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Review

Metal–organic-framework-based catalysts for hydrogenation reactions

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ARTICLE INFO

Article history:

Received 21 March 2017

Accepted 30 April 2017

Published 5 July 2017

Keywords:

Metal-organic framework

Hydrogenation

Heterogeneous catalysis

Nanoparticle

Chemoselectivity

Synergistic effect

ABSTRACT

Metal–organic-framework (MOF)-based materials with novel physicochemical properties have emerged as promising catalysts for various hydrogenation reactions. In addition to metal clusters and multifunctional organic ligands, MOF-based catalysts can incorporate other functional species, and thus provide various active sites for hydrogenation processes. The structural properties of the catalysts play significant roles in enhancing the interactions among the reactants, products, and catalytic sites, which can be rationally designed. Because of the synergistic effects between the active sites and the structural properties, MOF-based catalysts can achieve higher activities and selectivities in hydrogenation reactions than can be obtained using traditional heterogeneous catalysts. This review provides an overview of recent developments in MOF-based catalysts in the hydrogenation of alkenes, alkynes, nitroarenes, cinnamaldehyde, furfural, benzene, and other compounds. Strategies for improving the catalytic performances of MOF-based catalysts are discussed as well as the different active sites and structural properties of the catalysts.

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1. Introduction

Hydrogenation is one of the backbones of the chemical industry because of its wide range of applications in the synthesis of various products such as fine chemicals [1], pharmaceuticals [2], food [3], dyes [4], functional polymers [5], and perfumery [6]. Various chemical compounds, including alkenes, alkynes, carboxylic acids, aldehydes, and ketones, can be hydrogenated with high conversions and selectivities under relatively mild conditions. Since the last century, much pioneering research has been performed to exploit more opportunities in this area by optimizing reaction systems, including catalysts, reductants, and solvents. Catalysts, in particular, play a significant role in

enhancing the activities and selectivities of hydrogenation reactions. However, traditional hydrogenation catalysts such as metal particles [7], metal oxides [8], and metal sulfides [9] have various critical drawbacks and therefore need to be optimized. For example, metal particles, which have higher activities than metal oxides and sulfides, react easily with S, N, As, and P and lose their activities because of poisoning [10]. Metal oxides and sulfides are more chemically stable but usually require higher temperatures and pressures during hydrogenation reactions. Moreover, although some supports such as carbon materials [11], silicas, and zeolites [12] have been used to stabilize traditional catalysts and increase their hydrogenation activities and selectivities, the poor tunability of these supporting materials

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This work was supported by the National Natural Science Foundation of China (21322606, 21436005, 21576095), China Postdoctoral Science Foundation (2016M590771), and Guangdong Natural Science Foundation (2016A030310413, 2013B090500027, 2014A030310445, 2016A050502004).

DOI: 10.1016/S1872-2067(17)62852-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 7, July 2017

limits the achievement of high activities and selectivities under mild reaction conditions.

Metal–organic frameworks (MOFs), which consist of metal clusters and multifunctional organic ligands, have emerged as a new class of porous materials over the last two decades. Because of their properties such as ultrahigh porosities and surface areas, and designable and tailorable structure, MOFs perform well in a range of applications such as catalysis [13], gas storage and separation [14], sensing [15], luminescence [16], and drug delivery [17]. The integration of MOFs with other functional materials to give well-defined composite materials can trigger excellent synergistic effects, affording properties that are superior to those of any of the individual components [18]. These MOF-based catalysts, which have two or more types of active site in one system, are potential catalysts for hydrogenation reactions.

Compared with traditional catalysts, MOF-based materials have novel properties and superior tunability, and can be rationally designed for use in hydrogenation processes. (1) MOF-based catalysts have multiple and specific active sites [19]. In addition to the individual active sites in pristine MOF materials, MOF-based catalysts can have other active sites as a result of encapsulation of organic and inorganic guests or coating with other functional materials. A synergistic effect usually occurs and promotes the hydrogenation process when these additional active sites coexist in the unified system. (2) The sizes and distributions of the active sites in MOF-based catalysts can be controlled, and this significantly affects their activities and selectivities in hydrogenation reactions. The confinement effect in MOF materials plays an important role in the reaction process, and enhances the stability and durability of the active sites. (3) Their high specific surface areas increase the catalytic activities of MOF-based catalysts. A high specific surface area could not only increase the amounts of active sites, but also improve adsorption of reactants and reductants, increasing their local concentrations. These two factors have important effects on the activity [20]. (4) The easily tunable structures of MOF-based catalysts enable accurate control of the hydrogenation process. Adjusting the sizes of the pore windows and channels in MOF materials provides an efficient method for changing diffusion of the reactants to the active sites, and affects the activity and selectivity of the reaction [21].

Despite their physicochemical properties and superior tunability, the development of MOF-based catalysts for industrial applications has been slower than that of other commercial catalysts. MOF-based catalysts have some non-negligible disadvantages that hinder their practical applications. One major drawback of MOF-based catalysts is their poor stability, which can strongly affect their catalytic abilities, especially in harsh reaction environments such as high temperature and pressure, humid air, and organic solvents [19], in which some fragile frameworks can be easily destroyed. The other two key obstacles are their higher costs compared with those of traditional catalysts, and their reusability [22]. The design and synthesis of stable, economical, and durable catalysts are therefore important for the development of MOF-based materials for industrial applications. Developments in modern synthetic

techniques and our understanding of crystal engineering have enabled the fabrication of MOF materials with considerable stabilities using hard metal ions and organic ligands; these materials can maintain their original structure at temperatures up to 758 K, which is higher than the usual decomposition temperature range for most MOFs, i.e., 623–673 K [23]. In addition, the relative instability of MOFs can be used to fabricate MOF-derived porous carbon materials. This can extend the potential applications of MOF materials, as evidenced by the increasing number of research reports [24]. From these aspects, MOFs and MOF-based catalysts are promising and attractive for use in various fields.

This review summarizes recent developments in the use of MOF-based catalysts in the hydrogenation of alkenes, alkynes, nitroarenes, cinnamaldehyde (CAL), furfural (FAA), benzene, and other compounds. First, the types of active sites in MOF-based catalysts are introduced. Then strategies for improving the activities and selectivities of different hydrogenation reactions are discussed, including synergy among various active sites, optimization of the structure, and the interactions between reactants and catalysts. The synergistic effects among the favorable properties of MOF-based catalysts are also presented.

2. Active sites in MOF-based catalysts

MOF-based materials have been widely accepted as promising heterogeneous catalysts [25]. The active sites of MOF-based catalysts can be classified as metal ions/clusters, and functional ligands from the parent MOF materials and other exotic functional materials (Fig. 1). MOF materials can be used directly in some catalytic processes, or functional hybrid materials can be constructed by encapsulating active species within the frameworks or wrapping the framework with a shell material. The latter strategy combines the merits, and mitigates the shortcomings, of the parent components, and expands the range of MOF-based catalysts with superior performances for use in practical catalytic reactions. This section introduces the various active sites present in MOFs and MOF-based materials. Their use in typical hydrogenation reactions will be selectively illustrated in related sections.

2.1. Active sites in parent MOF materials

MOF materials can be used directly as catalysts because of

Fig. 1. Different types of active sites in MOF-based catalysts.

their coordinatively unsaturated sites (CUSs) and multifunctional organic ligands, which can both act as catalytic sites. As well as providing intrinsic sites, the CUSs and functional organic ligands can also coordinate with other active species such as homogeneous catalytic species to create new catalytic sites in MOF-based catalysts (Fig. 1) [26].

2.1.1. Metal nodes

Generally, the metal ions/clusters in MOFs coordinate with organic ligands and solvents during self-assembly and become CUSs after removal of the solvent molecules ligating the metal centers [27]. CUSs are Lewis acid sites and can serve as electron-pair acceptors in interactions with reactants and reductants, resulting in an increased reaction rate. A great number of CUSs in MOF materials have been reported with various metal ions, e.g., Cu^{2+} in HKUST-1 [28], Cr^{3+} in MIL-101 (Cr) [29], Fe^{3+} in MIL-100 (Fe) [30], Mg^{2+} in MOF-74 (Mg) [31], Co^{2+} in CPO-27 (Co) [32], and Zr^{4+} in UIO-66 [33]. Their unique activities have enabled their use in different chemical reactions. The CUSs in HKUST-1 and MIL-101(Cr) are typical CUSs and they are widely used in designing Lewis acid catalysts. HKUST-1, which is constructed using dicopper paddle-wheel secondary building units as nodes and benzene-1,3,5-tricarboxylate (btc) as linkers, contains free coordination sites on the Cu^{2+} ions [34]. Unlike the four-connected paddle-wheel clusters in HKUST-1, those in MIL-101(Cr) are six-connected trigonal-prismatic clusters with pseudo-octahedral coordination. The water molecules coordinated to Cr^{3+} can be easily removed at elevated temperatures in a vacuum and therefore the CUSs can be exposed during the activation process. Other methods such as introducing defective or unstable organic ligands [35] and partial decomposition of the MOF material [36] are also efficient methods for introducing CUSs into MOF-based catalysts.

2.1.2. Organic ligands

Various organic ligands contain functional groups that provide another typical type of active site in MOFs. For example, an NH_2 motif linked to the organic ligand of a MOF is an active group that can cooperate with a metal node in catalytic reduction of CO_2 [37]. Another two functional groups, namely SO_3H [38] and NO_2 [39], are Brønsted acid sites, and can be grafted onto the framework of MIL-101(Cr) to promote the catalytic performance by cooperation with the CUSs in MIL-101(Cr). Other functional groups, including OH and COOH, have also been explored as active sites [40]. These functional groups are usually linked to organic ligands before the fabrication of MOFs, but are sometimes grafted onto the MOFs during post-modifications.

2.2. Active sites in exotic functional materials

MOFs can act as host matrices for the encapsulation of active species in internal voids; this increases the availability of the active species, and promotes contact between reactants and catalysts [13]. The size and spatial dispersion of active species in MOFs can be adjusted, providing electronic effects that enhance the catalytic activity of the active species. The fixation

and confinement effect offered by the framework structure of MOFs can also efficiently prevent active species from leaching and agglomerating during a reaction. For example, a combination of MOFs and metal nanoparticles (NPs) can prevent the NPs from agglomerating and leaching during the reaction and limit the NP size during the growth stage [41]. MOFs can also be coated with other functional materials (e.g., zeolites, semiconductors, and another type of MOF) to fabricate core-shell-structured MOF-based composites. Rational design enables the coated composites to retain the original characteristics of the pristine MOFs, coupled with the properties of the shell materials, such as mechanical strength, hydrophobicity or hydrophilicity, and photoelectric properties. The shell materials can also serve as active sites and cooperate with the MOF core to catalyze hydrogenation reactions.

