Application of hierarchically porous metal-organic frameworks in heterogeneous catalysis: A review

Chongxiong Duan^{1,4}, Kuan Liang¹, Jiahui Lin¹, Jingjing Li¹, Libo Li², Le Kang³, Yi Yu^{2*} and Hongxia Xi^{2*}

ABSTRACT Hierarchically porous metal-organic frameworks (H-MOFs) with micro-, meso- and macropores have emerged as a popular class of crystalline porous materials that have attracted extensive interests, and they have been studied in diverse applications, especially in heterogeneous catalysis. The hierarchical structures enable sufficient diffusion and accessibility to the active sites of the molecules and permit the encapsulation of catalytic guest molecules to exploit more possibilities with enhanced catalytic performance. In this review, we have summarized the recent representative developments of H-MOFs in the field of heterogeneous catalysis, which includes oxidation reaction, hydrogenation reaction, and condensation reaction. Emphasis is placed on the multiple functions of hierarchical structures, and the catalytic activity, selectivity, stability, recyclability, etc. of the industrial utility of H-MOFs. Finally, the prospects and challenges of H-MOFs in heterogeneous catalysis and the remaining issues in this field are presented.

Keywords: hierarchically porous metal-organic frameworks, heterogeneous catalysis, industrial practicability

INTRODUCTION

Metal-organic frameworks (MOFs) are a novel class of porous crystalline materials that are self-assembled with metal ions (or clusters) and organic linkers through coordination bonds [1,2]. MOFs possess exciting structures and unique physiochemical features such as ultra-high specific surface area, permanent nanoscale porosity, tunable pore environment, uniformly structured cavities, and abundant active sites [3,4]. As such, MOFs have been commonly utilized in adsorption or separation [5–7], catalysis [8,9], supercapacitors [10–12], and biomedicine [13,14]. Among these applications, heterogeneous catalysis is one of the earliest proven applications, and MOFs as catalysts have cemented an unparalleled status in this field [15]. Despite the decades of rapid development, many reported MOFs are primarily restricted to the microporous structure with pore size below 2 nm [16,17]. This structure limits the diffusion of small molecules and prevents the larger molecules from accessing the catalytic active sites in the channels. Due to this limitation, the use of MOFs in industrial-scale applications is still greatly restricted [18–20].

Hierarchically porous MOFs (H-MOFs) with tunable porosity have emerged as attractive catalysts with high catalytic efficiencies [21–23]. With regards to heterogeneous catalysis, hierarchically porous structures are superior to their conventional microporous counterparts due to the following three aspects: (i) the total porosity of the hierarchically porous material is higher due to the introduced mesoporosity and preserved microporosity, which provides more active sites [24,25]; (ii) the sizes of the pores are big enough to allow the access of large reactant molecules to diffuse into, and a large amount of product molecules can also easily move out of the network [26,27]; (iii) hierarchical environment allows catalytic multifunctional modification by encapsulating metal nanoparticles (MNPs), polyoxometalates (POMs), and macromolecules (e.g., porphyrins). They cannot diffuse outside from the cavities due to their size limiting effects, which therefore can significantly minimize their possibility of leaching or aggregation even in liquid-phase systems [28,29]. It is worth noting that H-MOFs species discussed in this review mainly refer to H-MOFs with inherent hierarchical structures, H-MOFs with introduced meso- or macroporosity and MOFs on hierarchical supports. For all of these groups, the catalytic active centers are mainly on (i) the Lewis acid centers and/or active group on the organic linkers in the pristine framework [30], (ii) the active sites grafted onto metal ions or organic linkers *via* functionalized modification [31], and (iii) additional catalytic guest species in the pore space through pore confinement/encapsulation [32]. Nowadays, catalysts with single active sites can no longer satisfy the challenging catalytic systems in industry settings. Hence, exploring multifunctional active species and their synergistic catalytic effects have become an important research consideration to achieve heterogeneous catalysis associated with H-MOFs [33–36].

In general, the activity, selectivity, and lifetime of catalysts are important metrics to evaluate their performances. These metrics become even more stringent when the catalyst is used in industrial settings. In the past decades, researchers have been dedicated towards the development of highly active catalysts with better sensitivity, while mildly enhancing the reaction systems, shortening periods, and aiming at the maximized output at minimal energy utilization [37–39]. For example, PW₁₁@MIL-101 (PW₁₁ = [PW₁₁O₃₉]^{7–}), when used as a catalyst for the epoxidation of *cis*-cyclooctene, could achieve a superior turnover frequency (TOF) of 1922 h^{–1} [40]. Other reported

¹ School of Materials Science and Hydrogen Engineering, Foshan University, Foshan 528231, China

² School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

³ School of Materials Science and Engineering, Xi'an University of Science and Technology, Xi'an 710054, China

⁴ Guangdong Key Laboratory for Hydrogen Energy Technologies, Foshan University, Foshan 528000, China

* Corresponding authors (emails: ceyuicy526@mail.scut.edu.cn (Yu Y); cehxxi@scut.edu.cn (Xi H))

catalysts also showed high TOF values, e.g., MIL-101@Pt@FeP-CMP (CMP = conjugated micro- and mesoporous polymers) (1516.1 h^{-1}) for cinnamaldehyde hydrogenation [41], or NU-1000 (490 h^{-1}) catalyst for the oxidation of benzyl alcohol [42]. MOF industrialization has started as we witness the commercialization of MOF-based products, TruPick and ION-X from NuMat Technologies [43], and Basolite series produced by BASF [44,45]. However, hierarchically porous structure was not adequately considered, and the efforts focused on what we call holy grail applications such as CO_2 capture, hydrogen storage, and methane storage. In this regard, the employment of H-MOFs in industrial-scale production and application is imminent, and this will require more attention to conceptualize numerous possibilities in this exciting area.

To date, the application of MOFs as heterogeneous catalysts has been covered in several in-depth reviews [2,18,46–48]. However, a comprehensive overview of the research focused on the application of H-MOFs in heterogeneous catalysis remains lacking, and this review aims to fill this missing gap. Even though there are limited reports on the heterogeneous catalysis of H-MOFs, we will give a brief outline of the most representative examples instead of listing them all. We will offer a brief outlook on the oxidation reaction, hydrogenation reaction, and condensation reaction, including oxidation/oxidative dehydrogenation, dehydrogenation, hydrogenation, condensation, esterification, alkylation, coupling, and Knoevenagel condensation. The advantages and disadvantages of some classical H-MOF systems are compared and discussed from the view of industrial practicability. Finally, the prospects of using H-MOF heterogeneous catalysts and some unsolved problems are proposed.

APPLICATION OF H-MOFs IN HETEROGENEOUS CATALYSIS

H-MOFs for catalytic oxidation reactions

Oxidation reactions are very frequently used in the synthesis of fine chemicals [49,50]. Generally, the metal nodes in MOFs play a crucial role in the oxidation process mainly *via* two typical reaction mechanisms: acting as Lewis acid sites and reversible transition between two oxidation states [51]. According to the specific routes for the target product, we introduce the current research progress on H-MOFs in the oxidation field based on oxygenation/oxygenation-dehydrogenation and dehydrogenation reactions. In this section, we will mainly focus on four important substrates, i.e., alkanes, alkenes, alcohols, and sulfonyl-based compounds.

