are often activated under high temperature and high pressure, which would make the catalysts with small nanoparticles suffer deactivation from metal sintering and coke deposition. As can be seen from Table 1, YCSNs have been designed for CO\(_2\) hydrogenation to various products such as CO, methane, light olefins, methanol, and ethanol. For the CO synthesis, Xu and co-workers assembled a Pt/Au@Pd@UiO-66 catalyst with monodispersed Au@Pd and isolated Pt NPs as active sites.\[77\] About 70% selectivity for CO can be obtained via reverse-water-gas-shift reaction (RWGS). The authors then further optimized the structure to a multilayered spherical sandwich structured Au@Pd@UiO-67/Pt@UiO-67.\[78\] The CO\(_2\) conversion and CO selectivity were found to be marginally increased. The above complicated core-shell structure with noble metals and MOFs may be not promising for future industrial applications. Herein, a Fe-based catalyst with a partially graphitized carbon shell has been reported for highly efficient and stable CO synthesis and high selectivity toward light olefins in hydrocarbons.\[79\]

For hydrocarbons synthesis over YCSNs, the Ni-based catalysts are applied for CO\(_2\) methanation with superior catalytic performance. However, the stability of Ni-based catalysts is poor due to the prevalence of coke formation tied to increasing particle size; highly dispersed and ultrasmall Ni NPs as well as low reaction temperature are needed for CO\(_2\) methanation. One such study used a Ni@UiO-66 catalyst to achieve 100% selectivity of methane for 100 h at 300 °C.\[80\] The material was found to possess a 20 wt% nickel loading while the average size of Ni was still \(\approx\) 2 nm, indicating uniformly dispersed Ni NPs in the core–shell structure. Also, the activation energy of Ni@UiO-66 was lower than the conventional Ni/ZrO\(_2\) and Ni/SiO\(_2\) catalysts through the Arrhenius plot analysis. The problem with Ni@UiO-66 was its conversion and gas hourly space velocity (GHSV) being much lower than that reported for other CO\(_2\) methanation catalysts. A detailed study of the relationship between catalyst structure and product selectivity was undertaken by Zhan and Zeng.\[81\] Different structures of ZIF-67-derived nanoreactors with different gas diffusion pathways were fabricated for CO\(_2\) methanation, as shown in Figure 9. It was found that the surface area and retention time played significant roles in regulating product distributions. The sandwich-structured ZIF-67@Pt@mSiO\(_2\) possessed both a large surface area and long diffusion pathways which were beneficial for CO\(_2\) methanation. Another example of product
selectivity controlled by nanoporous environment was demonstrated for Rh@molecular sieve system. Rh@S-1 exhibited high CO selectivity while the Rh@HZSM-1 showed high CH₄ selectivity under the identical conditions, which was due to further CO hydrogenation inhibited by minimal hydrogen spillover on the pure silica MFI (S-1). To upgrade the products, a bifunctional CuZnZr@Zn-SAPO-34 catalyst was synthesized to suppress light olefin formation, achieving 72% selectivity toward light olefins via a tandem reaction. The authors proposed that the contact interface between CuZnZr and SAPO-34 was reduced much compared to that for physically mixed CuZnZr/Zn-SAPO-34 sample, which can restrain hydrogenation of light olefins. Catalysts with different compositions and similar reaction mechanisms, such as CuO–ZnO–ZrO₂@SAPO-11, CuO–ZnO–Al₂O₃@HZSM-5, and CuO–ZnO–Al₂O₃@SiO₂–Al₂O₃ have been applied for the synthesis of dimethyl ether. Additionally, a promising strategy for the direct synthesis of aromatics, especially p-xylene (PX) was provided by Wang et al. When the bifunctional Cr₂O₃/H-ZSM-5 was upgraded to Cr₂O₃/H-ZSM-5@silicalite-1, the isomerization reaction of PX was suppressed by the core-shell structured H-ZSM-5@S-1 zeolite with neutralizing acidic sites, promoting the PX selectivity from 76% to 25.3%.

YCSNs have also been applied to synthesize alcohols via CO₂ hydrogenation. For example, copper nanocrystals have been encapsulated into UiO-66, while Cu/ZnO₂ NPs were confined into UiO-bpy for the production of methanol. These novel Cu-based catalysts exhibited strong metal-support interactions and confinement effects, achieving 100% methanol selectivity alongside considerable stability (Table 1). These marked improvements over the current benchmark Cu/ZnO/Al₂O₃ catalyst, which shows competitive formation of CO. Due to the secondary building units, large surface area, regular pores and cavities, MOFs have been shown to be advantageous materials for coating NPs. Compared to MIL-101 (Cr) and ZIF-8, UiO-66 was proved to an excellent support for Cu nanocrystals. Recently, An et al. further extended previous research on methanol synthesis to include the selective conversion of CO₂ to ethanol, reporting selectivity higher than 99% (Figure 10a,b). Also, the turnover number (TON) reached 4080 at supercritical conditions of 30 MPa. This superior catalytic performance was achieved over a Cs⁺-modified Cu–Zr₁₂–MOF catalyst placed in a Teflon-lined stainless-steel reactor. The authors proposed a

![Figure 10. Scheme for CO₂ hydrogenation over a) Cu/ZrO₂ and b) Zr₁₂-bpdc-Cu. c) Proposed reaction mechanism for CO₂ hydrogenation over Zr₁₂-bpdc-Cu. Reproduced with permission. Copyright 2019, Springer Nature.](image-url)
catalytic cycle and assigned the high activity to the synergism of bimetallic Cu$_2$ centers and the effect of the alkali promoter (Figure 10c). This work further highlights significant applications of Cu-MOFs-based toward hydrogenation of small energy-related molecules.