More importantly, combining MOFs with other active species usually generates synergism among the properties of the parent components, providing a new material with particular functions that the individual components do not have.

The use of MOF-based materials has achieved considerable success in various catalytic hydrogenation reactions, e.g., the hydrogenation of compounds such as alkenes, alkynes, nitroarenes, CAL, and FFA, and MOFs have potential industrial applications. The following section describes several typical examples of exploiting MOF-based catalysts to enhance the activities and selectivities of hydrogenation reactions, including strategies for adjusting the types of active sites and the structural properties of MOF-based materials.

3. Hydrogenation reactions

3.1. Hydrogenation of alkenes

Alkene hydrogenation is widely used in organic synthesis and the chemical industry [42]. Numerous catalytic systems have been developed for this transformation, including homogeneous and heterogeneous catalytic systems. High-efficiency alkene hydrogenation can potentially be achieved using MOF-based catalysts. The type, distribution, relative strengths, and environment of active sites significantly affect the performances of MOF-based catalysts.

3.1.1. Active sites in hydrogenation of alkenes

3.1.1.1. Metal nodes in MOFs as active sites

CUSs readily catalyze alkene hydrogenation. Four MOF compounds (Fig. 2) consisting of alkaline-earth metal ions and anthraquinone-2,6-disulfonate (2,6-AQDS) ligands showed high activities and selectivities in alkene hydrogenation [43]. The metal ions in these MOFs were coordinated to organic ligands and water molecules, therefore CUSs could be generated after removing the coordinated solvent molecules. The formed CUSs could then act as acid sites to drive the heterolytic cleavage of H_2 molecules to produce hydride-type species for substrate hydrogenation. In catalytic activity tests, 1 mol% of $[\text{Mg}(2,6\text{-AQDS})(\text{H}_2\text{O})_2]$ (AEPF-2) catalyzed the selective conversion of styrene to ethylbenzene at 373 K under 0.5 MPa H_2 ,

Fig. 2. Structures of alkaline-earth-metal based MOFs: AEPF-2 (Mg), AEPF-3 (Ca), AEPF-4 (Sr), and AEPF-5 (Ba) [43].

with a turnover frequency (TOF) of 38.8 h⁻¹. The catalytic activities of [Ca(2,6-AQDS)] (AEPF-3), [Sr(2,6-AQDS)(H₂O)] (AEPF-4), and [Ba(2,6-AQDS)] (AEPF-5) were lower than that of AEPF-2, with TOF values of 12.3, 14.3, and 36.5 h⁻¹, respectively. The strengths of the Lewis acid sites in these MOFs greatly affected the catalytic activity. The order of the catalytic activities was AEPF-2 > AEPF-3 > AEPF-4 > AEPF-5, in direct correspondence with the Lewis acid strengths of the metal ions in the MOF compounds, i.e., Mg(II) > Ca(II) > Sr(II) > Ba(II).

In addition to being generated by removing solvent molecules coordinated to metal centers, CUSs can be introduced into MOF-based catalysts during MOF synthesis using a mixed-linker solid-solution approach [44]. This approach was used to produce structurally defective MOF compounds [Ru₃(btc)_{2-x}(pydc)_xX_y] (Fig. 3, **D1–D4**), from mixtures of benzene-1,2,3-tricarboxylic acid (H₃btc) and pyridine-3,5-dicarboxylic acid (H₂pydc) containing organic ligands at various

Fig. 3. Defect-engineered [Ru₃(btc)_{2-x}(pydc)_xX_y] (X = Cl, OH, OAc; x = 0.1 (**D1**), 0.2 (**D2**), 0.6 (**D3**), 1 (**D4**); 0 ≤ y ≤ 1.5) (left) and parent [Ru₃(btc)₂Cl_{1.5}] (**1**) (right) [44].

ratios. The size and structure of pydc (the deprotonated form of H₂pydc) are similar to those of btc (the deprotonated form of H₃btc), but with one less carboxylate ligation site. This defective linker can lead to the formation of an isostructural analog of the Ru^{II/III} mixed-valence compound [Ru₃(btc)₂Cl_{1.5}], as shown by powder X-ray diffraction. However, the X-ray photoelectron spectra (XPS) of **D1–D3** contained an extra doublet, at about 280.3 and 284.5 eV, indicating the presence of additional Ru⁶⁺ species, and confirming that the pydc ligand partly replaces the parent btc ligand and causes defective CUSs. Under 0.8 MPa H₂, 1 mol% of **D1** and **D3** both gave full conversion of 1-octene at 323 K, within 2 h for **D1** and in less than 1 h for **D3**, after pretreatment with H₂ at 423 K. Both showed higher activity than the parent defect-free [Ru₃(btc)₂Cl_{1.5}]. The superior performance of **D3** can be explained by the higher concentration of the pydc ligand leading to a larger number of defect sites, which would assist heterolytic activation of H₂ molecules.

3.1.1.2. Cooperation with homogeneous catalytic species as active sites

To the best of our knowledge, there are few reports of pure organic ligands in MOFs acting as direct catalytic sites for alkene hydrogenation. The introduction of other active ingredients into MOFs is an efficient way of extending the use of MOFs in alkene hydrogenation. Organic ligands in MOFs can coordinate with homogeneous catalytic species, which can be concurrently dispersed in MOF frameworks with protection. 2,2'-Bipyridyl (bpy) and its derivatives can act as chelating ligands and have strong binding affinities with metal precursors or metal-containing groups because of the N atoms in the bpy ligand. Lin's group [45] used bpy and its derivatives as organic ligands to synthesize bpy-MOFs, bpyv-MOFs [bpyv = 5,5'-bis(carboxyethenyl)bpy], and two MOFs with mixed ligands, i.e., mPT-MOF and mBPP-MOF (Fig. 4). These can be combined with the homogeneous catalytic species CoCl₂ to give a series of earth-abundant metal catalysts that can be used in alkene hydrogenation after activation with NaEt₃BH. Compared with the other Co catalysts, mBPP-MOF-Co (Co loading 2.5 × 10⁻⁵ mol%) had high activity with a turnover number (TON) of 2.5 × 10⁶ in the hydrogenation of 1-octene at 4 MPa H₂ and room temperature (RT). The effects of the organic ligands in MOFs were explored by treating a homogeneous analog, Co(Me₂bpy)Cl₂, with NaEt₃BH in tetrahydrofuran (THF) in an inert atmosphere at RT. Co-(Me₂bpy)₂, Co NPs, and H₂ molecules were formed by intermolecular deactivation of the highly active metal centers. Protection of the organic ligands in MOFs ena-

Fig. 4. Structures of MOF-CoCl₂ precatalysts [45].

bles MOF–CoCl₂ catalysts to recruit active sites after reductive elimination of the intermediate MOF–Co(H)(R) species generated during hydrogenation. In the absence of chelating ligands such as bpy and its derivatives in the parent MOF materials, the incorporation of homogeneous catalytic species can be achieved using a post-synthetic metalation approach. A Au³⁺-containing MOF-based material was prepared by modifying the parent amino groups on IRMOF-3 with salicylaldehyde and then reacting with a Au precursor, NaAuCl₄ [46]. The resulting catalyst was used in the selective hydrogenation of 1,3-butadiene, and gave a better catalytic performance than a Au/TiO₂ catalyst in terms of both activity and selectivity. This IRMOF-3-SI-Au stabilized Au(III) species well and gave complete use of the active Au sites, indicating that MOFs could provide novel platforms for stabilizing solution-inaccessible species and therefore prevent possible intermolecular deactivation. This approach therefore has good potential for developing MOF-based catalysts incorporating homogeneous catalysts.

In addition to catalyzing hydrogenation reactions, the metal clusters in MOFs can also coordinate with homogeneous catalytic species. The MOF Zr-MTBC (MTBC = methane-tetrakis(*p*-biphenylcarboxylate) was deprotonated with ⁿBuLi and then reacted with CoCl₂ in THF to afford Zr-MTBC-CoCl [47]. The homogeneous CoCl₂ catalyst can be loaded onto the sterically open Zr₂–μ₂-OH ligand sites in the Zr₈(μ₂-O)₈(μ₂-OH)₄ nodes of Zr-MTBC. After treatment with NaEt₃BH in THF, the catalytic activity of Zr-MTBC-CoH was tested. At a Co loading of 0.05 mol%, it showed high activities in the hydrogenation of a range of alkenes at RT with quantitative yields. Zr-MTBC-CoH gave complete conversion of bulky substituted alkenes such as 2,3-dimethyl-2-butene within 48 h, and afforded 2,3-dimethylbutane with a TON > 8000 at 4 MPa H₂ and 296 K.

Ion exchange is another approach to introducing homogeneous catalytic species into the frameworks of MOFs (Fig. 5). Alkene hydrogenation catalysts with good recyclability can be prepared using this method. Two different anionic MOFs, ZJU-28 with a negative charge at the metal node and MIL-101-SO₃ with a negative charge centered on the organic

linker, were loaded with the cationic Rh complex (dppe)Rh(cod)BF₄ (**1a**) (dppe = 1,2-bis(diphenylphosphino)ethane; cod = 1,5-cyclooctadiene), using a simple shaking method to force ion exchange [48]. After exchange, the resulting materials, i.e., MIL-101-SO₃-**1a** and ZJU-28-**1a**, were tested in 1-octene hydrogenation. These catalysts gave similar TONs (~4000) in the solvent-free hydrogenation of 1-octene to 1-octane at 348 K and 1 MPa H₂, and had satisfactory recyclabilities. In the fifth cycle, the catalysts both gave TONs of ~4000, which is the same as that in first run after 24 h. Hydrogenation of 2,3-dimethylbutene was used to investigate the effects of different MOF supports on the catalytic performance. MIL-101-SO₃-**1a** (Rh loading 0.003 mol%) showed much higher initial activity, with a TON of 8800 after 24 h, compared with 1500 for ZJU-28-**1a**. More importantly, the activity of MIL-101-SO₃-**1a** increased greatly to 13500 turnovers after four cycles, whereas a significant decrease in the TON to 289 was observed in the case of ZJU-28-**1a** during recycling. Furthermore, when these two catalysts were used in a reaction with two calixarene-tethered alkene substrates, which had different kinetic diameters (0.95 and 1.6 nm, respectively), distinct hydrogenation selectivities were observed. MIL-101-**1a** gave complete conversion with the smaller substrate, but only partial conversion was achieved with the larger substrate, which has a kinetic diameter close to the pore window size of the MOF. In contrast, with ZJU-28-**1a**, which has a pore window of size 0.9 nm × 0.9 nm, no hydrogenation product was detected with these two substrates. These results effectively show that size-dependent catalysis can be achieved by two structurally different MOFs supporting the same catalyst.