Oxygenation/oxygenation-dehydrogenation reactions

(1) Oxidation of alkanes

C–H activation is an attractive and crucial chemical process since it allows the full utilization of multifarious low-cost hydrocarbons, e.g., methane, ethane, propane, hexane, or cyclohexane, to produce useful organic chemicals. It can also be used to probably shorten the multi-step synthetic pathways that are widely used [52]. However, catalytic activation of stable C–H bonds is typically the most energetically demanding step in the reaction process. Simons *et al.* [53] used cluster-based density functional theory (DFT) calculations to show the variations in the energy barriers ($56.9\text{--}9.3 \text{ kcal mol}^{-1}$) for C–H activation of propane on two-atom Co–M oxide clusters supported on NU-

1000(Zr) matrix based on the identity of the dopant. When dopant was involved, the spin density and positive charge on the oxygen atoms bridging Co–M increased, which gave lower enthalpic barriers to C–H scission.

In addition, Cr- and Fe-MIL-101 have been proven to be the actual heterogeneous catalysts with superior catalytic activity and selectivity during the oxidation of cyclohexane with O_2 and/or *tert*-butyl hydroperoxide (TBHP) under mild solvent-free conditions [54]. However, the low conversion (36% for Cr-MOF and 38% for Fe-MOF) remains to be an issue. MIL-101 offers tremendous possibilities for catalyst engineering due to its outstanding properties, such as the inherent mesoporous channels (ca. 30 to 34 Å) that can ensure adequate diffusion of molecules and dispersion of nanoparticles (NPs) [55,56]. In a report [37], a highly heterogeneous catalyst system was developed by depositing Au/Pd bimetallic nanoparticles on MIL-101 to achieve liquid-phase aerobic oxidation of various saturated hydrocarbons without adding any promoters. Based on their results, the synergistic effects between Au/Pd and H-MOF conferred remarkable selectivity and good stability against metal agglomeration and leaching. However, when >80% selectivity to cyclohexanone was achieved in the absence of solvent, the cyclohexane conversion could not exceed 30%. Therefore, the attainment of high selectivity at elevated conversion for H-MOF catalysts remains to be a significant challenge.

(2) Oxidation of alkenes

The oxidation of alkenes has a wide range of industrial applications to produce feedstocks for high value-added products [57]. This section covers the epoxidation of cycloolefins and allylic oxidations of alkene substrates, which are carried out in the presence of an oxidant such as O_2 , H_2O_2 , TBHP, or peracids. Metal complexes with Schiff bases are well-known oxidation catalysts [58]. However, their main drawback lies in their subsequent recycling and product separation. It was reported that Co(II)-based complexes were anchored to Cr-MIL-101- NH_2 *via* strong coordination interaction by tightly bonding the Schiff base moiety groups. This was achieved by the condensation process of salicylaldehyde, pyridine-2-aldehyde, or pyridine-3-aldehyde with the amino group of Cr-MIL-101- NH_2 [59]. The high dispersion of Co(II) species promoted the adequate contact between the substrates and active sites, which could afford good applicability towards various olefins, such as cyclic olefins, tri-substituted olefins, aliphatic olefins, or aromatic olefins. Nevertheless, catalytic systems required aldehydes as sacrificial co-reductants to accelerate the oxygen transfer process. For instance, with isobutyraldehyde as a co-catalyst under air atmosphere, the final product achieved 99% conversion and 99% selectivity during the oxidation of *cis*-cyclooctene.

The concept of uniform immobilization of MNPs on H-MOFs is always very attractive in the heterogeneous catalysis field. However, there remains a significant technical challenge due to the aggregation of MNPs arising from the high cohesive energy and low melting points [60]. To address this issue, Zhang *et al.* [61] proposed a strategy to *in situ* synthesize sub-nanometer metal particle/H-MOF composite in the emulsion. In the reaction system, water droplets acted as both a solvent of metal precursors and a template for the mesoporous structures of MOFs. The metal precursors were then *in situ* reduced on the MOFs *via* the assistance of surfactant sorbitol-alkylamine (SAAS- C_{12}). Hence, based on such a strategy, MNPs could be uniformly immobilized on the hierarchical pores of H-MOFs.

Among the various prepared MNP-H-MOF materials, Au/Zn-MOF and Au/Cu-MOF exhibited outstanding catalytic performances for the selective aerobic oxidation of cyclohexene to 2-cyclohexen-1-one without an initiator. Unsurprisingly, the catalyst with smaller MNPs (0.8 nm) was able to exhibit higher catalytic activity than its counterparts.

Developing new catalytic systems through forward-thinking approaches has shown to be another viable strategy to convert POMs into H-MOFs [62]. Explorations were made into the viability of adding monovacant phosphotungstate PW_{11} or silicotungstate SiW_{11} to the MIL-101(Cr) cavities [40]. The structures of H-MOF and POM remained well preserved and the novel composites were shown to be active, robust, and selective heterogeneous catalysts. During the epoxidation of *cis*-cyclooctene into 1,2-epoxycyclooctane, PW_{11} @MIL-101 catalyst exhibited a complete conversion and 98% yield after the first 10 min of reaction with a high TOF of 1922 h^{-1} . However, one significant limitation of employing MOFs in related reactions with hydrocarbons is that the hydrocarbon is hydrophobic while the surface and pore channels of certain MOFs are hydrophilic. This difference results in the difficulty of hydrophobic substrate aggregation, which greatly hindered their practical application for heterogeneous catalysis. By coating NH_2 -MIL-101(Fe) with hydrophobic NTU-COF, this modification could alter the hydrophilic-hydrophobic property. Consequently, the composite exhibited a significantly enhanced catalytic conversion (32%) and selectivity (84%) during styrene oxidation, which were superior to those of the core materials (24% and 26%), respectively [63]. This improvement in the performance was mainly ascribed to NH_2 -MIL-101(Fe) that provided coordinative unsaturated catalytic sites and hierarchical environments to facilitate the diffusion of molecules. Also, the NTU-COF shell gathered the hydrophobic substrates to promote the radical mechanism for the oxidation process (as demonstrated by the free radical quenching experiment). Based on the previous reports, the formation of the target product, i.e., benzaldehyde, can be realized through two distinct routes. As shown in Fig. 1, the by-product, i.e., styrene oxide, was produced only *via* path B, and COF shell paired with MOF core promoted free radical mechanism mainly *via* path A.

(3) Oxidation of alcohols

Selective oxidation of alcohols to aldehydes or ketones is a critical transition in organic chemistry, but the use of H-MOFs for such reactions remained to be rarely reported. In this regard,

developing a suitable catalyst to catalyze the oxidation of alcohols is a long-term research objective. To target a specific mesoporous structure design in H-MOFs, Peng *et al.* [30] took advantage of the unique property of compressed CO_2 (that it can be dissolved in organic solvents to form CO_2 -expanded liquid (CXL)) and used CO_2 -expanded dimethyl formamide (DMF) as a switchable solvent to introduce large mesopores (13–23 nm) into $\text{Cu}_3(\text{BTC})_2$ crystals. This strategy can be performed under an ambient temperature within 3 h due to the enhanced mass transport rates that arise from the viscosity-lowering effect of CO_2 . Such a strategy is considered to be more efficient and less time-consuming when compared with the traditional method that requires high temperatures (70–180°C) and long preparation duration (>10 h). The resultant mesocellular MOFs were shown to be effective and reusable catalysts for the aerobic oxidation of benzylic alcohols under mild conditions (75°C and O_2 atmosphere). A co-catalyst (TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxyl) was needed to achieve >99% selectivity during the oxidation of benzyl alcohol to benzaldehyde. Notably, $\text{Cu}_3(\text{BTC})_2$ synthesized at higher pressure (6.6 MPa) could achieve a complete conversion within a shorter duration (3 h). Compared with the previous studies that employed microporous $\text{Cu}_3(\text{BTC})_2$ to catalyze benzyl alcohol [64,65], the higher efficiency recorded in their study greatly stimulated the industrial application associated with H-MOF-based catalysts.