4.1.2. Indirect Hydrogenation of CO

Ethanol (EtOH) and ethylene glycol (EG) are widely used as solvents, fuels, gasoline additives, antifreeze, as well as feedstocks for the synthesis of chemicals and polyester. EtOH and EG are chiefly produced through: 1) petroleum-based routes, i.e., via hydration of ethylene, 2) a biomass-based route via the fermentation of sugar or cellulose. However, countries like China are oil deficient, gas lean but coal rich. Therefore, the production of alcohols through a coal-based route would be hugely beneficial in these places. It is difficult to directly produce ethanol or EG via one-step from syngas at large scale. Nowadays, the novel indirect synthesis of ethanol and ethylene glycol from syngas that is itself produced from coal, biomass, and natural gas has been successfully realized in industry. In 2009, the world’s first coal to EG plant with an annual output of 200 000 tons was built by Tongliao GEM Chemical Co., Ltd., China and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences. In 2017, Shaanxi Yanchang Petroleum (Group) Corp. Ltd., China and Dalian Institute of Chemical Physics, Chinese Academy of Sciences collaborated to build the world’s first coal to ethanol plant with a capacity of 100 000 tons per year. The coal to EG or EtOH processes exhibit a similar pathway, which involves the production of dimethyl oxalate (DMO) or methyl acetate (MA) from CO first, followed by hydrogenation of the esters to alcohols (Figure 6). This is an economic and mild approach to produce alcohols, which hinges on the hydrogenation of the esters to regulate the yield of final product. Therefore, it is essential to develop efficient and stable catalysts for gas-phase hydrogenation of esters in industry.

Cu-based catalysts are extensively employed in hydrogenation of esters. The esters can be hydrogenated to many products over different active sites and reaction conditions. Taking DMO hydrogenation as an example, DMO can be hydrogenated to methyl glycolate (MG), ethylene glycol, ethanol, 1,2-propanediol, 1,2-butanediol, and so on. Also, as the reaction is conducted at the high temperatures, the copper NPs are prone to sintering and aggregation through the Ostwald ripening process. The research in the field of catalytic ester hydrogenation focuses on the improvement of target alcohol selectivity and catalyst stability. The conventional Cu-based catalysts reported for the hydrogenation of esters are typically supported on silica, zeolites, and metal oxides. Through encapsulating Cu NPs in nanoreactors, an exceptional performance (Table 2) can be achieved for ester hydrogenation over YCSNs.

**Dimethyl Oxalate (DMO) Hydrogenation:** The hydrogenation of DMO is a process of significant interest owing to the chemical properties that make DMO more easily transportable and solid at room temperature, thus more attractive than the other commonly produced material (from CO coupling), diethyl oxalate. Copper is commonly used as the active phase for this process as it is highly effective at converting carbonyl containing compounds into alcohols. A recent study found that copper oxides can be autoreduced when encapsulated into the channels of nanotubes (CNTs), removing the need for costly catalytic pre-reduction. The autoreduced Cu@CNTs catalyst can then be directly used in hydrogenating DMO to EG or ethanol via changing the calcination temperature. Ma’s group reported that hydrogen was also saved in a copper silicate nanoreactor with the H$_2$/DMO ratio as low as 20 (Figure 11a), when conventional materials require much higher ratios, typically between 50 and 200. This significant reduction is attributed to the local increase concentration of hydrogen inside the nanotube-assembled hollow spheres (NAHS). Cu@NAHS-232 showed an excellent stability over 300 h period of DMO hydrogenation. The authors further explored the effect of nanotube

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**Table 2.** Catalytic performance of YCSNs applied in hydrogenation of esters in industry.