A MOF with a high surface area and appropriate pore size can adsorb homogeneous catalysts and encapsulate the molecular catalyst inside cages. The formed heterogeneous catalyst can be reused in certain reactions without contamination of the products [49]. The chiral homogeneous catalyst [Rh(Me-BPE)(cod)]OTf (Me-BPE = 1,2-bis(2,5-dimethylphospholano)ethane; OTf = triflate) is highly effective and enantioselective in the asymmetric hydrogenation of alkenes such as dimethyl itaconate, methyl 2-acetamidoacrylate, and methyl (*Z*)-α-acetamidocinnamate. Typically, aprotic solvents such as dichloromethane and toluene favor this reaction. Significantly improved conversions were achieved in toluene by addition of achiral MOFs. With dimethyl itaconate as the substrate, UCM-1 gave an almost threefold-enhanced conversion of 27%, compared with 10% in the absence of UCM-1. The addition of UCM-1-NH₂ gave the highest enantiomeric excess (*ee*) value. Similar results were obtained for hydrogenation of the other two substrates on addition of MOFs. Adsorption experiments to quantify the amount of adsorbed Rh catalyst showed almost complete adsorbance in toluene; however, in dichloromethane, some of the Rh catalyst remained in the reaction solvent (Fig. 6). The catalytic hydrogenation results suggest that the enhanced activity achieved using MOF additives can be ascribed to enhanced stability of the molecular catalyst inside the MOF cages. Protection by MOFs could prevent the formation of inactive dimers or Rh–arene complexes from the homogeneous catalysts during the reactions.

Fig. 5. Catalyst loading via ion exchange using MOFs with anionic nodes or pendant anionic organic linkers [48].

Fig. 6. Schematic diagram of $[\text{Rh}(\text{Me-BPE})(\text{cod})]\text{OTf}$ adsorbed on IRMOF-3 or MIXMOF-5-NH₂ (a) and UCMCM-1 or UCMCM-1-NH₂ (b) [49].

When the unsaturated bond in an alkene connects with four different substituents or atoms, hydrogenation produces two products with different chiralities. Unlike size and shape selectivities, which are based on the intrinsic properties of MOFs, asymmetric selectivity can be affected by the chirality of the MOF-based catalyst. A common strategy for fabricating asymmetric MOFs is use of a privileged chiral ligand to coordinate with an achiral metal in an achiral synthetic environment [49]. After treatment with $\text{Ru}(\text{cod})(2\text{-Me-allyl})_2$ followed by HBr, a BINAP-MOF containing a chiral ligand [BINAP-derived dicarboxylate linker (L) (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl)] was post-synthetically metalated to give a highly enantioselective MOF-based catalyst **1-Ru** [51]. X-ray absorption fine structure studies showed that the Ru coordination environment in **1-Ru** was the same as that in the homogeneous complex $\text{Ru}(\text{Me}_2\text{L})(\text{DMF})_2\text{Cl}_2$ (DMF = dimethylformamide). At RT and appropriate pressures of H₂, **1-Ru** catalyzed the asymmetric hydrogenation of substituted alkenes to give quantitative yields with up to 85%, 72%, and 91% *ee* values for methyl α -acetamidoacrylate, methyl α -acetamidocinnamate, and dimethyl itaconate, respectively. Although these *ee* values are slightly lower than those of the homogeneous Ru catalyst, this work is valuable for producing single-site solid catalysts capable of asymmetric hydrogenation.

3.1.1.3. Supported metal NPs as active sites

Metal NPs usually give good catalytic performance in hydrogenation and are promising active sites in MOF-based catalysts [41]. When metal NPs are loaded on the frameworks or encapsulated in the cages of MOFs, the nano-sized metal particles are stabilized because MOFs, which have high surface areas and robust structures, are reliable supports; this greatly affects their activities in hydrogenation reactions. Our group rationally designed a one-step method for encapsulating metal NPs in the cages of MOFs and successfully obtained small metal NPs [52]. Pd precursors, i.e., $\text{PdCl}_2(\text{CH}_3\text{CN})_2$, were introduced into the cages of MOFs by coordination with 2,2'-bipyridine-5,5-dicarboxylate (bpydc) in the MOFs at a relatively low temperature of 353 K. Under a controlled temperature program, the solvent, i.e., DMF, mildly reduced the Pd precursors at a higher temperature, 403 K, forming Pd NPs of size 1.5 ± 0.3 nm. The catalyst Pd@MOF, with Pd NPs of size 5.4 ± 1.2 nm, was synthesized for comparison by rapidly heating to 403 K without an intermedi-

ate-temperature stage. Pd-in-UiO-67 (Pd loading 1 wt%) formed using a controlled temperature program, gave full conversion of styrene with >99% ethylbenzene selectivity after 25 min at RT and 0.1 MPa H₂; however, Pd@MOF needed a longer time (60 min) to achieve total conversion of styrene. The superior performance of the Pd-in-UiO-67 catalyst can be ascribed to the smaller size of the Pd NPs confined in the MOF cavities.

The metal NPs in a MOF tend to agglomerate during hydrogenation reactions because of their high surface free energies. Introducing metal NPs and other functional materials into the pores of MOFs can effectively prevent migration and agglomeration of NPs and increase the service lives of the catalysts. Glucose and Pd precursors were impregnated into an as-prepared MOF, i.e., ZIF-8, and then the intermediate glucose-Pd²⁺/ZIF-8 was reduced by heating at 573 K under an Ar/H₂ flow [53]. The attained C@Pd/ZIF-8 catalyst consisted of ZIF-8-supported carbon-stabilized Pd NPs. The average particle size of C@Pd/ZIF-8 (210 nm) was larger than those of ZIF-8 (165 nm) and Pd/ZIF-8 (175 nm). This can be ascribed to the formation of a porous carbon material by pyrolysis of glucose on the ZIF-8 surface. In cycling experiments, C@Pd/ZIF-8 (Pd loading 2.7 wt%) was continuously tested at 353 K and 2 MPa H₂ five times; only a slight loss of catalytic activity in styrene hydrogenations was observed (89.70% in the first run and 85.3% in the fifth run). Pure Pd/ZIF-8 without porous carbon gave a styrene yield of 98.5% in the first run and 25.5% in the fifth run. This is because Pd particles loaded on pure ZIF-8 aggregate or leach out of the MOF during the reaction, as shown using transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (Fig. 7). In contrast, those on C@Pd/ZIF-8 are completely protected by the confinement effect, giving improved durability of the catalyst in cyclic hydrogenation reactions.

The performance of different active sites in MOF-based catalysts is affected by the structural properties of the MOF sup-

Fig. 7. TEM (a) and HRTEM (b) images of C@Pd/ZIF-8 after five runs; TEM (c) and HRTEM (d) images of Pd/ZIF-8 after five runs [53].

ports. MOFs with the high specific surface areas and porous structures are widely used in gas adsorption. These properties can result in increases in the concentrations of gas reactants around the active sites in MOF-based catalysts, and therefore enhance the catalytic efficiency in alkene hydrogenation. The catalytic efficiency of a Pd nanocubes@ZIF-8 catalyst synthesized by forming ZIF-8 on pre-prepared Pd nanocubes (NCs) with plasmonic photothermal effects was higher than that of the parent Pd NCs in the hydrogenation of various alkenes [54]. Under light irradiation at 100 mW cm^{-2} and 0.1 MPa H_2 , Pd NCs@ZIF-8 (Pd loading 8.7 wt%) gave almost complete conversion of 1-hexene in 90 min at RT, whereas Pd NCs gave only 58% conversion. In a H_2 sorption study at 298 K, the sorption isotherms for Pd NCs@ZIF-8 and Pd NCs (Fig. 8) clearly indicated that the H_2 enrichment capacity of Pd NCs@ZIF-8 is higher than that of Pd NCs. This increases the concentration of H_2 around the Pd NC active sites in MOFs and improves the catalytic activity.

Another key factor in the catalytic activities of MOF-based catalysts is substrate diffusion inside the catalyst, i.e., internal diffusion, which significantly affects the accessibility of the substrate to the active sites. The microporous regime of most MOF-based catalysts inherently limits the transport of chemical species and their contact with active sites, resulting in decreased substrate conversion efficiency. The fabrication of MOFs with mesopores is a constructive method for enhancing internal diffusion in MOF-based catalysts. For example, metal NPs were added to the solution in which ZIF-8 had self-assembled, and then the NPs were etched to produce mesopores in the MOF (Fig. 9). This concept was used to fabricate meso-ZIF-8-Pt by encapsulating two types of NP; Au NPs served as sacrificial templates and were removed by the etching procedure, and Pt NPs were used as the catalytic active sites for alkene hydrogenation inside the ZIF-8 [55]. The N_2 adsorption-desorption isotherm of meso-ZIF-8-Pt, which shows behavior intermediate between type I and type IV, showed that the catalyst had the characteristics of both microporous and mesoporous materials. The pore size and Brunauer-Emmett-Teller specific surface area were both larger than those of the ZIF-8-Pt catalyst without the mesopores. As expected, at 308 K

Fig. 8. H_2 sorption isotherms for Pd NCs@ZIF-8 and Pd NCs at 298 K [54].

Fig. 9. Preparation of functionalized meso-MOFs [55].

and 0.1 MPa H_2 , the conversions of various substrates (*n*-pentene 44%, *n*-hexene 16%, and *n*-heptene 11%) catalyzed by meso-ZIF-8-Pt were higher than those obtained using the ZIF-8-Pt catalyst (*n*-pentene 30%, *n*-hexene 9%, and *n*-heptene 7%). These experiments were specifically performed under static conditions without external stirring, suggesting that the conversion depended solely on molecular self-diffusion. The results clearly show the capacity of mesopores to promote internal diffusion in MOF-based catalysts. This encapsulation-etching method for the fabrication of meso-MOFs can be extended to other MOFs and NPs with various sizes, shapes, and compositions, showing the versatility of this method for the rational design and synthesis of mesoporous materials.