MOFs possess an important characteristic of enabling isostructural MOF based on metallic nodes. This feature comes from the custom reticular chemistry [66]. This concept involved the pre-synthesis of several isomeric mesoporous MOFs, M-NU-1200 ($M = \text{Zr}, \text{Hf}, \text{Ce}, \text{Th}$), and their subsequent utilization as supports for vanadium catalysts *via* a collaborative action between the single ion vanadium and the oxo group in MOFs [67]. The results showed that the catalytic performance, i.e., TOF, was correlated to the electronegativity and oxidation state of the metallic supports when using the aerobic oxidation of 4-methoxybenzyl alcohol as a model reaction. For example, the TOF of V-Zr-NU-1200 was 20 times higher than that of the V-Ce-NU-1200. Based on the controlled reaction with V-Zr-NU-1200 in the presence or absence of an organic base, alkali-free and alkali-assisted mechanisms are proposed and shown in Fig. 2. $\text{V}=\text{O}$ is the active site for the base-free process (Fig. 2a), while the active site is $\text{V}-\text{OH}$ when base is involved (Fig. 2b). It is noteworthy that both mechanisms indicate that metal nodes with strong electron retraction drive the vanadium catalyst to

Figure 1 Proposed mechanism of (a) path A and (b) path B for styrene transformed to benzaldehyde. Reprinted with permission from Ref. [63]. Copyright 2019, Wiley-VCH.

Figure 2 Proposed (a) base-free and (b) base-assisted mechanism of V-M-NU-1200 for catalyzing the oxidation of 4-methoxybenzyl alcohol. Reprinted with permission from Ref. [67]. Copyright 2019, American Chemical Society.

start the reaction easily, and therefore achieving a higher initial rate. Therefore, their study can offer a feasible way to design isostructural H-MOFs with controlled catalytic performance.

(4) Oxidation of sulfides

Oxidizing sulfides is the most direct method to synthesize sulfoxide/sulfone. This is particularly important since sulfoxides and sulfones are vital chemicals that have been used in industrial and pharmacological applications. Oxidative desulfurization (ODS) is a beneficial method because it requires mild condition which is easy to operate. In addition, ODS is highly effective at the removal of sulfur-containing compounds, which makes it attractive due to the increasing demand for eco-friendly low-sulfur fuel products [68,69]. For example, Li *et al.* [70] reported a series of modified-POM($\text{H}_2\text{PMo}_6\text{W}_6\text{O}_{40}$)@MOF-199@MCM-41 composite catalytic materials that could achieve highly efficient ODS of dibenzothiophene (DBT) in recent years. The attractive catalytic performance exhibited by POM in ODS processes has gradually garnered worldwide attention, and the attempt to incorporate POM in porous MOF can give rise to a novel strategy to pursue enhanced properties. The structural characteristic was confined to MOF-199 capturing modified POM, which was the whole encapsulated by mesoporous MCM-41 to ensure the fixed solid effects. Consequently, it led to an improved deep ODS process. In one report [71], the catalytic performance of M-POM@MOF-199@MCM-41 (Metal-PMM, M = Cr, Mn, Fe, Co, Ni, Cu, Zn, and Cd) was evaluated in the DBT removal of model oil. It was shown that metal ions showed the key factors in affecting the catalytic activity due to their electronic configurations. The maximal DBT removal capacity (99.1%, 180 min, 80°C) was achieved after modifying the material with Co. The mechanism of ODS catalyzed by Co-PMM in O_2 atmosphere was proposed and shown in Fig. 3: $\text{M}(\text{O})_n^-$ (M = Mo or W) in Co-PMM reacts with oxygen molecules to yield active species $\text{M}(\text{O}_2)_n^-$, followed by the combination with DBT molecules to produce sulfoxide; then sulfone can be obtained soon after the oxidation of sulfoxide, and the catalytic cycle is completed after the regeneration of oxygen molecule. In another report [72], Cs-PMM stood out and

Figure 3 Possible mechanism of Co-PMM for the oxidation of DBT. Reprinted with permission from Ref. [71]. Copyright 2017, Elsevier.

realized 99.6% DBT conversion under the same conditions and it could be cycled for 10 times without significant loss in its catalytic activity. Furthermore, considering the unique structure of amphiphilic quaternary ammonium micelles of POMs with a surfactant surface and a POM core, its large lipophilic hydrocarbon part facilitated the hydrophobic distribution of the catalyst in oil to reduce mass transfer resistance and increase the reaction rate. In this context, SRL-PMM (SRL, a kind of surfactant) was successfully fabricated and it was testified as an outstanding catalyst that achieved complete conversion of DBT in 150 min at 60°C [73]. It is worth noting that the reaction duration to reach 100% conversion was further shortened to 90 min by modifying POMs with cyclic N type of quaternary ammonium salt ionic liquid [74]. With the deepening concept of cost reduction and efficient output, the operating conditions needed for desulfurization were well optimized to meet the requirements of practical industrial applications.

In particular, to overcome certain issues of pore-blocking and complex diffusion of substrates arising from the involvement of POM, Farha's group [75] directly used a hierarchical Zr-MOF (NU-1000) with micro- and mesopores as the support for POMs. The as-synthesized Zr-MOF (NU-1000) possessed small triangular channels (12 Å) that permitted the incorporation of specified POMs (10 Å), while the larger hexagonal channels (31 Å) provided an auxiliary pathway for substrate diffusion. When $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was employed as an archetypal POM, the nodes of NU-1000 could behave as its counterion to prevent POM from leaching once the nodes were protonated. The composite was examined as a catalyst during the oxidation of 2-chloroethyl ethyl sulfide (CEES) and it was able to demonstrate complete conversion within 20 min with H_2O_2 as the oxidant. However, owing to the accessibility of the nodes in H-MOF, this catalytic system was not selective towards CEES oxidation. To address this issue, other metal oxide-based catalysts were used and light-activated processes were required [76,77]. Recently, Farha's group [78] encapsulated another POM, i.e., $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, in the mesoporous channels of NU-1000 via a simple impregnation strategy. Interestingly, upon heating at 80°C without bulk solvent, POMs migrated to the microporous channels. However, when using cyclohexane as a solvent, such transformation could be inhibited. The composite exhibited higher conversion and selectivity without using light and a sacrificial reductant when compared to POM alone. Importantly, the composite could be recycled while POM showed no activity after reactions. However, the selectivity of the products (CEESO, 2-chloroethyl ethyl sulfoxide and CEESO₂, 1-chloro-2-(ethylsulfonyl)ethane) was not mentioned.

In general, researchers have made significant progress in the development of H-MOF catalysts for oxygenation/oxygenation-dehydrogenation reactions; however, there is still a long way to go before its industrialization. We believe that the main reason is that the stability of H-MOFs is still not as good as some widely used industrial catalysts such as molecular sieves and metal oxides. In terms of the oxygenation reaction, oxidants are essential, whereby organic oxidants are the most commonly used. However, they are toxic, polluting, and difficult to recycle. As such, H_2O_2 and O_2 are advocated. In addition, the avoidance or reduction of a co-catalyst or sacrificial agent is also a major effort in promoting the commercialization of H-MOFs.

Dehydrogenation reaction

Oxidant-free catalytic dehydrogenation of compounds is a green and atom-economical process to protect the catalysts and avoid hazards in a complex industrial environment [79]. H-MOFs used in catalytic dehydrogenation currently target the production of organics, such as ketones from dehydrogenated alcohols or olefins from dehydrogenated light alkanes and hydrogen production.