| Catalyst          | Substrate | Conv. [%] | Product  | Select. [%] | Lifetime [h] | Keywords                              | Refs. |
|-------------------|-----------|-----------|----------|-------------|--------------|---------------------------------------|-------|
| Cu/SiO$_2$        | DMO$^{a}$ | 99.6      | EG$^{b}$ | 88.6        | 30           | Cu sintering                          | [141] |
| Cu/SiO$_2$        | DMO       | 95.0      | EG       | 53.0        | 75           | Low temperature                       | [142] |
| Cu@CNTs-350       | DMO       | 99.3      | EG       | 88.0        | 200          | Auto-reduction                        | [98]  |
| Cu@NAHS-232       | DMO       | 100.0     | EG       | 95.0        | 300          | Nanotube-assembled hollow sphere      | [99]  |
| Cu NPs            | DMO       | 35.6      | EG       | 16.9        |              | Cu–O–SiO$_2$ interface, the best performance | [101] |
| Cu-NP@m-SiO$_2$   |           | 95.8      |          | 93.3        |              | NG                                    |       |
| Cu-PSNT           |           | 33.7      |          | 22.6        |              | NG                                    |       |
| Cu-PSNT@m-SiO$_2$ |           | 99.9      |          | 96.0        | 200          |                                       |       |
| Ag$_2$N$_2$/SBA-15| DMO       | 100.0     | MG$^{c}$ | 91.0        | 50           | Bimetallic Ag–Ni                      | [103] |
| Cu/SiO$_2$        | MA$^{d}$  | 95.0      | Methanol, Ethanol | – 95.0 | 96           | Core–shell structure                  | [105] |
| Cu@CeO$_2$        | MA        | 100.0     | Ethanol  | 100.0       | 160          | Facile synthesis                      | [104] |
| Cu-ZnO/SBA-15     | MA        | 84.3      | Ethanol  | 81.8        | 192          | Encapsulation                         | [106] |

$^a$DMO, dimethyl oxalate; $^b$EG, ethylene glycol; $^c$NG, not given; $^d$MG, methyl glycolate; $^e$MA, methyl acetate.
lengths (63–238 nm) and hollow-sphere size (69–361 nm) on the catalytic performance, finding that the longer nanotubes would enhance the hydrogenation performance due to spatially restricting the reactants to increase contact between them. Interestingly, the larger hollow spheres did not exhibit a similar enhancement in their performance due to a balancing effect between adsorption and diffusion on the reaction rate (Figure 11b).[100] Further studies regarding these balancing effects in YCSNs provide more effective methods for the reactor design. Also, Xu et al. encapsulated Cu microparticles, Cu nanoparticles, and copper phyllosilicate nanotubes (PSNT) within mesoporous silica to produce a large Cu–O–SiO$_x$ interface, and reported that Cu-PSNT@m-SiO$_2$ exhibits the best performance among all reported Cu-based catalysts (Figure 12).[101] The exceptional performance was attributed to the large active Cu–O–SiO$_x$ interface, which originates from strong metal–support interactions. Similarly, Wang et al. reported a Co@Si$_x$ nanoreactor with abundant Co–O–SiO$_x$ interfaces for hydrogenation of CO$_2$ to methanol instead of CO.$^{[102]}$ Besides, when the core–shell structured Ni@Ag NPs were encapsulated into mesoporous SBA-15, the strong interaction and electronic charge transfer between nickel and silver facilitated DMO hydrogenation to MG or EG with a yield of >90% for 50 h.$^{[103]}$

**Methyl Acetate (MA) Hydrogenation:** MA hydrogenation is similar to DMO hydrogenation and is the key step in the synthesis of ethanol from syngas. As regards DMO hydrogenation, Cu-based catalysts are favored due to the presence of Cu$^+$ and Cu$^0$, which are generally considered as the active sites for hydrogenation of carbon–oxygen bonds.$^{[104]}$ However, the balance between Cu$^+$ and Cu$^0$ can be disturbed due to the migration and aggregation of Cu$^0$ under high temperature and rich H$_2$ conditions, resulting in the reduction of Cu$^+$. Therefore, methods to stabilize Cu$^+$ and Cu$^0$ during reaction are important. Recently, a core–shell structured Cu@CeO$_2$ catalyst was reported to possess impressive stability for MA hydrogenation (160 h), while the conventional Cu/CeO$_2$-IM catalyst prepared by the impregnation method
was deactivated in 11 h (Figure 13). The improved stability and ethanol selectivity were attributed to the specially located and strongly synergistic Cu⁺ and Cu⁰, which were distributed at the interface between the core and shell, increasing the contact area.⁸⁴ Another work reported the encapsulation of copper NPs within a thin layer of SiO₂, detailing high MA conversion (95%).⁸⁵ Owing to the synergism between the geometry and electronic effects, the core–shell structured Cu/SiO₂ catalyst was stable for about 100 h. Although the size of Cu NPs remained unchanged following the reaction, the ratio of Cu⁺/(Cu⁰ + Cu⁺) was increased, indicating that the stability can be improved further. Despite impressive stability, the selectivity of ethanol (~60%) was relatively low with nearly 35% methanol selectivity over Cu/SiO₂. Wang et al. further revealed that the turnover frequency (TOF) was linearly related to the Cu⁺/Cu⁰ ratio for Cu–ZnO@SBA-15 catalysts, suggesting that a high Cu⁺/Cu⁰ ratio is beneficial for MA hydrogenation.⁸⁶ Therefore, the distribution and ratio of Cu⁺ and Cu⁰ in the core-shell structured catalysts are different than those on the conventional catalysts.