3.1.2. Selective hydrogenation of alkenes

In addition to the optimizing the catalytic activities of MOF-based catalysts in alkene hydrogenation, the pore structures of MOFs can act as size- and shape-limiting windows for selective hydrogenation of different alkene molecules. A Ca-MOF (AEPF-1) showed different selectivities for styrene and α -methylstyrene, giving an almost full conversion yield (95%) of styrene but a low yield (60%) of α -methylstyrene under the same conditions, i.e., 398 K and 0.5 MPa H_2 [56]. UiO-66 with encapsulated Pt NPs gave high activity with 100% conversion of hexane, with a molecular size of 0.25 nm , after 24 h at 0.1 MPa H_2 and 308 K, but showed low activity, with 8% conversion, for triphenylethylene, with a larger molecular size of 0.58 nm [57]. These results can be attributed to the large pore apertures in the Pt/UiO-66 frame (0.6 nm), which are big enough to allow hexane diffusion without significant restraint. In contrast, triphenylethylene diffusion is limited.

The results described above suggest that hydrogenation of triphenylethylene, with a molecular size of 0.58 nm , would be catalyzed to some extent by Pt/UiO-66 with an aperture size of 0.6 nm . A MOF-based catalyst with a smaller pore aperture should be used to prevent conversion of triphenylethylene. However, a smaller pore aperture generally limits chemical

species diffusion and decreases the catalytic activity. Coating with another type of MOF with smaller pore apertures satisfactorily enhances size and shape selectivity by shell MOFs with smaller pore apertures and ensures favorable internal diffusion by core MOFs with larger pore apertures. For example, UiO-66-NH₂ with encapsulated Pd NPs was placed in a solution containing the raw materials for the synthesis of ZIF-8 and cetyltrimethylammonium bromide as a surfactant to fabricate a conformal Pd-UiO-NH₂@ZIF-8 catalyst [58]. In the hydrogenation of ethylene at 293 K, there were no significant differences between catalysis by Pd-UiO-NH₂@ZIF-8 (conformal shell) and that by Pd-UiO-NH₂. The ethylene molecule (0.25 nm) is small enough to diffuse into ZIF-8 with an aperture size of 0.34 nm and UiO-66-NH₂ with an aperture size of 0.6 nm and therefore reached the Pd NP active sites. In cyclohexene hydrogenation at 343 K, Pd-UiO-NH₂@ZIF-8 (conformal shell) showed almost no activity because of the large size of cyclohexene (0.55 nm), but high catalytic activity was observed with Pd-UiO-NH₂.

The example of MOF@MOF suggests that coating with other active species is a useful method for expanding the selective properties of MOFs in alkene hydrogenation. MOF shells can act as molecular sieves to screen reactants, and the active species, i.e., the core, catalyzes the hydrogenation reaction. Compared with encapsulation, coating with active species can broaden the type and size of active species and ensure the activity and selectivity of a MOF-based catalyst. However, a well-defined shell is needed to achieve good selectivity. For example, the integrity of the MOF shell is significant in the selectivity; this was confirmed by the catalytic performance of two analogous structures, i.e., Pd-UiO-NH₂@ZIF-8 with a fractured shell and Pd-UiO-NH₂@ZIF-8 with a conformal shell (Fig. 10). The latter

limited cyclohexene hydrogenation to a greater extent, giving lower conversions. These results can probably be attributed to the presence of substrate diffusion pathways created by the fractured shell of ZIF-8 [58].

In addition to the integrity of the shell, the thickness of the shell [59], the contact between the shell and the core [60], and the diffusion of reactants in the shell and core layer [60,61] can also affect the catalytic efficiency and durability of MOF-based catalysts in alkene hydrogenation. For example, a well-defined Pd/ZnO@ZIF-8 core-shell catalyst was fabricated using an in situ method to enhance the interactions between the shell and the core. This catalyst showed lower cyclohexene selectivity compared with that of Pd/SiO₂@ZIF-8 at 0.1 MPa H₂ and 308 K. The poor performance of Pd/SiO₂@ZIF-8, which was prepared using a traditional method, is thought to be the result of weak adhesion between the shell and the core [60]. MOF-based catalysts with yolk-shell structures are therefore considered to be effective materials for promoting internal diffusion. Pd@ZIF-8 hollow nanospheres were reported to show a high TOF of 2150 h⁻¹ in 1-hexene hydrogenation at 1 MPa H₂ and 298 K; this is almost seven times that for Pd/CPS@ZIF-8 (310 h⁻¹), which contained a solid core of carboxylate-terminated polystyrene spheres (CPS) [61].

3.2. Hydrogenation of alkynes

Selective hydrogenation of alkynes is essential in industry for improving the quality of alkene streams by removing acetylene impurities generated by steam-cracking of hydrocarbons. In the presence of a catalyst, alkyne hydrogenation involves chemisorption of the dissociative H₂ and sequential addition of the dissociated H atoms to the unsaturated bond, resulting in alkenes (semi-hydrogenation) and alkanes (over-hydrogenation) [61]. When using a MOF-based catalyst in alkyne hydrogenation, it is therefore necessary to ensure alkyne conversion but also control the yields of alkenes, to prevent over-hydrogenation to alkanes.

According to previous reports, MOFs with encapsulated metal NPs can be used to catalyze alkyne hydrogenation. For example, Ir NPs@ZIF-8, synthesized by immersing ZIF-8 in a solution of Ir(cod)(MeCp) precursor followed by heating in a H₂ atmosphere, was tested in the hydrogenation of phenylacetylene. At 0.3 MPa H₂ and 313 K, Ir NPs@ZIF-8 with an Ir loading of 1.5 wt% gave full conversion and >90% selectivity after 16 h [63]. Ir NPs@ZIF-8 showed impressive catalytic activity in the hydrogenation of alkynes, but over-hydrogenation occurred during the reaction.

The over-hydrogenation of alkynes in catalysis with active metal NPs may be caused by the presence of adjacent sites in large NPs. To improve the selectivity of alkyne semi-hydrogenation, rationally depositing another metal on the pristine metal NPs is a feasible but challenging strategy for diluting and separating the metal active sites. A recently developed seed-mediated growth method was successfully used to fabricate Pd@Ag core-shell NPs encapsulated in MOFs (Fig. 11) [64]. This catalyst with an optimized Pd/Ag ratio gave highly efficient partial hydrogenation of phenylacetylene. The intro-

Fig. 10. TEM images of conformal Pd-UiO-NH₂@ZIF-8 (A) and fractured Pd-UiO-NH₂@ZIF-8 (B). (C) Size-selective hydrogenation of conformal Pd-UiO-NH₂@ZIF-8, fractured Pd-UiO-NH₂@ZIF-8, and Pd-UiO-NH₂ (from left to right); back columns are for ethylene hydrogenation at 293 K, front columns are for cyclohexene hydrogenation at 343 K. Reproduced from Ref. [58].

Fig. 11. Schematic diagram of fabrication of Pd@Ag core-shell NPs encapsulated in MOF pores [64].

duction of Ag on the surfaces of Pd NPs in UiO-67 enhanced the selectivity for styrene compared with that of pure Pd NPs in UiO-67. Pd@Ag-in-UiO-67 (Pd loading 1.0 wt%) gave 91% selectivity for styrene in quantitative phenylacetylene conversion, whereas monometallic Pd-in-UiO-67 gave 75% selectivity for styrene and >99% phenylacetylene conversion at 298 K and 0.1 MPa H₂. The enhanced selectivity of Pd@Ag-in-UiO-67 can be attributed to the isolated and electronegative Pd sites on the surface, which were diluted and modified with electrons by Ag deposition on Pd.

The introduction of selective ingredients with metal NPs into MOFs can also improve the selectivity for semi-hydrogenation products. Nitrogen-containing compounds used as surface modifiers to enhance the selectivity of the catalyst for alkyne semi-hydrogenation have been reported [65]. 1,1,3,3-Tetramethylguanidinium trifluoroacetate, which is a type of ionic liquid (IL) and contains N was integrated into Cu₃(btc)₂ MOF with Pd NPs to obtain a Pd/IL/MOF catalyst (Fig. 12). The designed catalyst, with a Pd loading of 13.2 wt%, gave almost complete conversion (>99%) of phenylacetylene in 40 min and

Fig. 12. Structure of Pd/IL/MOF catalyst and its catalytic activity in selective hydrogenation of phenylacetylene [65].

high selectivity (>99%) for styrene at 303 K and 0.1 MPa H₂; other catalysts with different supports were less active and selective. For example, Pd NPs loaded on a porous carbon material gave 57.3% conversion of phenylacetylene and 93.8% selectivity for styrene in 40 min under the same reaction conditions.

In addition to incorporating other functional components into MOFs with encapsulated metal NPs, the selectivity can also be improved by regulating the MOF structure. A noble metal@MOF yolk-shell composite, Pd@H-Zn/Co-ZIF, was fabricated by the encapsulation of Pd in hollow H-Zn/Co-ZIF [66]. The hollow structure was formed by mild phase transformation of a ZIF-67 core coated with a ZIF-8 shell; this catalyst has played a significant role in semi-hydrogenation of acetylene. Pd@H-Zn/Co-ZIF showed improved activity with higher selectivity (>80%) for ethylene compared with a solid ZIF catalyst, Pd@S-Zn/Co-ZIF (<65%), prepared using a coprecipitation method, under a mixed gas flow at 323 K. The enhanced selectivity can be attributed to the hollow nucleus of H-Zn/Co-ZIF, which accelerates acetylene diffusion and the privileged desorption of ethylene from the Pd NP surfaces.

The products of semi-hydrogenation of alkynes may also undergo *cis-trans* isomerization and display different configurations [67]. These molecules with different geometric isomers can have distinct physicochemical properties, making additional purification processes necessary. MOFs could play a significant role in the size limitation of product molecules and used in *cis-trans* configuration selection. MOF-74(Ni) was chosen as a shell to coat a flower-like Rh-Ni alloy, giving a core-shell-structured catalyst Rh₁Ni₁@MOF-74(Ni) [68]. In the hydrogenation of diphenylacetylene, Rh₁Ni₁@MOF-74(Ni) with a porous shell gave enhanced selectivity for *cis*-stilbene; the selectivity was about three times that of the parent alloy Rh₁Ni₁. Because *trans*-stilbene is larger, isomerization from *cis*-stilbene to *trans*-stilbene is limited by steric hindrance in the cavities of MOF shells. This was confirmed by the increased selectivity for *cis*-stilbene as the shell thickness increased.

3.3. Hydrogenation of nitroarenes

Hydrogenation of nitroarenes has attracted much interest because the resulting anilines and their derivatives are important raw materials in the industrial production of polymers, pharmaceuticals, and various fine chemicals [68]. This process generally involves the splitting of H₂, reduction of the nitro group and other intermediates, and condensation of hydroxylamines and nitroso species. In addition to reduction of the nitro group, other functional groups in nitroarenes can be reduced during hydrogenation, e.g., halide, carbonyl, and cyano groups. The control of side reactions has therefore always been one of the difficulties in selective hydrogenation of nitroarenes. Some catalysts with favorable chemoselectivities have been reported but they had intrinsically low catalytic activities [70,71]. MOF-based catalysts, which show considerable activities in hydrogenation reactions, have given impressive performances in nitroarene hydrogenation systems.