(1) Ketones from dehydrogenated alcohols

Ortuño *et al.* [80] used DFT to computationally evaluate the first-row transition metals (Fe, Co, Ni, Cu, Zn) deposited on NU-1000 with Zr- and Hf-based nodes as catalysts for acceptorless cyclohexanol dehydrogenation. Taking Fe^{II} -NU-1000 as an example, the proposed catalytic mechanism included three main steps: (i) proton transfer, (ii) β -hydride elimination, and (iii) H-H bond formation. The specific process and the change in free energy are shown in Fig. 4. Based on the computational screening of the examined metals, Ni- and Co-derivatives were

Figure 4 Proposed mechanism for Fe^{II} -NU-1000-catalyzed dehydrogenation of cyclohexanol to cyclohexanone (ΔG_s in kcal mol⁻¹). Reprinted with permission from Ref. [80]. Copyright 2016, American Chemical Society.

predicted as the potential catalysts due to their excellent catalytic activities being about 2000 times more active than the Fe-based catalysts at 298 K. This study provided an essential theoretical reference for H-MOFs, especially with Co or Ni species, in the practical experiments towards dehydrogenation reactions.

In addition, Tilgner *et al.* [81] reported a Pd/TiO₂@MIL-101 composite. Ti species were distributed into the layer structure of MIL-101 using metal organic chemistry vapor deposition (MOCVD) and then it was thermally decomposed to TiO₂ in the presence of a water atmosphere by loading with Pd NPs. By combining the catalytic performance of MIL-101 with TiO₂ and Pd NPs, there was an increased amount of active sites for C-H bond activation during the acceptorless dehydrogenation of high conversion aromatic alcohols. Based on their result, the composite catalyst was able to exhibit high conversions of over 90%, which were much higher than those reported for Pd@MIL-101 and other commercial palladium catalysts. It is worth mentioning that the reactions were performed below 100°C, which is rare and has often been observed for homogenous catalysts [83]. In addition, Huang *et al.* [83] adopted a Pluronic F-127 supramolecular template, whereby mesopores were incorporated into the microporous MOFs (MIL-53(Al)) and highly dispersed bimetallic NPs (PtPd) were immobilized in the mesoporous structure. Based on the results, the catalytic activities of the oxidant-free dehydrogenation alcohol series were enhanced, which was partially attributed to the synergistic effect of the bimetallic NPs. The sizes of the alcohols were examined (from 2-pentanol to 2-octanol, and cyclohexanol, cyclooctanol), and the corresponding ketones were found to be smaller than the mesopores of the catalyst, which thus led to free diffusion and moderate yields (46.3%–63.7%).

(2) Olefins from dehydrogenated light alkanes

Selective dehydrogenation of light alkanes (e.g., ethane and propane) is a thermodynamically unfavorable process which needs a significant amount of energy [84]. In this regard, H-MOFs should have extraordinary stability and excellent performance. Li *et al.* [38] reported the anchoring of Co(II) ions onto NU-1000(Zr) material via two routes, i.e., solvothermal deposition in MOF (SIM) and atomic layer deposition in MOF

(AIM), which were later denoted as Co-SIM+NU-1000 and Co-AIM+NU-1000, respectively. After being activated in O₂ flow at 230°C for 4 h, both materials could catalyze the oxidative dehydrogenation of propane to propene at experimental temperature as low as ~200°C. Such an experimental temperature was much lower when compared with the commonly used 300–500°C for ODH catalyzed by VO_x catalysts [85]. Using lower temperatures can help to propel the reduction of propane dehydrogenation, which minimizes coke deposition and increases the lifetime of the catalyst. However, the catalytic activity and selectivity of these two catalysts for propane dehydrogenation were different under the same reaction conditions, which was ascribed to the different Co species formed during the activation process (as observed from the *in situ* X-ray absorption spectroscopy). In particular, the authors proposed the ODH mechanism (Fig. 5) based on computational modeling with a reasonable catalytic cycle that matched well with the experimental observation, and this process could further facilitate the design of high-performing catalysts.

(3) Hydrogen production

Even though tremendous achievements in enhancing the catalytic oxidation reactions by H-MOFs have been achieved, the development of relatively low-cost heterogeneous catalysts with high hydrogen production activity remains to be a significant challenge [86]. As mentioned above, catalysts with considerable activity and selectivity can be realized by depositing NPs (Ag or Pd) into the hierarchical channels without triggering aggregation. Formic acid (FA) and ammonia borane (AB) are commonly used as potential H₂ generation materials based on the reactions: HCO₂H → CO₂ + H₂ and NH₃BH₃ → NH₂=BH₂ + H₂, respectively [87,88]. Ke *et al.* [89] proposed a three-step FA decomposition process based on AgPd@MIL-100(Fe) core-shell catalyst: (i) porous MIL-100 shells provided high concentrations of FA, especially near AgPd core, followed by the dissociation of O–H bonds of FA and metal formate species with a generated H⁺ ion; (ii) metal formate species underwent β-hydride elim-

ination to produce CO₂ and metal hydrides; (iii) metal hydrides reacted with H⁺ ions to release H₂. The synergistic effect between Ag and Pd in the catalyst could enhance the catalytic performance (~180 mL H₂, 10 mL FA⁻¹) when compared with the monometallic catalysts. Furthermore, the lifetime of the catalyst was extended due to the inhibited adsorption of CO by-product on Pd, and the pro-longed catalyst lifetime is essential for its practical application. In the report by Yamashita's group [90], they attributed the incorporated amine functional group (instead of NPs) as the most important factor behind the high catalytic activity of Pd-NH₂-MIL-125. This was because amine could prevent the aggregation of MNPs, and scavenged proton to form ⁺HNH₂, which later could react with Pd hydride species to generate hydrogen molecules.

In general, when compared with the traditional dehydrogenation catalysts, H-MOFs exhibited certain merits: (i) as a solid catalyst, H-MOFs can address the issues of high cost and environmental pollution caused by the use of homogeneous bases in industry setting; (ii) composite catalysts can effectively maintain the heterogeneous phase in homogeneous environment and improve their reusability; (iii) H-MOFs as precursors can generate more fascinating meso-MOFs for targeted catalysis. Stability remains to be an unavoidable topic. For example, propane dehydrogenation process is executed under the conditions of 0.05–3.0 MPa and 500–650°C in industry setting.

H-MOFs for the catalytic hydrogenation reactions

In general, hydrogenation reaction is a reversible process with a negative chemical reaction heat and a reduction in the number of molecules. Hence, according to Le Chatelier's principle, relatively low temperature and high pressure are favorable factors to shift the equilibrium to hydrogenation so as to ensure the enhanced conversion of specific substrates [91]. However, higher temperature facilitates the reaction rate. The optimal temperature in practical operation relies on the activity of the catalyst. In addition, the excess hydrogen can accelerate the reaction rate

Figure 5 The computed ODH mechanism using activated A-1 (formed by losing a ligand and releasing water in Co-SIM+NU-1000). Reprinted with permission from Ref. [38]. Copyright 2017, American Chemical Society.

and improve the conversion rate and contribute to the heat removal during the process. Notably, the surplus hydrogen can be recycled, which conforms to the economic principle in the industry.

H-MOF@MNPs is a popular material used to catalyze hydrogenation reactions [61]. For example, Park *et al.* [92] described the formation of Ni NPs in MesMOF-1 with two meso-cages (3.9 and 4.7 nm in diameter). Nickelocene-containing MesMOF-1 was obtained by immobilizing nickelocene onto the evacuated MesMOF-1 *via* sublimation at 85°C for 1–3 h. Subsequently, the sample was treated with H₂ and washed with methanol, leaving the Ni particles inside the pores of MesMOF-1. Ni@MesMOF-1 was tested for its catalytic activities during the reduction of nitrobenzene or styrene. The results showed that the conversion of styrene to ethylbenzene was completed within 4 h under H₂ in methanol at room temperature. The conversion of nitrobenzene to aniline was undetectable under the same experimental conditions. However, when changing the hydrogen source into NaBH₄, such conversion was completed within 15 min. It is worth noting that the enhanced reaction rate was mainly attributed to the Ni particles, but not the solid reducing agent.