### 4.2. Liquid-Phase Hydrogenation of Other Compounds

Liquid-phase hydrogenation reactions have been extensively used for upgrading alkenes,⁸⁷ alkenes,⁸⁸ aromatics,⁸⁹ and biomass,⁹⁰ as summarized in Table 3. Both direct hydrogenation (DH) with hydrogen and transfer hydrogenation (TH) with other hydrogen sources (e.g., isopropanol) have been used for the liquid-phase hydrogenation reactions.⁹¹

#### 4.2.1. Hydrogenation of Alkenes and Alkynes

The size-selective hydrogenation of alkenes such as 1-hexene, cis-cyclooctene, and tetraphenylethylene can be employed as a

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**Figure 12.** A copper silicate nanoreactor with large Cu–O–SiO₂ interface for DMO hydrogenation. a) Illustration of the preparation of Cu-PSNT@m-SiO₂. b) The long-term stability test of Cu-PSNT@m-SiO₂. Reaction conditions: LHSV = 2.0 h⁻¹. Reproduced with permission.⁹¹ Copyright 2018, Springer Nature.

**Figure 13.** Representative catalysts for methyl acetate hydrogenation. a) Scheme of Cu/CeO₂-IM prepared by impregnation method and b) Cu@CeO₂ prepared by sol-gel method. c) Cu⁰ and Cu⁺ distribution over reduced Cu@CeO₂. d) Stability test of Cu@CeO₂ and Cu/CeO₂-IM at 215 °C. Reproduced with permission.⁹⁴ Copyright 2017, Wiley-VCH.
model reaction to prove the catalyst structure. It is more challenging to selectively hydrogenate acetylenic compounds to alkenes in the petrochemical industry, for example, hydrogenation of phenylacetylene (PA) to styrene, which is an important monomer for the synthesis of polystyrene. Recently, some novel YCSNs materials have been developed for the hydrogenation of alkenes and alkynes.

YCSNs that utilize MOFs as shells to encapsulate metal NPs (NPs@MOFs) have been vigorously studied due to their highly tunable structures and properties. A layered hollow nanosphere with two MOF shells, namely void@HKUST-1/Pd@ZIF-8 (Figure 14), was designed and produced by the “ship in a bottle” and “bottle around the ship” methods.\[107\] This multifunctional nanostructure possesses a hollow space for accelerating mass transfer, an inner HKUST-1 shell for hosting the active sites of Pd NPs, and an outer ZIF-8 shell as both a shield and sieve that protects active sites and screens reactants. The role of the various parts of the multifunctional hollow void@HKUST-1/Pd@ZIF-8 was further demonstrated by hydrogenation of different olefins. The authors also pointed out that the composite materials can be composed of other metals and porous materials, improving the functionality of YCSNs. The hierarchically structured and porous NPs@MOFs can be fabricated by a simple and universal method; an annealing process can be used to collapse the internal defect units while leaving the external shell intact. The resultant Pt@UiO-66-NH2 that was treated at 250 °C for 2 h, exhibited higher reaction rates and selectivity for 1-hexene when compared to Pt@UiO-66-NH2.\[112\] Similarly, a yolk–shell structured Pd&ZnO@carbon was synthesized by a solvothermal treatment and subsequent carbonization process of the resin polymer (Figure 15).\[108\] The reported Pd&ZnO@carbon catalyst exhibited around 95.5% PA conversion and

Table 3. Catalytic performances of YCSNs applied in liquid-phase hydrogenation reactions.

| Catalyst | Substrate | Conv. [%] | Product | Select. [%] | Cycle | Keywords | Refs. |
|----------|-----------|-----------|---------|-------------|-------|----------|-------|
| Pt-Cu@HKUST-1 | 1-hexene | 90.00 \[a\] | 1-hexane | NG \[b\] | 4 | Size-selective catalysis | [114] |
| Pt@Uio-66-NH2-2h | 1-hexene | 97.4 | 1-hexane | NG | 3 | Hierarchically porous | [112] |
| 3DOM-Pt@ZIF-8/SiO2 | 1-hexene | 80.0 | 1-hexane | NG | 7 | 3D-ordered macroporous structure | [143] |
| Pd@ZIF-8 | 1-hexene | >87.0 | 1-hexane | NG | 5 | Mechanosynthesis-assisted encapsulation | [144] |
| Pd@Ag@CeO2-1.5 | PA \[c\] | 96.0 | Styrene | 99.0 | 5 | Autoredox reaction | [116] |
| Pd@ZnO@carbon | PA | 95.5 | Styrene | 99.0 | 5 | Yolk–shell particles | [108] |
| Pd NCs@NCM | PA | 98.9 | Styrene | 92.8 | 4 | Mott–Schottky effect | [143] |
| CN@Pt/CNTs | PA | 100.0 | Styrene | >90.0 | 4 | DFT calculations | [118] |
| Ru@C-Al2O3 | LA \[d\] | 100.0 | GVL \[e\] | 99.9 | 7 | C-Al2O3 supported Ru | [146] |
| Ru/ZrO2@C | LA | >96.0 | GVL | >94.0 | 6 | UO-66 derived carbon | [110] |
| Al2Zr5@Fe2O4 | FFA \[f\] | 95.9 | FA \[f\] | 87.4 | 5 | Recyclable catalyst | [147] |
| Ni@N/C-800 | FFA | 99.0 | FA | 98.0 | 5 | Nitrogen-rich carbon | [148] |
| PtCeO2@Uio-66-NH2 | 1-hexene | 97.4 | 1-hexane | NG | 3 | Hierarchically porous | [112] |
| Ru@C/ TiO2, 500 | FFA | 100.0 | THFA \[f\] | 98.0 | 5 | Ultrasmall Ru NPs | [149] |
| 4Li-Co@NC | FFA | 100.0 | CPR \[f\] | 97.0 | 6 | Multishell hollow | [123] |
| CeO2/Pd@MIL-53(Al) | CAL \[g\] | 100.0 | HCAL \[h\] | 96.0 | 10 | Atomic layer deposition | [121] |
| PtNi20NWs@Ni@Fe2-MOF | CAL | >92.9 | COL \[i\] | 82.5 | 5 | Pt-Ni nanowires | [32] |
| (Pt-enriched cage)@CeO2 | CAL | >81.0 | COL | >82.0 | 8 | Pt-enriched cage | [21] |
| MIL-101(Cr)@Pt @MIL-101(Fe) | CAL | 99.8 | COL | 95.6 | 5 | Sandwiching platinum nanoparticles | [38] |
| MIL-101Pt@Fe-P-CMP | CAL | 97.6 | COL | 97.3 | NG | Hydrophobic hybrids | [120] |
| PtCeO2@SG-ZSM-5 | NB \[m\] | 100.0 | Aniline | >100.0 | NG | Converting hierarchical to bulk structure | [150] |
| 0.64Pd/C-Nc-MIL-101 | NB | >99.9 | Aniline | >99.9 | 5 | NPs encapsulated in MOFs | [130] |
| Au@CeO2 YSNs | NB | 100.0 | Azobenzene | >80.0 | 5 | Hybrid-structure-effect | [132] |
| Pd@PPh3@FDU-12 | NB | >99.9 | Aniline | >99.9 | 5 | Electronic modulation using PPh3 | [133] |
| Ru@PCF | 4-NP \[l\] | >99.9 | 4-AP \[l\] | >99.9 | 10 | Sub-3 nm NPs | [126] |
| Au@YS-MMS-35 | 4-NP | >93.0 | 4-AP | NG | 10 | Plasmolysis-inspired nanoengineering strategy | [41] |
| Fe2O4/C@Au | 4-NP | >90.0 | 4-AP | NG | 10 | RF resin derived carbon | [151] |