A series of lanthanide-based MOFs, [Ln₂(C₂H₄C₂O₄)₂(SO₄)

(H₂O)₂] (RPF-16), where Ln = La, Pr, Nd, and Sm, were synthesized and used to catalyze nitrobenzene hydrogenation [72]. The reactions were performed in toluene at 0.5 MPa H₂ and 363 K. The activity of RPF-16-La, with a TOF of 29.7 h⁻¹, was much lower than those of the other catalysts, with TOF values of 146.8 h⁻¹ for RPF-16-Sm, 161.2 h⁻¹ for RPF-16-Nd, and 175.2 h⁻¹ for RPF-16-Pr. All these catalysts gave aniline as the sole product within the desired reaction time. The activity order was in agreement with the increasing Lewis acid strengths of the corresponding lanthanide metals, i.e., La < Sm < Nd < Pr. Further experiments were performed with RPF-16-Pr as the catalyst to investigate the hydrogenation of nitroarenes that differed structurally and electronically. Nitroarenes with *p*-NH₂, *p*-CH₂CN, *p*-CHO, *p*-Br, and *p*-I substituents all gave full nitroarene conversions and high selectivities for the corresponding amines. Dehalogenation was detected only for 4-iodonitrobenzene, with 30% nitrobenzene as a by-product. These results show that the Lewis acid sites in MOFs can provide active sites for nitroarene hydrogenation.

Several metal NPs encapsulated in the frameworks of MOFs, such as Pt@MIL-101 [73], Pd/DUT-67 [74], Pd-in-Uio-67 [75], and Pd@MIL-101 [76], were synthesized by various methods and used in nitrobenzene hydrogenation reactions. Our group developed a novel synthetic strategy for encapsulating Pd precursors through ligand design prior to MOF assembly followed by reduction in a H₂ atmosphere, to give uniformly distributed Pd NPs inside the MOF cavities [75]. This Pd-in-Uio-67 catalyst, with a Pd loading of 1.0 wt%, gave superior catalytic activity (conversion >99%) and selectivity (>99%) within 3 h at 0.1 MPa H₂ and RT. The outstanding catalytic performance can be attributed to the electron-donating effects of the aryl rings and the carboxylate moiety to Pd in the MOFs, and the confinement in nanocavities offered by the framework of the MOF.

Jiang's group [76] reported an example that used a coupling effect with dehydrogenation of ammonia borane (NH₃BH₃) to boost the hydrogenation efficiency. Pd@MIL-101 was obtained by encapsulating a Pd precursor in MIL-101 via a double-solvent approach and then using NH₃BH₃ to reduce the Pd precursor. Unlike the case using Pd@MIL-101 with small Pd NPs (~3 nm) as the catalyst for nitroarene hydrogenation in a H₂ atmosphere, NH₃BH₃ was added to a solution containing Pd²⁺@MIL-101 and the nitroarene to perform a tandem reaction involving ammonia borane dehydrogenation and nitroarene hydrogenation. The tandem reaction over Pd@MIL-101 (Pd loading 0.87 wt%) achieved almost full conversion at RT of various nitroarenes within a short period of time. For example, nitrobenzene and its methyl, amino, *p*-methylol, or *p*-hydroxyl derivatives were reduced to give excellent yields (>99%) of their corresponding amine products within 1.5 min; the reaction rate was 20 times slower when NH₃BH₃ was replaced with a H₂ flow while keeping the other conditions the same. Further experiments to explore uncoupled dehydrogenation of NH₃BH₃ showed that the effect of NH₃BH₃ was significant, suggesting that fast H₂ generation from NH₃BH₃ greatly enhances the local concentration of H₂, facilitating contact between hydrogen and the nitro compounds and increasing the reaction efficiency.

In addition to monometal-encapsulated MOF-based catalysts for adjusting the reductant in hydrogenation systems, bimetallic NPs in MOFs are being developed. Different types of bimetallic NPs have been successfully introduced into MOFs, e.g., PdNi alloy NPs (PdNi-in-Uio-67) [77], PdCu alloy NPs (PdCu@Fe^{III}-MOF-5) [78], Au@Ag core-shell NPs (Au@Ag/ZIF-8) [79], Pd@Pt core-shell NPs (PdPt@Uio-66) [80], and Pd^{II}Ni crown-jewel NPs (Pd^{II}Ni-in-Uio-67) [81]. Because of the synergistic effect achieved by incorporating two different metals, MOF-based catalysts with encapsulated bimetallic NPs give higher catalytic activities and chemoselectivities in nitroarene hydrogenation. In particular, because of the modified electronic structures of the bimetallic NPs, the MOF-based catalysts give performances superior to those of their analogs with immobilized monometallic NPs. For example, Pd₁Pt₁@Uio-66 with a Pt/Pd molar ratio of 1:1 gave complete hydrogenation of nitrobenzene within 3 h at 0.2 MPa H₂ and RT, whereas Pt@Uio-66 needed 6 h to complete the conversion [80]. XPS (Fig. 13) showed that an additional signal, from Pt 4f, appeared after sputtering for Pd₁Pt₁@Uio-66, indicating modification of the electronic structure of the Pt NPs. Differences between the performances of monometallic and bimetallic NPs encapsulated in MOFs were also observed for other catalytic systems such as Pd-in-Uio-67 and PdNi-in-Uio-67 [75], and Au@Ag/ZIF-8 and Au/ZIF-8 [79].

It is worth noting that crown-jewel metal NPs, which consist of one type of metal NP decorated with other metal atoms on the surface, are different from alloy NPs and core-shell metal NPs. Density functional theory (DFT) calculations were used to identify the electronic states of the Pd and Ni atoms in

Fig. 13. (a) Full survey XPS of PdPt@Uio-66 (core-shell) before (black) and after (red) sputtering. Pt 4f spectrum of sample before (b) and after (c) sputtering [80].

Pd^ΔNi-in-UiO-67, which is a crown-jewel Pd-based bimetallic nanostructure encapsulated in UiO-67 via hydride-induced reduction [81]. Bader charge analysis showed that the Pd atoms were negatively charged, which is the opposite of the Ni atoms (about +0.20e), indicating electron denotation from Ni atoms to Pd atoms. Furthermore, the change in the electronic structure was accompanied by a shift in the calculated binding energy of nitrobenzene (BE-NB) on the Pd^ΔNi surface from 1.66 to −2.22 eV with increasing Ni content (for Pd/Ni molar ratios of 40:1, 32:1, 24:1, 16:1, and 8:1) on the Pd surface. These results suggest that nitrobenzene adsorption changed from endothermic to exothermic, which is thermodynamically favorable. However, when the BE-NB is more negative, nitrobenzene desorption becomes difficult, which limits the adsorption of other reactants. Based on these two factors, there was an optimum Pd/Ni molar ratio for nitrobenzene hydrogenation. Pd^ΔNi-in-UiO-67 with the optimum Pd/Ni molar ratio of 24:1 gave 70.5% conversion of nitrobenzene and 99.3% selectivity for aniline at 298 K and 0.1 MPa H₂, whereas the monometallic Pd-in-UiO-67 gave only 36.5% conversion and 98.6% selectivity. Similar results were obtained for Pd^ΔM NPs, where M is a transition metal atom, e.g., Cu and Fe. The controlled decoration of Pd NPs with M can be used to manipulate the *d*-band electronic structure, which further affects the catalytic performance by influencing the binding strength between the reactants and active sites.

In addition to Lewis acid sites, monometallic NPs, and bimetallic NPs, sulfides can be used as the active sites in MOF-based catalysts. Because of the high specific surface areas of MOFs, functionalizing the nodes of MOFs with active components is an efficient way of isolating the active sites. Atomic layer deposition was used to deposit cobalt sulfide on NU-1000. The resulting CoS-AIM (Co/S molar ratio = 1.2:1.1) was more catalytically active in the selective hydrogenation of *m*-nitrophenol to *m*-aminophenol (Fig. 14) than other materials such as NU-1000, Co₉S₈ films supported on Si, and amorphous CoS_x (Co/S molar ratio = 0.87) [82]. NU-1000 and Co₉S₈ films were inactive in the transformation using NaBH₄ as the reductant at RT, whereas CoS-AIM gave almost full conversion of *m*-nitrophenol and selectivity for *m*-aminophenol in 15 min, and CoS_x gave 70% conversion but only 30% of *m*-nitrophenol was transformed to *m*-aminophenol. All these results imply a strong synergistic effect between NU-1000 and cobalt sulfide. An analogous material, CoO-AIM, was tested to clarify the specific role of S in CoS-AIM; CoO-AIM was almost inactive (less than 1% conversion).

Fig. 14. Schematic diagram of fabrication of CoS-AIM catalyst and its selective hydrogenation of *m*-nitrophenol [82].

The presence of various active sites expands the applications of MOF-based catalysts; however, some of the catalysts show relatively low mechanical strengths in harsh environments, and this prevents exploitation of their full potential. Coating the catalysts with mechanically harder composites is an efficient approach to enhancing the mechanical properties of MOF-based catalysts to extend their range of practical applications. Mesoporous silica (mSiO₂) was chosen as the shell material because its large porosity ensures that reactant molecules can move into or out of core materials without altering their pristine properties [83]. ZIF-8 was used as the core for mSiO₂ coating. The resulting nanocomposite ZIF-8@mSiO₂ and pure ZIF-8 were examined using atomic force microscopy nanoindentation. A direct comparison of the projected areas under an identical indentation force showed that the projected area for ZIF-8@mSiO₂ was smaller than that for pure ZIF-8, indicating that ZIF-8@mSiO₂ was harder. When Au or Cu NPs were anchored on the ZIF-8 exterior surface before coating with mSiO₂, the resulting ZIF-8@Au@mSiO₂ and ZIF-8@Cu@mSiO₂ gave good performances in the hydrogenation of 4-nitrophenol with NaBH₄ as a reductant in real reaction environments.