Hydrogenation of nitroaromatic hydrocarbons is a direct way to prepare the corresponding anilines and dicyclohexylamines. Chen *et al.* [93] incorporated Pd NPs into the pores of MIL-101 and used it as a bifunctional catalyst for the solvent-driven selective hydrogenation process. A near-thorough selectivity to aniline was recorded in a strongly polar solvent (DMF), and a remarkable selectivity of 99.1% to dicyclohexylamine occurred in a non-polar solvent (*n*-hexane). The polarity of the solvent was the key to the successful hydrogenation, which acted as a regulating factor for the link between reactants/intermediates and Pd/MIL-101. A plausible reaction mechanism can be observed in Fig. 6. Pd NPs have been previously proven to be able to stimulate certain hydrogenation processes. Meanwhile, the unsaturated metal sites in MIL-101 can serve as Lewis acid sites to provide active imines and quench released ammonia, which

Figure 6 Proposed routes for the hydrogenation of nitrobenzene in polar or non-polar solvent over Pd/MIL-101. Reprinted with permission from Ref. [93]. Copyright 2018, American Chemical Society.

promote the cross-coupling process and further hydrogenate the generated phenylcyclohexyl-amine to achieve a high-yield production of dicyclohexylamine.

In addition, Zhao *et al.* [94] synthesized H-MOF composites by sandwiching Pt NPs between a core and a shell composed of MIL-101(Fe), MIL-101(Cr), or both for the efficient hydrogenation reaction of pentadiene or aldehydes. The sandwich structure could incorporate Pt NPs well, therefore, leading to the improvement of the catalytic performance when recycled. Compared with Pt NPs, both MIL-101@Pt and MIL-101@Pt@MIL-101 exhibited a remarkable enhancement in the selective hydrogenation for cinnamaldehyde, which was attributed to the Lewis acid sites in MIL-101 crystals that activated the C=O bonds. Nevertheless, the enhanced selectivity was accompanied by a sharp decrease in TOF values. For example, 16.9 h⁻¹ was recorded for MIL-101(Cr)@Pt/MIL-101(Fe)^{2,9} which is lower than 372.4 h⁻¹ for Pt NPs. Such a result was attributed to the limitation of reactant and product diffusion in MIL-101 shells. However, the conversion of cinnamaldehyde could achieve up to 99.8% in 20 h. Theoretical calculations and reaction processes are shown in Fig. 7. Moreover, the sandwich-like design could be realized in another mesoporous material, i.e., MOF-525(Zr)@Pt/MOF-525(Zr), with high selectivity towards furfural (85.0%). The considerable potential of H-MOFs in its structure and high catalytic activity was confirmed, and later, Yuan *et al.* [41] made some further innovations to the structural design. Considering that practically, the cinnamaldehyde substrate was hydrophobic, while the surface and channels of MIL-101 were hydrophilic. They then adopted a conjugated micro- and mesoporous polymer (CPM) with iron(III) porphyrin (FeP-CMPs) as a shell to construct a sandwich-like MIL-101@Pt@FeP-CMP^{sponge} composite *via* liquid epitaxial growth. The hydrophobic surface facilitated the enrichment of the hydrophobic matrix around the catalytic site during the transition of cinnamaldehyde hydrogenation to cinnamyl alcohol [95], thereby improving the conversion (97.6%). In contrast, the iron sites on the shell can be active C=O bonds to regulate selectivity (97.3%). It is worth mentioning that the catalyst could achieve a state-of-the-art TOF value of 1516.1 h⁻¹, which provided sig-

Figure 7 Mechanism of cinnamaldehyde hydrogenation by MIL-101@Pt. A: cinnamaldehyde; B: cinnamyl alcohol; C: hydrocinnamaldehyde. Brown: C, pink: H, red: O, gold: Fe, blue: Cr, green: Cl. Reprinted with permission from Ref. [96]. Copyright 2016, Nature Publications.

nificant reference values for the development of hetero-architectures in the field of efficient heterogeneous catalysis.

Recently, Wang *et al.* [96] proposed a novel and facile modulator-induced approach to synthesize transitional H-MOFs, which was an intermediate state of MOFs that gradually transitioned to a metal-based compound by removing the partial linkers. Mesoporous Pt/ST-UiO-66 and Pt/FT-UiO-66 were obtained when *m*-phenylenediamine (MPDA) and *p*-phenylenediamine (PPDA) were used as the modulators, respectively. Interestingly, Pt/ST-UiO-66 possessed the highest conversion of 96.43% in liquid-phase hydrogenation of *n*-hexene, which was attributed to its larger pore size and higher ratio of mesopore volume to micropore volume. Overall, selective hydrogenation catalysts are mainly divided into noble-metal catalysts (Pd, Pt series) and non-noble-metal catalysts (Cu, Ni series). Most studies on H-MOF hydrogenation catalysts are focused on loading these metal species on H-MOF supports [97], and they have shown satisfactory catalytic performance. From MNPs to MNPs@H-MOFs and even monoatomic metal@H-MOFs, every improvement is accompanied by an enhancement in catalytic properties. Notably, the catalytic performance will be greatly improved if the morphology regulation at nanometer scale and the controllable preparation of metal catalysts at the atomic scale can be realized.

H-MOFs for the catalytic condensation reaction

CO₂ cycloaddition reaction

Cycloaddition of CO₂ to epoxides is considered to be one of the most common and promising approaches in carbon capture and sequestration (CCS) technology [98]. For H-MOF, the mesopores provide a space to ensure the sufficient diffusion of molecules, while the vacant or partially coordinated metal ions are distributed at Lewis acid sites to activate the epoxides. The organic ligands can be then functionalized with Lewis basic sites to achieve enhanced catalytic activities [99,100]. Currently, only a small amount of pure H-MOFs without additional modification with functional groups or species have been reported to demonstrate impressive CO₂ fixation efficiency. For example, Peng *et al.* [101] proposed the fabrication of hollow and mesoporous Zn-BTC (BTC = 1,3,5-benzenetricarboxylic) *via* a CO₂ ionic liquid (IL) interfacial templating route for the first time. With *n*-Bu₄NBr as the promoter, the material catalyzed CO₂ cycloaddition with a high yield of 97.4% at 80°C.

Most reaction systems require multi-functionalization to fabricate highly efficient and pure H-MOFs, which are not mainstream for CO₂ cycloaddition. Inversely, the co-existence of metal nodes and basic functional groups is popular and promising in cycloaddition. For example, Babu *et al.* [102] constructed micro-mesoporous amine-functionalized MOFs (UMCM-1-NH₂) using mixed ligands ((2-aminoterephthalic acid (NH₂-BDC) and 1,3,5-tris(4-carboxyphenyl)benzene (BTB)). The as-synthesized micro-mesoporous UMCM-1-NH₂ was used as a catalyst in the cycloaddition of CO₂. Its outstanding performance for propylene oxide (90% conversion and TOF of 141 h⁻¹) can be attributed to appropriate acidity/basicity and the hierarchical architecture. Similarly, in a later report, the hierarchically porous MIL-88-NH₂(Fe) showed a higher conversion when used in reactions with similar substrates [103]. For example, the mechanism by which amine-functionalized H-MOFs functioned during the cycloaddition of epoxide with co-catalyst tetrabutylammonium bromide (TBAB) was proposed:

epoxide is activated *via* the interaction between its O atom and metal Lewis acid sites. Subsequently, Br⁻ ion on TBAB attacks the least hindered C atom of the epoxide, which results in the negative charge of its O atom and ring-opening. Concomitantly, the amine groups of the catalyst polarize CO₂, and then its O atom attacks β-carbon of the ring-opened epoxide to form an intermediate with the elimination of Br⁻. Finally, the ring closure takes place to form the product, and the regenerated catalyst moves to the next cycloaddition cycle. The Lewis acid site is not limited to the inherent metal nodes, but can also be constructed by modification processes. Chang *et al.* [104] proposed a facile strategy to introduce hierarchical channels into MOFs *via* a competitive coordination method using Cu(BF₄)₂, where Cu acted as both etching agent and additional active sites. Combining the bifunctional active site of Lewis acid sites and bipyridine N basic sites as well as the hierarchical structure, the catalyst exhibited a strong affinity to CO₂ and faster catalytic efficiency than that of the corresponding microporous material.