*Data taken from literature; \[a\] NG, not given; \[b\] PA, phenylacetylene; \[c\] LA, levulinic acid; \[d\] GVL, γ-valerolactone; \[e\] FFA, furfural; \[f\] FA, furfuryl alcohol; \[g\] THFA, tetrahydrofurfuryl alcohol; \[h\] CPL, cyclopentanol; \[i\] COL, cinnamaldehyde; \[j\] HCAL, hydrocinnamaldehyde; \[k\] COL, cinnamyl alcohol; \[l\] NB, nitrobenzene; \[m\] 4-NP, 4-nitrophenol; \[n\] 4-AP, 4-aminophenol.

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99% selectivity toward styrene in five runs. Interestingly, a Pd@Zn-MOF-74 catalyst without calcination process also exhibits full conversion of PA and 92% selectivity of styrene.\(^{[113]}\) The active sites are Pd NPs and open Zn(II) sites that undergo coordination interactions with the reactants, though analysis of the relevant literature suggests that the Zn(II) sites are more effective when incorporated into the shell. Another core@shell Pt–Cu frame@HKUST-1 catalyst was synthesized in situ by a microwave irradiation method, showing size-selective hydrogenation of alkenes with stable property.\(^{[114]}\)

In addition to MOFs derived YCSNs, the other shell media have been reported for the hydrogenation of alkenes and alkynes. For example, silica, ceria, or N-doped graphene have been used to confine noble metal NPs. The hydrophilic silica shell has been used to encapsulate hydrophobic Pd/SF. The Pd/SF@NS\(_x\) catalyst can be well dispersed in water and adsorbs acrylate substrates with a facile recycling operation, resulting in high activity for olefins hydrogenation.\(^{[115]}\) Although single-component NPs@CeO\(_2\) materials have been extensively studied, a recent bimetallic asymmetrical (Pd@Ag)@CeO\(_2\) catalyst has been prepared by a new modified autoredox reaction and a seeded growth strategy.\(^{[116]}\) The (Pd@Ag)@CeO\(_2\) catalyst displayed high selectivity toward styrene (>99%) in PA hydrogenation. Ag in the structure regulates reaction selectivity toward styrene, thus successfully addressing the trade-off between the selectivity and activity. The authors developed another bimetallic Au–Pd@CeO\(_2\) catalyst that showed synergistic effects between Au and Pd for NH\(_2\)BH\(_3\) initiated hydrogenation of PA.\(^{[28]}\) There is also a report on a nanoframe possessing multiple Pt–Ni–Ag\(_{1.9}\) cores with a CeO\(_2\) shell, which achieved full conversion of PA with a styrene selectivity of 86.5%.\(^{[117]}\) Another novel use of Pt in a catalyst that confines Pt NPs within N-doped graphene sheets that are in turn supported on carbon nanotubes (CN@Pt/CNT) was reported too.\(^{[118]}\) The catalyst exhibits ≈90.0% styrene selectivity at 100% conversion of PA. Density functional theory (DFT) calculations performed in this study indicate that the styrene desorption over CN@Pt(III)