3.4. Hydrogenation of cinnamaldehyde (CAL)

α,β -Unsaturated alcohols and saturated aldehydes are important because their hydrogenation products are widely used in producing fine chemicals for medicines, perfumes, and food additives [84]. The hydrogenation of α,β -unsaturated aldehydes generally faces the problem that competitive reductions of the C=O bond and C=C bonds result in low selectivity for the target product. CAL, a typical α,β -unsaturated aldehyde, is difficult to hydrogenate efficiently with satisfactory selectivity for the target product because of the potential formation of cinnamal alcohol (COL), hydrocinnamaldehyde (HCAL), and hydrocinnamal alcohol (HCOL) (Fig. 15). The distributions of the various products of CAL catalytic hydrogenation mainly depend on factors such as the catalyst, solvent, and additives. For MOF-based catalysts, catalyst design is one of the keys to achieving selective hydrogenation of either the C=O bond or the C=C bond, and avoiding over-hydrogenation.

The hydrogenation of a C=C bond is more thermodynamically favorable than that of a C=O bond, but it is still hard to achieve 100% selective hydrogenation of CAL to HCAL. It has been reported that larger active metal NPs favor C=O bond hydrogenation [85], therefore MOF-based catalysts encapsulating small NPs could increase selectivity for hydrogenation of

Fig. 15. Reaction pathways in hydrogenation of CAL.

the C=C bond. Pd-based catalysts are among the most active and selective catalysts for the hydrogenation of CAL to HCAL. Pd⁰-MIL-101-NH₂(Cr) with Pd NPs of size 2–3 nm was tested in CAL hydrogenation; the performance was compared with that of a commercially available Pd/C catalyst with larger Pd NPs at 0.1 MPa H₂ and RT [86]. Pd⁰-MIL-101-NH₂(Cr) (Pd loading 8 wt%) gave higher selectivity (95%) for HCAL, with >99% conversion of CAL in 90 min, as expected. In contrast, the Pd/C catalyst gave only 41% selectivity and 69% conversion. The increased catalytic activity can be attributed to the wider pore windows (1.6 nm) of MIL-101-NH₂(Cr), which enhance mass transfer of the reagents into the catalyst framework, as well as the smaller and highly dispersed Pd NPs.

Generally, good dispersion of metal NPs in MOF-based catalysts is essential for the hydrogenation reaction, and significantly influences adsorption and desorption of the substrate on the catalyst. The reactants have to diffuse into the MOF-based catalyst framework to reach the metal NPs if the NPs are encapsulated in the cavities, which may cause further hydrogenation of the reactants. Pd was loaded on ZIF-8 using a wet impregnation method and then reduced by heating in H₂ [87]. This gave a Pd/ZIF-8 catalyst with Pd NPs located on the external surface of ZIF-8, as shown by the N₂ adsorption and TEM results. At a Pd loading of 1.0%, Pd/ZIF-8 gave 90.4% selectivity for HCAL at 313 K and 2.0 MPa H₂; reported selectivities achieved using other supported Pd catalysts with Pd NPs in the pore cavities of the supports were Pd/MIL-101(Cr) 78.2%, Pd/MIL-53(Cr) 67.8%, and Pd/γ-Al₂O₃ 70.6%. During the reaction, the subsequent hydrogenation of HCAL to HCOL is avoided because the formed HCAL is removed quickly from the catalyst surface in the Pd/ZIF-8 system, giving a lower conversion to HCOL; further hydrogenation of HCAL to HCOL occurred in other systems with Pd NPs inside the pores, which limited diffusion. However, loading metal NPs on the external surfaces of MOFs can lead to problems with NP leaching because the NPs do not benefit from the confinement effect offered by MOFs. Pd/ZIF-8 lost 15% of its original activity after the fourth run, although it retained its selectivity.

Our group developed a Pd@MOF1 catalyst in which the metal NPs are mainly inside the MOFs. The catalyst gave selective hydrogenation of CAL to HCAL based on π–π stacking interactions between the aromatic rings of CAL and the aromatic ligands of MOF1 [88]. The bpydc ligands adsorbed on the surfaces of the pre-prepared Pd NPs were reduced by NH₃BH₃ and assembled with [Zr₆O₄(OH)₄(CO₂)₁₂] clusters to fabricate Pd@MOF1. The resulting Pd NPs were encapsulated in the MOF

network. CAL tends to diffuse into the Pd@MOF1 pores in the direction of the aromatic rings because of the π–π stacking interactions. The C=C bond is preferentially hydrogenated because it is nearer the aromatic ring of CAL than the C=O bond is. At 298 K and 0.1 MPa H₂, the Pd@MOF1 catalyst with a Pd loading of 2.0 wt% gave full chemoselectivity for HCAL and full CAL conversion within 6 h. It is worth noting that the N atom in bpydc plays an important role in preventing agglomeration of NPs. Pd@MOF2, which was prepared using biphenyldicarboxylic acid, which does not have a N atom, as the ligand under similar conditions, suffered from high aggregation of Pd NPs and showed lower chemoselectivity (75%) and activity in CAL hydrogenation. Pd@MOF1 showed no essential losses of activity and selectivity after five runs.

Another strategy for controlling the selectivity for HCAL is based on the strong interactions between CAL and the Lewis acid sites in Pt/MIL-101 [89]. A simple colloidal deposition method was used to fabricate a Pt/MIL-101 catalyst with small Pt NPs (2.3 ± 0.55 nm). The total amount of Lewis acid sites in Pt/MIL-101 was 1.91 mmol g⁻¹ after removing the terminal water molecules in the MOF structure. In situ attenuated total reflection infrared (ATR-IR) spectroscopy showed that under the desired reaction conditions with Pt/MIL-101 as the catalyst the C=O bond stretching vibration of CAL underwent a clear red shift (12 cm⁻¹), whereas no band shift of the C=C bond was observed. This result can be attributed to coordination between the C=O bonds and the Cr Lewis acid sites of MIL-101. Observations of the entire reaction process showed the appearance of a peak from HCAL at 1715 cm⁻¹, the intensity of which increased with increasing reaction time, indicating hydrogenation of the C=C bond. On the basis of these ATR-IR studies and other catalyst characterization studies, it can be speculated that a Pt/MIL-101 catalyst with small Pt NPs would favor reduction of the C=C bond, as well as coordination between the C=O bond and the Lewis acid sites in Pt/MIL-101, enhancing the chemoselectivity for CAL hydrogenation (Fig. 16). As expected, the catalyst gave superior selectivity (>99.9%) for HCAL in various solvents such as isopropyl alcohol (IPA), hexane, toluene, and ethyl acetate, with different activities. Pt/MIL-101 gave almost full conversion and selectivity (>99.9%) in IPA at 298 K and 0.1 MPa H₂ within 1 h.

The development of effective catalysts for selective hydrogenation of the C=O bond is more challenging than in the case of the C=C bond because hydrogenation of the latter is more thermodynamically favorable. Because of the molecular structure of CAL and the different locations of the C=C and C=O

Fig. 16. Plausible mechanism for hydrogenation of CAL over Pt–Lewis acid collaborative Pt/MIL-101 catalyst [89].

bonds in CAL, using the structural confinement effect of MOFs could be an effective way of achieving selective hydrogenation of the C=O bond. Pt NPs were confined in the cavities of UiO-66-NH₂ by coordinating the amine group on the MOF organic ligand to fabricate a Pt@UiO-66-NH₂ catalyst [90]. The Pt NPs were encapsulated in cages, therefore the CAL molecules had to pass through the pore windows (0.6 nm) to reach the NPs. CAL molecules are long and were therefore forced to adsorb on the Pt NPs via the terminal C=O bond, which was selectively hydrogenated, instead of the C=C bond in the middle of CAL, because of the narrow channels in the MOF. Pt@UiO-66-NH₂ (Pt loading 10.7 wt%) gave 85.9% conversion of CAL and 87.9% selectivity for COL after 42 h at 298 K and 4 MPa H₂. In comparison, the analogous catalyst Pt/UiO-66-NH₂ in which the loading of Pt NPs of similar size was controlled to achieve loading on the external surface of UiO-66-NH₂, gave a lower selectivity of 71.6% with 52.2% conversion; this confirmed the significant restriction effect of the framework. Along with the structural confinement effect, the pore walls of MOFs can affect product adsorption on the Pt surface and control the selectivity for COL.

Coating with a MOF shell can enhance the structural confinement and increase CAL transformation to COL. Based on this concept, a core-shell-structured catalyst, Pt/MIL-100@MIL-100, was fabricated by coating the Pt/MIL-100 surface with the same MOF by homoepitaxial growth [91]. Choosing the same MOFs for producing the hybrid ensures favorable diffusion of reactants and a well-defined shell. The shell thickness of the Pt/MIL-100@MIL-100 (Pt loading 0.82 wt%) catalyst was adjusted using four assembly cycles; the obtained catalyst gave 95% CAL conversion and 96% selectivity for COL in 4 h at 298 K and 0.1 MPa H₂. The uncoated Pt/MIL-100 (Pt loading 0.93 wt%) achieved only 55% selectivity for COL, although it gave almost full conversion of CAL in less time (2 h) under the investigated conditions. These results clearly show that a MOF shell coating enhanced the selectivity but decreased activity. The former effect can be attributed to steric hindrance of the possible products and Pt NPs with higher electron densities as a result of electron donation from aryl ligands in the MOFs. The latter effect was caused by unavoidable diffusion limitation caused by coating with a 24 nm thick shell material.

To optimize the strategy for developing a core-shell-structured catalyst for CAL hydrogenation, two analogous MOFs with the same topological structures but different metal centers, i.e., Fe and Cr, were used to build a sandwich nanostructured catalyst (Fig. 17). The different CUSs in MOFs interact in various ways with reactants, which can influence the activity and selectivity in hydrogenation of CAL [92]. DFT calculations suggested that the hydrogenation of CAL to COL was more favorable on Fe because of the lower reaction energy, whereas the catalytic activity in CAL hydrogenation decreased because of stronger surface binding of the H atoms on the Pt NPs loaded on MIL-101(Fe). Pre-experiments on CAL hydrogenation agreed with the calculation results, i.e., MIL-101(Fe)@Pt (Pt loading 5.1 wt%) gave higher selectivity for hydrogenation to COL, whereas MIL-101(Cr)@Pt (Pt loading 4.8 wt%) was more active in CAL conversion. A combination of the advantages of

Fig. 17. Synthetic route for sandwich MIL-101@Pt@MIL-101, comprising Pt NPs sandwiched between a core and shell of MIL-101 [92].

the two catalysts, achieved by coating MIL-101(Fe) on the surface of MIL-101(Cr)@Pt, could be the optimum choice for improving both the activity and selectivity in CAL hydrogenation to COL. MIL-101(Cr)@Pt@MIL-101(Fe) with a shell of thickness 8.8 nm gave 94.5% selectivity for COL with 45% conversion of CAL in 6 h at 3 MPa H₂ and RT, whereas MIL-101(Fe)@Pt@MIL-101(Fe) with a 9.2 nm thick shell needed a longer time (8.5 h) to achieve the same selectivity at the same conversion level, and MIL-101(Cr)@Pt@MIL-101(Cr) with a 5.1 nm thick shell displayed lower selectivity (79.2%) at 45% conversion. MIL-101(Cr)@Pt@MIL-101(Fe) (Pt loading 4.6 wt%) with a 2.9 nm thick shell only required 2 h to complete 45% conversion of CAL and gave a selectivity of 94.2% for COL; decreasing the thickness of the MIL-101(Fe) shell optimizes reactant diffusion. Furthermore, exceptionally high selectivity (95.6%) and conversion efficiency (99.8%) were achieved within 20 h using MIL-101(Cr)@Pt@MIL-101(Fe) with a 2.9 nm thick shell; this performance is better than those of state-of-the-art catalysts. The design of a sandwich catalyst with a more active core and a more selective shell could not only improve the selectivity but also reduce the diffusion limitation caused by the shell coating, providing a potential strategy for designing selective catalysts for important yet challenging transformations.