In addition, incorporating imidazolium-based ionic ligands into the porous structure could catalyze the fixation of CO₂ into cyclic carbonates with self-supported nucleophilic halogen ions [105]. Liang *et al.* [106] designed a mesoporous cationic MOF (FJI-C10) that contained imidazolium moieties, Lewis acidic Cr³⁺ sites, and free halogens. During the chemical fixation of CO₂ into cyclic carbonates, epoxide was adsorbed by Cr³⁺. Its ring-opening step was driven by the activation effect of Cr³⁺ sites and the nucleophilic attack by a halogen ion on the less hindered side of the epoxide. Subsequently, an acyclic carbonate formed *via* the nucleophilic attack of alcoholate on CO₂, and it was later converted to a cyclic carbonate through intramolecular cyclization (Fig. 8). Based on the optimization of the experimental factors, the reported catalyst could achieve a high yield of 87% and a remarkable TOF of 494 h⁻¹ for chloropropene carbonate at 60°C and 1 atm. Recently, another H-MOF with Mn²⁺ Lewis acid sites was functionalized with an imidazolium bromide (ImBr) ionic liquid, and the resultant ImBr-MOF-545(Mn) was used in a catalytic one-pot cascade epoxidation-cycloaddition reaction of styrene to styrene carbonate. During the process, the catalyst exhibited a high conversion of 99.1% and selectivity of 94.8% at 60°C, without adding any co-catalysts. In particular, the catalyst demonstrated sufficient reusability of up to five runs without

Figure 8 Mechanism of FJI-C10 for catalyzing cycloaddition reaction of CO₂ with epoxides (the hashed bonds represent weak coordination interactions). Reprinted with permission from Ref. [106]. Copyright 2018, Royal Society of Chemistry.

any significant loss in its catalytic activity [99].

There have been many excellent studies on CO₂ cycloaddition, and this process has been achieved at ambient temperature and pressure with high conversion (>90%) [107]. We think that the selective tandem transformation of olefins and CO₂ into cyclic carbonates can be adopted to optimize the process so as to provide a safe, economic, and energy-efficient pathway by reducing the need of synthesizing toxic epoxides externally [108,109]. Moreover, avoiding the use of co-catalysts is also a significant improvement.

Esterification reaction

Esterification reaction combines two substrates to form an ester, and a typical example is the esterification of alcohol and acid (carboxylic acid, oxygen-containing organic acid, or anhydrides) [110]. According to the report by Yaghi and other excellent studies [111–114], acid-modified H-MOF catalysts used in esterification can be mainly divided into three categories. (i) Encapsulating catalyst species within the inner pores of MOFs, such as directly embedding 12-tungstophosphoric heteropolyacid (HPW) in the mesoporous cages of MIL-101 [112]. (ii) Fixing catalytic functional groups onto open metal sites. For example, stabilizing an HPW with amino groups of ethylenediamine (ED) grafted on the unsaturated metal sites of MIL-101 [113]. (iii) Modifying functional groups on the organic linkers, such as sulfonic acid-functionalized MOFs [114].

Zang *et al.* [117] prepared a sulfonic acid-functionalized MIL-101 crystalline material using one-pot synthesis, and used it for the catalytic liquid-phase esterification of monocarboxylic acids with monohydric alcohols. Based on their experimental results, the resultant catalyst showed an excellent yield of 99.5% for acetic acid with *n*-butanol and 95.2% for oleic acid with *n*-hexanol, and it demonstrated good reusability. Recently, Alavi-jeh *et al.* [116] provided a modification strategy to develop dual-functionalized mesoporous H-MOFs, [Cr₃O(BDC-SO₃H)_{2.4}-(BDC-SO₃NH₃Bu)_{0.6}]_n using sulfonic acid-functionalized MIL-101 (MIL-101(Cr)-SO₃H) and butyl amine (BuNH₂). The esterification of phthalic anhydride with hydrophilic and acidic alcohols was catalyzed by the product obtained from the acidic hydrophobic groups, and investigations were conducted on various parameters such as catalyst amount, alcohol types, reactant molar ratio, solid acid hydrophobicity, synthetic time, and reaction temperature. According to their results, the multifunctional catalyst exhibited a higher yield (97%) than other previously reported catalysts [117], without any significant loss in catalytic activity after being recovered and reused for several consecutive reactions. Notably, excellent conversion was achieved rapidly with a small amount of catalyst, which translated to more economically beneficial catalysis.

Another route to synthesize esters is to directly combine organic carboxylic acids with olefins, and it is regarded as one of the most economically and environmentally friendly strategies for esterification reaction [118]. Amino groups were used to anchor HPW on MIL-101 *via* the charge effect to form HPW/EDG-MIL-101 catalyst for olefin esterification [113]. The results showed that with 40 wt% HPW loading, HPW/EDG-MIL-101 featured the highest sec-butyl acetate (SBAC) yield of 30.67 wt% (8 h) when compared with the catalyst synthesized by direct encapsulation of HPW in the mesopores of MIL-101. The superior activity and stability of the catalyst were attributed to the enhanced dispersion and stability that arose from the strong

Figure 9 Mechanism for HPW/Uio-66-NH₂ to catalyze the esterification of 1-butene with acetic acid. Reprinted with permission from Ref. [119]. Copyright 2019, American Chemical Society.

interaction between HPW and ED. Similar functional design and application were achieved in another robust MOF, i.e., UiO-66 crystal [119]. As shown in Fig. 9, the number of amino groups was controlled by the mole ratio of terephthalic acid to 2-amino terephthalic acid, while the acidity of the catalysts was adjusted by changing the amount of HPW loaded. More importantly, SBAC yield on the product with 40 wt% HPW reached 39.4%, which exhibited no obvious change even after three cycles. Although a certain gap exists between the laboratory data and industrial level [120], they avoided the corrosion of equipment caused by catalysts with strong acidity, which will lead to more eco-friendly SBAC catalysts with high performance.

Moreover, few pure H-MOFs have been tested as promising catalysts for esterification. Heterogeneous ZIF-8 catalyzed the selective monoglyceride synthesis *via* the esterification of oleic acid with glycerol under mild reaction conditions, and it was both active and recyclable [121]. The restructuring of the local framework was dominated by fatty acid, which led to the generation of permanent mesopores. It further enhanced the conversion of the catalyst to 57%, which outperformed a reported excellent catalyst, i.e., ultrastable Y zeolite (30%). ZIF-8 could be recovered easily and reused in two runs without appreciable loss in catalytic activity. However, it was noted that there was a significant change in the morphology and crystallinity of the catalyst after cycling.