![Figure 14. The illustrated of hollow structured void@HKUST-1/Pd@ZIF-8 with double MOFs shells. Reproduced with permission.\(^{[107]}\) Copyright 2017, Wiley-VCH.](image)

![Figure 15. A yolk-shell structured Pd&ZnO@carbon for hydrogenation of phenylacetylene to phenylethylene. a,b) Schemes for the preparation of ZnO@carbon and Pd&ZnO@carbon, respectively. c,d) Catalytic performance with recycling tests for Pd&ZnO@carbon, Pd/ZnO and Pd/C particles. Reproduced with permission.\(^{[108]}\) Copyright 2018, Wiley-VCH.](image)
is easier than that over Pt(111), avoiding the complete hydrogenation of PA. Therefore, the confinement effect of N-graphene is beneficial for promoting styrene selectivity.

4.2.2. Hydrogenation of Biomass

Increasing attention has been paid to the upgrading of biomass-derived platform molecules such as furfural (FFA), cinnamaldehyde (CA), and levulinic acid (LA) to high-value products. The key challenge for biomass hydrogenation is the design of highly active, selective, and stable catalysts, as there are a number of competitive reactions, thus complex reaction mechanisms, which create a multitude of different products. For example, CA is a typical \( \alpha,\beta \)-unsaturated aldehyde, which can be hydrogenated to hydrocinnamaldehyde, cinnamyl alcohol, and hydrocinnamyl alcohol. Therefore, tuning selectivity toward any one of these compounds is a challenging task to make materials capable of producing targeted molecules. Given the effectiveness of the YCSN morphology with similar reactions, it is logical that these materials seem suitable for this specific process.

There are some interesting nanoreactor structures that have been developed for biomass hydrogenation. The conventional single-shell structure derived from MOFs can be designed to become a sandwich or a multishell hollow structure.[119] One example is Pt-CeO\(_2@\)UiO-66-NH\(_2\) that was prepared with the assistance of polystyrenesulfonate to alter the surface charge and microwave to adjust the nucleation process (Figure 16a). This single-shell MOF derived Pt-CeO\(_2@\)UiO-66-NH\(_2\) can convert 99.3% of furfural almost entirely to (>99%) furfuryl alcohol.[39] Similarly, Tang’s group designed a sandwich nanostructure of Pt NPs with MIL-101 as both inner core and outer shell (Figure 16b). The novel MIL-101@Pt@MIL-101 catalyst featured the exposed (111) planes of fcc platinum and showed an enhancement of the mass transport in highly selective hydrogenation of \( \alpha,\beta \)-unsaturated aldehydes to unsaturated alcohols.[38] Further modification of the sandwich material produced intriguing shell materials in the form of iron (III) porphyrin polymers (FeP-CMP). The new FeP-CMP shell was not only hydrophobic and porous, but also was able to enrich the local concentration of cinnamaldehyde. Furthermore, the authors attributed the higher selectivity toward cinnamyl alcohol to increased activation of the C=O bonds.[120]

Another sandwich-structured CeO\(_2@\)Pd@MIL-53(Al) was designed by employing atomic-layer-deposition-formed layers of Al\(_2\)O\(_3\) as a sacrificial template.[121] The MIL-53 shell can protect Pd NPs and tune the product distributions toward unsaturated alcohols in the hydrogenation of \( \alpha,\beta \)-unsaturated aldehyde.[121] Chen et al. precisely controlled a range of multishell hollow Co@NC nanoreactors from single to quadruple...
layer structures through a step-by-step crystal growth method (Figure 16c). When the Co@NC nanoreactors were applied to the hydrogenation of furfural, the yield of cyclopentanol was increased with each additional shell, with 4LH-Co@NC demonstrating the highest performance. The authors proposed a plausible mechanism and proved that Lewis and Brønsted acid sites in 4LH-Co@NC were useful in furfural hydrogenation. Compared with the solid S-Co@NC, the 4LH-Co@NC catalyst with the multishell hollow structure has several merits such as multiphase heterogeneous interface, improved mass transfer ability and highly dispersed Co NPs. A Co@N-doped graphene nanoreactor with obvious Mott-Schottky effect was reported for improving hydrogenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran.[122] These studies show that through precise structural control, the achieved morphology is capable for solving the challenges faced in this field.[123]

A tandem reaction, combining the aldol condensation reaction and hydrogenation reaction, was designed to demonstrate the different reaction routes under the various different catalyst architectures (Figure 17). A Pt@HZSM-5 catalyst with more than 90% of Pt NPs encapsulated into zeolites (rather than loaded onto the surface) is beneficial for the aldol condensation reaction between furfural and acetone, resulting in 87% selectivity toward C₈-hydrogenated aldol adducts. However, the Pt/HZSM-5 catalyst with most of the Pt NPs located on the external surface led to the conversion of furfural first.[47] The reaction routes of direct hydrogenation (DH) and transfer hydrogenation (TH) of levulinic acid with isopropanol as the H-donor were performed over a Ni₃Fe NPs@C catalyst.[124] Both the TH and DH route can efficiently convert levulinic acid with high selectivity toward GVL. In addition, a Co-CoO@SiO₂ catalyst with a tunable ratio of Co/CoO, which is controlled by varying reduction temperature, was developed for chemoselective hydrogenation of cinnamaldehyde. It was also noted that the core–shell architecture successfully protected Co NPs from leaching during the liquid-phase hydrogenation.[53] Another Co@C NPs catalyst derived by pyrolysis of glucose was also reported to be highly active and stable for hydrogenation of LA to GVL.[52]