As well as metal NPs, the CUSs inside MOFs can also be used as the active sites for CAL hydrogenation to COL via Meerwein-Ponndorf-Verley (MPV) reduction [93]. The use of HCl and trifluoroacetic acid as modulators in UiO-66 synthesis gave a more open framework structure; the UiO-66 with increased CUSs combined with IPA which is a hydride donor, and therefore acted as a hydrogen transfer catalyst. In the absence of H₂, UiO-66 was used to hydrogenate CAL with IPA as the solvent at 413 K, giving >99% conversion of CAL with 92% selectivity for COL.

3.5. Hydrogenation of furfural (FFA)

FFA, another typical α,β -unsaturated aldehyde, is a potential platform molecule in the chemical and fuel industries because of its potential to deal with the deficit in fuel resources and its use in the production of valuable chemicals such as furfural alcohol (FA), cyclopentanone (CPO), tetrahydrofurfuryl alcohol

(THFFA), furanoic acid, and THF [94]. The hydrogenation of FFA to such products is a significant challenge because of the undesired side-products formed during hydrogenation. Two functional groups in FFA, i.e., the C=O bond and the conjugated C=C–C=C system in the furan ring, can be chemoselectively reduced, depending on the reaction conditions. Metal NPs such as Cu, Pd, Ru, and Pt NPs are typically used in FFA hydrogenation and can be combined with MOFs to fabricate MOF-based catalysts for selective hydrogenation of FFA [95]. As a support, MOF can affect the behaviors of the reactants and the NPs, and therefore affect the catalytic efficiency in FFA hydrogenation, depending on the properties of the parent MOFs.

Based on the study of CAL hydrogenation with sandwich nanostructured catalysts, it was assumed that the incorporation of CUSs and Pt NPs in MOF-based catalysts would promote selectivity for hydrogenation of the C=O bond [92]. To confirm this speculation, FFA hydrogenation was performed using a MIL-101(Cr)@Pt@MIL-101(Cr) catalyst. MIL-101(Cr)@Pt@MIL-101(Cr) (Pt loading 4.4 wt%) with a 5.1 nm thick MIL-101(Cr) shell gave 98.5% conversion with 99.8% selectivity for FA in 5 h at RT and 3 MPa H₂. Even without a MIL-101(Cr) shell, MIL-101(Cr)@Pt still showed higher selectivity (91.2%) than that of pure NPs, with a selectivity of 85.7%. These results show the presence of strong interactions between FFA and MIL-101(Cr) via the C=O bond and the CUSs, which could promote hydrogenation of the C=O bond in this catalytic system.

Interactions between the C=O bonds and CUSs were also observed in the hydrogenation of FFA to CPO. Our group synthesized a Ru/MIL-101 catalyst with a 3% Ru loading and used it to hydrogenate FFA [96]. At the beginning of the reaction, FFA was quickly converted to FA, which was transformed into CPO in three steps. The Lewis acid–base interactions between the C=O groups in CPO and the CUSs in MIL-101(Cr) effectively limited over-hydrogenation of C=O (Fig. 18). Ru/MIL-101 (Ru loading 3 wt%) gave almost full conversion (>99) with 96% selectivity for CPO within 2.5 h at 433 K and 4 MPa H₂. Further experiments showed that in this system the CPO selectivity over Ru/MIL-101 was dependent on the H₂ pressure and the Ru loading. If either of these factors exceeded the optimum value in this system, over-hydrogenation of CPO clearly occurred.

The adsorption properties of MOFs can enhance the local concentrations of reactants around active sites and further increase the reaction rate; this has been observed in the hydrogenation of alkenes (Section 3.1) [54], and can also contribute to FFA hydrogenation. Two Al-based MOFs, Al-MIL-53-BDC

Fig. 18. Possible reaction pathways in FFA hydrogenation in water over Ru/MIL-101 [96].

Fig. 19. Thermogravimetric curves of Al-MIL-53-BDC and Al-MIL-53-ADP samples after FFA adsorption [97].

and Al-MIL-53-ADP, were synthesized using different organic linkers, i.e., 1,4-benzenedicarboxylic acid (BDC) and adipic acid (ADP), respectively [97]. These MOFs had different surface areas, which played a significant role in FFA adsorption. After saturation of adsorption, Al-MIL-53-BDC, with a large surface area (761 m² g^{−1}), lost 35% of its weight in the range 303 to 473 K, whereas only a 12% weight loss was observed for Al-MIL-53-ADP (4 m² g^{−1}) up to 373 K (Fig. 19). The weight loss is mainly attributed to loss of FFA. Both MOFs can support Ru NPs via a simple deposition–reduction method, and because of its adsorption capacity, Ru/Al-MIL-53-BDC with a 2.9% of Ru loading gave full conversion of FFA with >99% selectivity for FA in 2 h at 0.5 MPa H₂ and 293 K. In contrast, Al-MIL-53-ADP (Ru loading 3.0%) gave 44% conversion of FFA with a similar selectivity for FA. It is worth noting that although loading with Ru NPs changed the surface areas of these MOF-based materials, Ru/Al-MIL-53-BDC (497 m² g^{−1}) still had a larger surface area than Ru/Al-MIL-53-ADP (18 m² g^{−1}).

3.6. Hydrogenation of benzene

Hydrogenation of benzene is a significant industrial process because of the high consumption of its product, i.e., cyclohexane, in the synthesis of Nylon-6 and Nylon-66 [98]. Furthermore, the benzene level in the environment is important, especially in terms of air quality, and should be regulated to protect human health. Compared with the reduction of functional groups such as C=C bonds, C=O bonds, and nitro groups, the full hydrogenation of benzene is more difficult and generally requires rigorous conditions, with temperatures greater than 373 K and H₂ pressures greater than 3 MPa.

Hydrogenation of various aromatic compounds containing benzene rings and other reducible functional groups was performed using the MOF-based catalyst Zr-[IrL] [99]. At 313 K and 0.2 MPa H₂, the C=C bonds of styrene, the C=O bonds of benzaldehyde, the cyano groups of benzonitrile, and the nitro groups of nitrobenzene were all hydrogenated before reduction of the benzene ring occurred. These results show that MOF-based catalysts are promising catalysts for hydrogenation of benzene to cyclohexane, but benzene ring reduction is still

Fig. 20. General reaction pathway for hydrogenation of aromatic compounds [99].

more challenging than reduction of other unsaturated groups. At 333 K and 0.6 MPa H₂, the benzene rings of various aromatic substrates such as aniline, toluene, ethylbenzene, and phenol were hydrogenated with different activities. For example, toluene was quantitatively converted within 5 h, giving a 98 h⁻¹ TOF. The activity under the experimental conditions was attributed to cooperation between the CUSs of the Zr metal clusters and the immobilized Ir complexes in Zr-[IrL] (Fig. 20). The former could activate the benzene rings in aromatic compounds and the latter played an important role in assisting heterolytic activation of H₂ molecules.

The design of MOF-based catalysts should be rationalized to achieve high efficiency in catalytic hydrogenation of benzene. For MOF-based catalysts encapsulating NPs, the host-guest interactions between the framework of the MOF and the NPs should be considered. These interactions can confine and stabilize the NPs during the reaction, but also suppress the activity of the NPs if the interaction is too strong. For example, consumption of the reactant H₂ over the Ni NPs in Ni/MIL-120 and Ni/Al₂O₃ was determined using temperature-programmed H₂ reduction [100]. Ni/MIL-120 gave a more intense peak, which indicates that stronger interactions between Ni NPs and the Al₂O₃ support can suppress reduction. The performances of these two catalysts in the hydrogenation of benzene to cyclohexane were tested in a pulse fixed-bed microreactor; the activity of Ni/MIL-120, which has appropriate interactions, was superior to that of Ni/Al₂O₃.

The sizes and distributions of NPs in MOFs also affect the activity. The benzene hydrogenation catalytic activity of Ru@Zr-MOF prepared in a supercritical CO₂-methanol solution was almost double that of Ru/Zr-MOF synthesized using a simple impregnation method [101]. The poor performance of Ru/Zr-MOF can be attributed to the larger size and inhomogeneous dispersion of the Ru NPs.

Bimetallic NPs can also be used for benzene hydrogenation, and they can achieve high efficiency even under solvent-less conditions. Our group successfully deposited Ru-Pt bimetallic NPs on MIL-101 using a simple colloidal deposition method. The catalyst gave highly efficient hydrogenation of benzene to cyclohexane under solvent-less conditions [102]. Because of the synergistic effect of Ru-Pt catalysts, Ru-Pt/MIL-101 with the optimum Ru/Pt ratio of 2:1 showed superior catalytic activity, with a TOF of 2335 h⁻¹, compared with 1137 h⁻¹ for Pt/MIL-101 and 594 h⁻¹ for Ru/MIL-101. Furthermore, gram-scale reactions using 10 mL of benzene as the substrate and a benzene/(Ru/Pt) molar ratio of 8000:1 gave almost full conversion to cyclohexane (Fig. 21), suggesting the possibility of practical applications of the Ru-Pt catalytic system.

Fig. 21. Cyclohexane yield as function of time in gram-scale hydrogenation of benzene. Reaction conditions: benzene (10 mL), Ru-Pt (Ru:Pt = 2:1), benzene/metal = 8000:1, 1 MPa H₂, 333 K [102].

3.7. Hydrogenation of other compounds

In addition to the hydrogenation reactions described above, MOF-based catalysts can be used for the hydrogenation of other compounds such as CO₂ [103,104], phenol [105], γ -valerolactone (GVL) [106], ethyl levulinate (EL) [107], and nitriles [108]. In these reaction systems, the properties of the MOF-based catalysts greatly affect the selectivity and activity, as well as other aspects of hydrogenation.