To date, most H-MOFs used in esterification reactions (alcohol and acid) are acidic modified. There are varieties of organic functional groups and accessible guests that serve as acid active sites during catalysis [122]. Concentrated sulfuric acid is usually used in the traditional production process; however, some problems exist, such as the formation of by-products, corrosion, and pollution. Many novel catalysts have been reported in recent years, such as heteropolyacid [123], ionic liquids [124], and phenolic resins [125]. Consequently, considerable recent research interest has focused on the design of novel composites and their applications for esterification reactions.

Alkylation reaction

Alkylation reaction represents a widely used process in which an alkyl group can be introduced into organic substrates through addition or substitution reactions [126]. Alkylation engineering processes, such as the production of ethylbenzene (EB) through the alkylation of benzene with ethanol, employ Fe-based H-MOFs, especially MIL series, which makes them crucial to this

field [127]. Based on the results obtained from an investigation into the effects of weight hourly space velocity (WHSV) on raw material conversion and targeted product selectivity, it was shown that MIL-101 (72.9%, 150°C) and MIL-88 (72.1%, 175°C) at WHSV of 3.34 h⁻¹ exhibited the highest conversion. Compared with the traditional catalyst (zeolite) at high temperatures (390–450°C) [128], such a reaction was significantly less energy-intensive, and therefore it was considered to be a promising method to produce ethylbenzene. Kovačič *et al.* [129] proposed a strategy to prepare hierarchically porous, fully opened hybrid membranes which consisted of MIL-100(Fe) nanoparticles embedded into dicyclopentadiene (DCPD)-in-water high internal phase emulsion (HIPE). Due to the combination of the accessibility of Lewis acid sites in MIL-100 and the convective mass transfer of polyHIPE matrix, the conversion of *p*-xylene with benzyl bromide by the catalyst was 99% in 1.5 h based on a batch mode, and 7% in 2 s based on a flow-through mode at 110°C. A possible mechanism can be seen in Fig. 10. Such a result provided an approach for the future application of such hybrid materials.

Direct growth of MOF-5 on SBA-15 mesoporous silica has been demonstrated as an alternative compound strategy to prepare catalysts for alkylation. For example, Karimi *et al.* [130] explored the interesting structure-directing role of SBA-15 in the formation of MOF crystals, whereby oriented growth of MOF-5 on SBA-15 was a nucleation-controlled process. This allowed the formation of nucleation seeds through the linkages between the silanol groups of SBA-15 and the metallic centers of the MOF, and further controlled the expansion of the framework. The new design allowed higher microporosity in the MOF, which resulted in the availability of more Lewis acid sites. It is vital to note that smaller feature materials with rod-like morphology demonstrated superior catalytic performance that was more than twice that exhibited by pure MOF-5 in Friedel-Crafts alkylation of toluene with benzyl bromide to produce *p*-benzyltoluene with *o*-benzyltoluene as a by-product. As such, this feature rendered them as the best and most efficient catalysts.

Considering the inferior water stability of MOF-5, Kou *et al.*

Figure 10 Possible mechanism for alkylation, and dehydrogenation of ethanol. Reprinted with permission from Ref. [127]. Copyright 2017, Elsevier.

[131] constructed MOF-5 crystals in the nanopores of SBA-15 and limited their formation outside the pores. It is worth mentioning that this fabrication was achieved *via* a double-solvent approach, which provided a high interfacial tension between the hydrophilic and hydrophobic solvents to drive the precursors into the hydrophilic nanopores. Interestingly, the resultant composite exhibited superior hydrostability. In addition, the limitation of MOF filling the pores of the substrate caused a reduction in the crystal size and accelerated the mass transfer of silica mesopores, which consequently made the composite highly active during the Friedel-Crafts alkylation of benzyl bromide with toluene (100% conversion). Thus, these studies have presented insights into the effects of H-MOF structures on the catalytic activity so as to facilitate the future design of more efficient heterogeneous catalysts with environmentally friendly features. The catalysts involved in the alkylation reactions in industry, i.e. strong mineral acids or Lewis acids, are highly toxic and corrosive, and they are capable of corroding storage and disposal containers [134]. Currently, companies such as UOP and Mobil badger are using zeolites for the production of ethylbenzene [134]. Utilizing zeolites as catalyst can result in several problems such as high operating pressure and temperature. In this respect, H-MOFs displayed great promise, but more attention will be paid to their stability and recycling performance.

Coupling reaction

A coupling reaction is a process whereby two organic chemical molecules are combined to obtain an organic molecule. Palladium NPs or organometallic complexes have received tremendous interest as powerful catalysts for cross-coupling reactions in academic and industrial-scale applications [133,134]. The development of MOFs with immobilized Pd as catalysts to address its problematic recycling has always been a hot topic due to the excellent features of MOFs as supports. Zhang *et al.* [135] reported a facile immobilization strategy to anchor palladium bis(phosphine) complexes during MOF synthesis, which resulted in a mesoporous material, i.e., palladium-CP1 (CP = coordination polymer) without Pd NPs or cluster generation. During the Sonogashira coupling reaction of iodobenzene and phenylacetylene at room temperature, a yield close to 55% was achieved for toluene, which was attributed to the mesopores that improved the mass transfer process, the high density of metal sites, and homogeneous distribution of activity sites. Even though the yield was significantly lower than its homogeneous counterpart [Pd(PPh₃)₂Cl₂] (89%), the catalyst was highly stable as it could be reused more than four times without any metal leaching. Such a report is a huge step forward for the development of highly stable Pd-based catalysts in coupling reactions.

Pascanu *et al.* [136] demonstrated the importance of adjusting the NPs loading in the supports and optimized the experimental conditions to prepare efficient catalysts based on H-MOFs. A strong relationship between the amount of Pd loaded into MIL-101-NH₂ and the catalytic properties of its corresponding system was revealed. The catalyst with 8 wt% Pd and an average size of 2.6 nm displayed remarkable activities and recyclabilities during the Suzuki Miyaura cross-coupling reaction. Aryl and heteroaryl bromides and activated aryl chlorides were successfully coupled within short durations under mild conditions (ambient temperature/80°C, water/EtOH, and aerobic conditions). More

importantly, the catalyst could be recycled at least 10 times without altering its outstanding catalytic performance. In another report by the same group [137], the importance of the base on the stability of the support (MOFs) in the reaction system was considered. The authors compared different anions, e.g., carbonates and fluorides, and cations, e.g., potassium and caesium, of the base and explored their effects on the catalytic activity, crystallinity, porosity, and Pd distribution based on 8 wt% Pd@MIL-101-NH₂(Cr). Based on their study, the anions of the base exerted a significant impact on the support structure and catalytic activity, while the cations of the base contributed to the catalysis outcome and the distribution of Pd NPs. For example, the presence of carbonates, e.g., K₂CO₃ or Cs₂CO₃, could lead to high yields within a short time. However, the structure of the MOF was decomposed after the catalysis. Interestingly, the best results obtained in the catalysis were with caesium, which was attributed to the increased Pd migration and redeposition (Fig. 11). The redistribution and larger aggregates of active species opened a way for new catalytic pathways. Nevertheless, the resultant challenge regarding the stability and lifetime of the catalyst should be re-examined. Based on the optimized conditions, a diverse set of over 40 highly functionalized biaryls were synthesized *via* the above coupling process by using 8 wt% Pd@MIL-101(Cr)-NH₂ [138]. Some of the target products are important intermediates in pharmaceuticals, and they have shown the potential of the catalyst in various fields. Most importantly, this was the first report of a nanocatalyst supported on a MOF employed in a packed-bed micro-flow reactor. A small library of 11 was isolated and more challenging compounds in a single continuous flow experiment were constructed without replacing the catalyst. This research opened up a new paradigm in the design of immobilized catalytic systems using automated processes under a continuous-flow regime.