4.2.3. Hydrogenation of Nitro Aromatic Compounds

YCSNs have been widely used for selective hydrogenation of nitro aromatic molecules, which contain benzene rings and reducible nitro groups, to their corresponding aromatic amines, which are significant raw materials for the synthesis of fine chemicals, dyes and pharmaceuticals.[125] Special attention has been paid in this section to transfer hydrogenation of nitroarenes with the various H-donors that can best contact and react with nitroarenes.

Carbon-based materials are extensively applied for hydrogenation of nitroarenes. A general approach for constructing a highly dispersed active phase catalyst was developed by Ai et al.[126] The porous carbon was used to encapsulate sub-3 nm NPs including Fe, Co, Ni, Mo, Ru, Rh, Pd, and Pt by a organometallic conjunction strategy (Figure 18). The representative Pd@PCF nanocatalyst was reported to be active and selective for reduction of nitroarenes to their corresponding anilines, with NaBH₄ as a hydrogen source. Another method to produce the graphitic carbon (GC) with encapsulated Ni NPs (Ni@GC) involved the pyrolysis of Ni-MOFs. This technique produced materials that showed favorable performance in the reduction of 4-nitrophenol to 4-aminophenol.[127] Similarly, Zn₄Co₁Oₓ@carbon hollow catalyst derived by pyrolysis of Zn/Co-ZIF@polymer was reported to exhibit superior selectivity toward aniline in various nitroarene hydrogenation.[36]

Recently, tremendous efforts have been devoted to developing an effective technique for dispersion of metal NPs in nitrogen (and or phosphorus)-doped carbon materials. Some mesoporous N-doped carbon with encapsulated Co NPs (Co@CN-800) were derived by pyrolysis of a ZIF-67/SiO₂

Figure 17. a) The proposed reaction pathways of a model tandem reaction. b) Schematic illustration for sequential aldol condensation and hydrogenation of furfural with acetone over Pt@HZSM-5 and Pt/HZSM-5. Reproduced with permission.[47] Copyright 2018, American Chemical Society.
composite, followed by etching SiO₂ with hydrofluoric acid. The Co@CN-800 catalyst was reported to be active for transfer hydrogenation of nitroarenes by formic acid. The nitrogen atoms acted as basic sites to facilitate the formation of the Co-formate species. [128] Even single cobalt sites can be located in the N-doped carbon matrix to form Co-Nₓ active sites, which are active for hydrogenation of nitroarenes. [129] Similarly, a catalyst consisting of C-N-decorated Pd NPs encapsulated in MIL-101 (0.64Pd/C-Nₐ-MIL-101) exhibited Pd sub-nanoclusters and single atoms, achieving a high yield of aniline, with methanol as a solvent. [130] Another N-doped hollow carbon spheres catalyst was prepared through the reaction of C₆₀ and ethylenediamine (EDA) and subsequent carbonization. This metal-free carbon catalyst exhibited noteworthy activity and recyclability for hydrogenation of nitroarenes. [109] In another similar work, N,P-codoped carbon shells were used to encapsulate Co NPs, obtaining Co@NPC-800 catalyst with outstanding activity in the hydrogenation of functionalized nitroarenes. [131] The electron-negative P atom can affect the charge of Co and thus enhance the adsorption and hydrogenation of NO₂ group. [131]

Two core–shell and yolk–shell structured Au@CeO₂ catalysts have been reported for the transfer coupling of nitrobenzene, however, the catalytic rate and synthesized products were considerably different due to their structural distinctions. [132] When the Pd NPs were decorated with PPh₃, the Pd NPs surface would be enriched with electrons to more favorably react with the electrophilic nitrobenzene. Therefore, this Pd/PPh₃@FDU-12 catalyst displayed an excellent performance for nitrobenzene hydrogenation. [133] Furthermore, when Ru NPs were modified with PPh₃ and incorporated into a silica nanoreactor, the Ru/PPh₃@FDU catalyst showcased efficient catalytic performance in the hydrogenation of benzoic acid to cyclohexanecarboxylic acid. [134] With the development of covalent organic frameworks (COFs), a representative yolk–shell structured MNPs@COF, namely Pd@H-TpPa was also reported to exhibit superior catalytic performance than Pd@ZIF-8 for the transfer hydrogenation of 4-nitrophenol by NaBH₄. [135]

5. Conclusions and Perspectives

In summary, yolk/core–shell nanoreactors play an indispensable role in developing catalysts possessing small size and highly dispersed active NPs, which are simultaneously preventing deactivation and loss of NPs during the catalytic process. Herein, we have presented literature showing that a significant progress has been made in the synthesis of YCSNs, as well as their applications toward various gas-phase and liquid-phase hydrogenation reactions.