For example, the intrinsic photocatalytic properties of the Ti metal clusters in NH₂-MIL-125(Ti) give efficient photo-induced CO₂ reduction, in which only formate is produced. Loading noble metal NPs, i.e., Pt and Au, on NH₂-MIL-125(Ti) promoted photocatalytic hydrogenation, giving H₂ and formate as the products. The experimental differences between the performances of Pt and Au NPs combined with DFT calculations show that the H atoms can spill over from the Pt NPs to the frameworks of MOFs and reduce Ti⁴⁺ to Ti³⁺, which promotes CO₂ reduction [103]. The Ni CUSs in a Ni-MOF for nitrile hydrogenation strongly interact with nitriles and expedite the first step in nitrile hydrogenation, forming primary imines and generating amines by full hydrogenation [108]. In EL hydrogenation, the Zr metal clusters in Zr-MOFs such as UiO-66, MOF-801, and MOF-808 are the active sites in MPV reduction of EL to GVL. A combination of the high surface area and pore size of Zr-MOFs give high GVL formation [107].

In addition to the metal centers of MOF-based catalysts, the functional organic ligands can act as catalytic sites and improve the reaction efficiency. Compared with the parent MIL-101, functionalized MIL-101-SO₃H showed higher activity in GVL hydrogenation; this is because of the participation of the Brønsted acid SO₃H groups [106]. Furthermore, increasing the content of the SO₃H groups from 25% to 50% increased the GVL conversion from 8.0% to 35%.

The mesoporosity and hydrophilicity of MIL-101 enabled Pd precursors to be adsorbed in the framework and then reduced in the pores, resulting in small NPs (2.5 ± 0.5 nm) in MIL-101 [105]. In contrast, large NPs (4.3 ± 0.9 nm) were formed on the

Fig. 22. Structure (a), TEM (b) and scanning electron microscopy images (c) of $\text{Cu}_3(\text{btc})_2/\text{TiO}_2$ core-shell structures [104].

external surface of MIL-53, which can be attributed to the relative hydrophobicity of MIL-53. The differences between these two reduced materials are reflected in their catalytic performances, i.e., Pd/MIL-101 showed higher activity in phenol hydrogenation, with a 52 h^{-1} TOF at 0.5 MPa H_2 and 323 K, whereas Pd/MIL-53 gave a TOF of 40 h^{-1} at 0.5 MPa and 333 K.

The use of MOFs as core coatings in core-shell-structured catalysts (Fig. 22(a)) was also used to design a catalyst for CO_2 reduction [104]. TiO_2 nanocrystals were coated onto the MOF $\text{Cu}_3(\text{btc})_2$ with a small shell size of 10–20 nm (Fig. 22(b) and (c)). The $\text{Cu}_3(\text{btc})_2/\text{TiO}_2$ catalyst, with a porous surface, retained the ability of the parent $\text{Cu}_3(\text{btc})_2$ to capture CO_2 and combined it with the photocatalytic ability of bare TiO_2 . Furthermore, the hybrid $\text{Cu}_3(\text{btc})_2/\text{TiO}_2$ catalyst gave a higher photocurrent than bare TiO_2 ; this is attributed to improved separation of photogenerated electron-hole pairs. Pure $\text{Cu}_3(\text{btc})_2$ without a TiO_2 shell was inactive in CO_2 reduction under UV illumination. Bare TiO_2 gave low CO_2 selectivity because it also catalyzed the photoreduction of water. When $\text{Cu}_3(\text{btc})_2/\text{TiO}_2$ was used as the catalyst, the yield of CH_4 was over five times higher than that obtained using bare TiO_2 and no H_2 (produced by water reduction) was detected during hydrogenation. The results for hydrogenation of CO_2 show the importance of the developed $\text{Cu}_3(\text{btc})_2/\text{TiO}_2$ catalysts with hybrid structures.

4. Conclusions and perspective

MOF-based catalysts have emerged as promising catalysts for hydrogenation because of their novel properties. This review mainly introduces the design of MOF-based catalysts and their applications in the hydrogenation of alkenes, alkynes, nitroarenes, CAL, FFA, benzene, and several other compounds. MOF-based catalysts with various active sites and tunable structures have been used to achieve high activities and selectivities in hydrogenation reactions.

However, research on the use of MOF-based catalysts in hydrogenation reactions is still in its infancy. Much effort is needed to improve existing MOF-based catalytic systems to enable their use in practical applications. (1) The relatively low stability of most MOF-based catalysts in moist environments is still a major obstacle to their practical use in catalysis, and limits their use in hydrogenation reactions performed in aqueous solution. Coating with hydrophobic materials such as polydi-

methylsiloxane [109] to optimize the wettability of the core catalyst is an efficient approach; shell materials with appropriate porosities are needed to ensure substrate diffusion. Post-modification of hydrophobic groups on MOF materials is expected to be a supplemental strategy. (2) Research on encapsulating metal NPs into MOF-based catalysts is mainly based on noble metals such as Pt, Pd, Ru, and Au; practical application of these noble-metal-based catalysts in the chemical industry is limited by their diminishing sources and increasingly high costs. Base metals such as Fe and Co are ideal replacements for noble metals because of their low prices, abundant contents in the Earth's crust, and considerable catalytic activity in hydrogenation. More attention should therefore be focused on exploring new approaches to achieving activities comparable to those of noble metals. (3) Adjusting the morphology of the metal NPs in MOF-based catalysts is an efficient way of controlling hydrogenation reactions. In particular, metal NPs with different surface facets are promising for selectively catalyzing different hydrogenation processes, and NPs with hollow nanostructures have shown improved catalytic activities. The latter also offers an approach to decreasing noble metal loading and materials costs in MOF-based catalysts. (4) Enzymes offer significant advances in chemo- and enantio-selectivity in hydrogenation reactions, and their combination with MOF materials could be a potential solution to the shortcomings of enzymes such as difficulty of recovery. Furthermore, MOF-based catalysts containing enzymes as active species have potential for catalyzing reactions in aqueous solution if the water stability of the catalysts can be improved. (5) Scale-up of the production of MOF-based catalysts is a basic requirement for industrial processes. To achieve this goal, methods for large-scale catalyst production need to be developed based on achievements at the laboratory scale.

The results of a large number of previous studies show that the use of MOF-based catalysts in hydrogenation reactions has a promising future, despite the existing challenges. Practical applications of these catalysts will become increasingly promising when sustained research has been performed in this field.

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Graphical Abstract

Chin. J. Catal., 2017, 38: 1108–1126 doi: 10.1016/S1872-2067(17)62852-3

Metal-organic-framework-based catalysts for hydrogenation reactions

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This review summarizes recent progress in metal-organic-framework-based catalysts in various hydrogenation reactions, including hydrogenation of alkenes, alkynes, nitroarenes, cinnamaldehyde, furfural, benzene, and other compounds.

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金属有机骨架基催化剂在加氢反应中的应用

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摘要: 加氢是现代化工产业中的一类主干反应, 广泛应用于精细化学品、药物、食品、染料、功能聚合物及香料等制造产业中。高效催化剂的引入使得加氢反应能够在相对温和的条件下还原各类不饱和化合物。金属催化剂在加氢反应中活性

高,所需的反应温度较低,适用性广,但是容易和S, N, As和P等元素结合而“中毒”失去反应活性. 金属氧化物催化剂和金属硫化物催化剂具有一定的抗毒性,但活性相对较差,通常需要采用高温高压的反应条件,对催化剂本身和反应器的要求较为苛刻. 传统催化剂在反应中具有一定的局限性,所以亟需开发新一代高效的加氢催化剂,在保证高活性和高选择性催化效果的同时,降低对能源的消耗和对环境的负面影响.

金属有机骨架(MOFs)作为一种新型的多孔材料在过去二十年中受到相当大的关注,并在催化、气体存储和分离、传感器、发光材料和药物输送等众多领域的应用中表现出卓越的性能. 利用MOF材料良好的相容性,将MOF和其它功能材料结合形成新的复合材料可以在更大程度上扩大MOF材料的应用领域. 与传统的催化剂相比,MOF基材料具有优异的物理化学特性和结构可调性,通过合理的设计能够满足不同的催化加氢过程: (1) MOF基催化剂具有多样且特异性的活性位点. 除了组成MOF材料的金属离子/簇和功能有机配体之外,MOF材料可通过封装其他活性物质或者被活性物质包裹等方式引入其他类型的催化位点,进一步扩大MOF基催化剂在不同催化加氢中的适应性. 此外,不同的活性位点之间的协同作用又能特异性地促进反应的进行,对提高反应的选择性起到重要的作用. (2) 活性位点的尺寸大小和空间分布可以被有效控制. 这能影响到催化剂在催化反应过程中的活性和选择性,并且通过MOF材料的限域效应,同时能增强活性位点的稳定性和耐久性. (3) 高比表面积能提高MOF基催化剂的催化活性. 这种结构特性不仅可以增加MOF基催化剂的活性位点,而且能够吸附反应物和还原剂达到扩大其局部浓度的效果. (4) 反应分子的扩散可通过调节MOF基催化剂的结构实现控制. 通过调整MOF材料的孔窗口和通道的尺寸,能够改变反应物在催化剂内部的扩散途径,影响底物和活性位点的接触,能进一步影响反应的活性和选择性.

本文总结了近几年来MOF基材料在不同的催化加氢反应中的应用,其中包括烯烃、炔烃、芳硝基化合物、肉桂醛、糠醛和苯等化合物的加氢反应. 首先介绍了MOF基材料中不同类型的活性位点,除了MOF材料自身的金属离子/簇和功能有机配体外,MOF基复合材料中的金属纳米颗粒、金属硫化物、金属氧化物、均相催化剂等活性位点可以通过封装或包裹的方式引入. 在不同加氢反应中,着重介绍了MOF基催化剂中不同类型活性位点的加氢过程中的催化方式、催化剂本身的结构优化及催化剂与反应底物之间的相互作用,以及这些因素之间的协同作用对反应活性和选择性的影响. 最后,讨论了MOF基材料在加氢反应中应用存在的问题以及未来发展展望.

关键词: 金属有机骨架; 加氢; 多相催化; 纳米颗粒; 化学选择性; 协同效应

收稿日期: 2017-03-21. 接受日期: 2017-04-30. 出版日期: 2017-07-05.

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基金来源: 国家自然科学基金(21322606, 21436005, 21576095); 中国博士后科学基金(2016M590771); 广东省自然科学基金(2016A030310413, 2013B090500027, 2014A030310445, 2016A050502004).

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