The general synthetic methods for YCSNs and their unique features in regulating catalytic performance were introduced with the aim to provide a guide for design of novel YCSN materials and expand their applications into other catalytic fields. In this work, the application of YCSNs has been emphasized.
in heterogeneous hydrogenation reactions including the direct and indirect hydrogenation of CO/CO₂, as well as hydrogenation of alkenes, alkynes, aromatics, and biomass. The current difficulties in each of these hydrogenation reactions and the targeted development of YCSNs to overcome them have been discussed. This review shows the exceptional catalytic performance including high activity and selectivity as well as excellent stability or reusability can be achieved by using YCSN materials for hydrogenation reactions.

Although great achievements have been made in the field of YCSNs, the current challenges in the development of YCSNs for hydrogenation reactions can be summarized into three main aspects: 1) Synthesis of YCSNs to expand their application in hydrogenation reactions is still challenging because of difficulties in precise controlling the pore size distribution of the shell media, the size of the internal cavities and the distribution of metal NPs. The geometric uniformity of the YCSNs is also difficult to consistently regulate. The preparation should be simplified and the raw materials need to be reduced for large-scale production of YCSNs. The current “inside-to-outside” strategies involve tedious processing steps such as multi-step deposition and removal, which lead to high cost, synthetic duration, and difficulty for scaling up. Some reports of one-pot methods are only applicable to the preparation of particular materials and so lack versatility of material production. Moreover, the one-pot methods often emphasize the significance of material addition sequence. “Outside-to-inside” strategies face numerous other problems, but mainly suffer from the issue of precise control of the morphology and spatial distribution of NPs, as well as struggle with complete NP encapsulation into voids although great efforts have been made in this regard. Therefore, the facile and efficient construction method for YCSNs is still lacking. 2) Hydrogenation reactions: At present, the research concerning YCSNs focuses on the development of new preparation methods, new composition materials, and the control of spherical shell thickness. However, studies on the internal and external modification and functionalization of YCSNs, or targeted YCSN design and synthesis, in response to specific hydrogenation reactions and associated requirements are rare. There is a plethora of literature concerning MOF-based YCSNs; despite this, these materials still suffer deactivation in both liquid and gas-phase high temperature hydrogenations. A detailed overview of the field together with in situ analysis of the structural evolution of YCSNs during reactions is lacking. 3) Mechanistic studies: The mechanism of forming the core-shell structure and the mechanism of hydrogenation reactions on YCSNs remain poorly understood.

Considering these problems and the literature we have reviewed, several avenues for usage of YCSNs for hydrogenation reactions are suggested below.

1) For the synthesis of YCSNs, it is suggested to construct the nanoreactors according to the specific reaction requirements. For example, YCSNs with antisintering properties can be developed for gas-phase hydrogenation reactions at high temperatures, which could guide the development of industrial hydrogenation catalysts. The microenvironment of YCSNs can be improved to upgrade YCSNs by exploring their functionalization, such as modifying the hydrophilicity and hydrophobicity, or altering the electronic properties of internal metal nanoparticles/shell surface via ligand modification. The development of new synthetic methods and optimization of the preparation steps and raw material costs can regulate the size and morphology of metal NPs, optimize the thickness and pore size distribution of the shell layer and finally show ways toward large-scale preparation. In particular, it is useful to develop shell etching methods using mild conditions/solvents for convenient regulation of the porosity in shells and void/core/shell size.

2) For hydrogenation reactions, it is necessary to improve the product selectivity for direct hydrogenation of small C₁ molecules. At present, the selectivity of many products is low. YCSNs are expected to do more tandem reactions for CO₂ direct hydrogenation to C₂ molecules. When considering indirect conversion of CO via esters hydrogenation, research toward increased stability of copper-based catalysts would greatly enhance the field, especially efforts toward stabilization of the Cu⁺ species. Although synthetic studies will greatly increase our understanding of these materials, more attention should be paid to the mass transfer characteristics, as well as the separation and reuse of the catalyst in liquid phase hydrogenation or separation of the gas products. Furthermore, efforts should be made toward regulating the shape of the nanoreactors. For instance, tubular Cu–PSNT@m-SiO₂ is more active for DMO hydrogenation than spherical Cu-NP@m-SiO₂. In addition, since YCSNs are also widely used in photo- and electrocatalysis, it is suggested to combine with thermo-, photo-, and electrocatalytic hydrogenation in the future.

3) For mechanistic studies, it is possible to prepare nanoreactors with special yolk/core structures and specific active sites to study the hydrogenation reaction mechanisms, especially adsorption and dissociation of hydrogen. Advanced characterization techniques, DFT calculations and reaction kinetic studies stimulate research in this area. For example, a Cu@m-SiO₂ catalyst was designed to investigate the mechanism of interfacial effect in DMO hydrogenation with help of DFT calculations and experimental results.[101] After becoming familiar with the reaction mechanism, these studies would be beneficial toward rational design of high-performance nanoreactors and their applications to fields other than thermal gas or liquid phase catalysis, i.e., photo/electrocatalysis.

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Conflict of Interest
The authors declare no conflict of interest.
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