H-MOFs show a great huge advantage in loading Pd into their hierarchical channels towards Suzuki-Miyaura reaction. H-MOFs involved mainly focus on the loading of MNPs into pores of MOFs which makes them accessible by reactants for chemical transformations. As a precious metal, Pd's cost is highlighted in large-scale production. In fact, researchers have developed other novel metal catalysts involving Ni, Cu, Co or Fe [139,140]. Notably, the reaction can be achieved under transition-metal-free conditions [141]. Hence, there is still a long way to go on the design of Suzuki-Miyaura catalysts referring to H-MOFs.

Suzuki-Miyaura Reaction

Figure 11 Schematic diagram for the Suzuki-Miyaura reaction using Pd@MIL-101(Cr)-NH₂ catalyst. Reprinted with permission from Ref. [137]. Copyright 2015, Wiley-VCH.

Knoevenagel condensation

Knoevenagel condensation is one of the most compelling reactions to achieve C=C bond formation from aldehydes/ketones or other compounds with active methylene during organic synthesis [142,143]. Such a process is typically catalyzed by weak acids, bases, or acid-base sites of H-MOF catalysts. The design and synthesis of effective acid-base bifunctional catalysts continue to challenge the opposing active sites in the assembly process. In a recent pioneering study [144], amine-functionalized bimetallic MOFs (MIL-101(Al/Fe)-NH₂(X)) were prepared as the catalyst for the deacetalization-Knoevenagel condensation reaction. As shown in Fig. 12, the unsaturated aluminum and iron acted as adsorbed benzaldehyde dimethyl acetal to form benzaldehyde and activated the dehydrogenation of carbonyl, which was subsequently followed by the formation of an intermediate product with malononitrile. Then the intermediate was activated by the metal ions to induce the deprotonation of -CH₂- through the amine groups, which further generated the C=C bonds and formed the end product. The catalysts prepared with any experimental ratio of two metals could facilitate the complete conversion and enhance the condensation rate due to the synergistic effects between Al³⁺ and Fe³⁺. Furthermore, the large mesoporous pores (3.7 nm) also contributed to the catalytic performance of the catalyst. Thus, their work helps to promote the development of mixed-metal H-MOFs in the field of heterogeneous catalysis.

Similarly, various amino-functionalized H-MOFs, UPC-100-In, UPC-101-Al, and UPC-102-Zr, were evaluated as catalysts for Knoevenagel condensation using malononitrile and aromatic aldehydes to produce benzylidene malononitrile [145]. The amino groups (active sites) in the catalysts reacted with aldehydes to form an imine intermediate, followed by the reaction with malononitrile and the regeneration of the active sites. Obviously, the substrates with bulky groups could lead to low reaction rate and total yield due to the size selection of hierarchical structures. For the condensation of benzaldehyde and malononitrile, the total yields based on the three reported cat-

Figure 12 Proposed mechanism for the deacetalization-Knoevenagel condensation reaction catalyzed by MIL-101(Al/Fe)-NH₂(X). Reprinted with permission from Ref. [144]. Copyright 2020, Royal Society of Chemistry.

alysts were different (93.4%, 99.1%, and 88.9%, respectively) at room temperature with dichloromethane solvent. It was mainly due to the reduction of the porosity of the catalyst by the incorporated UPC-100-In. Also, the amino groups in UPC-102-Zr were unexposed in the larger hexagonal and triangular channels.

Recently, a novel shell-by-shell soft templating strategy to fabricate highly uniform mesoporous multi-shelled hollow MOFs (MSHMs) with Pt or Au NPs embedded was demonstrated [146]. Based on the structural perspective, designing a multi-shelled hollow architecture could provide a promising avenue for developing superior catalysts in three aspects. (i) The division by inner shells into several continuous regions could increase the collision probability of the reactants with the active sites, and the increased collision could further enhance the catalytic activity of the catalyst. (ii) Multi-shells could support the framework, which in turn enhances the structural stability of the material. (iii) Multi-shells could provide sufficient interspace to encapsulate or anchor the catalyst species to ensure better dispersion and stronger combination. In addition, the generation of mesopores self-assembled by the surfactant, i.e., tetradecyltrimethylammonium bromide ($C_{14}TAB$), could provide a new synthetic platform for the synthesis reaction. Based on the ingenious design, the material with triple-shells architecture showed excellent catalytic performance towards a one-pot oxidation-Knoevenagel condensation, with a higher α,β -unsaturated nitrile yield (59.6%) than those of the non-, single-, and double-shelled MOFs. Hence, based on their work, it is expected that developing multi-shelled hollow MOFs may open more possibilities in H-MOF engineering.

Solvent polarity in Knoevenagel condensation has been demonstrated to affect the transition state and the capacity of the catalyst for proton transfer [112]. For instance, during the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate with non-protic, polar DMF, MIL-101(Cr) with 10 wt% POM could produce over 90% conversion. More importantly, an excellent TOF of over 656 h^{-1} was achieved, which was in contrast to the lower activity exhibited in protic, polar ethanol under the same conditions. However, it should be noted that the use of organic solutions will inevitably increase the cost and worsen the pollution concerns [35]. In this regard, Yousefian *et al.* [147] created a solvent-free system for the Knoevenagel condensation between aromatic aldehydes with malononitrile. The composite, i.e., Cu-BTC constructed on citric anhydride (CA)-modified

chitosan (CS), was utilized as a highly effective and cost-effective mesoporous catalyst in a solvent-free environment. Their reported composite was able to achieve an outstanding yield of 100%, which was superior when compared with the relatively low yields in other solvents, e.g., water, ethanol, dichloromethane, and acetonitrile. Such a result might be due to the solvation of active functional groups in these solvents, or the formation of hydrogen bonds between the active proton sites in CS-CA/Cu-MOF and these solvents, which resulted in the reduced catalytic efficiency. Thus, the excellent performance exhibited by the catalyst can provide significant inspiration for the green and large-scale progress of H-MOFs.

Traditional Knoevenagel condensation requires organic amine as the catalyst, which exhibits poor stereoselectivity, and is difficult to separate and purify. To better serve the modern chemical industry and even the pharmaceutical chemical industry, it is necessary to optimize the conditions, especially the option of catalysts and solvent, to suit the large-scale industrial production path. At present, many examples of acid-base sites of H-MOFs have emerged, but their application in this field is limited. The challenge then is not to expand the number of examples but to deploy MOF-centric chemistry for evaluating ideas and developing attractive new catalysts that may be difficult or impossible to evaluate or develop by other means.

Other condensation reactions

As mentioned above, aldehydes are highly reactive to amine groups, which results in the formation of imine (Schiff base) linkages. In addition, the Lewis acidity of trimeric Al^{3+} clusters in the framework of MIL-101 or MIL-53 is known to be mild. Thus the impregnation of superacidic phosphotungstic acid (PTA) into MOFs appears to be an efficient method to enhance the uptake of acetaldehyde vapor due to the acceleration of repeated aldol condensation in the presence of water [148]. The kinetics of this conversion with $NH_2MIL101(Al)/PTA_{imp}$ (imp = impregnation) composite was significantly faster than that of $NH_2MIL101(Al)$, which was attributed to the dominance of acid-catalysis when PTA was involved (Fig. 13a). It was compared with the rate-limiting step of enamine or iminium through the Mannich condensation mechanism without PTA modification (Fig. 13b). The synergistic effect of heteropolyacid and mesoporous MOFs was also proven in another heteropolyacid-functionalized MOFs, i.e., HPW@MIL-101(Fe), whereby the reported material displayed good performance during the acet-

Figure 13 Mechanism of (a) acid-catalyzed aldol condensation of acetaldehyde with $NH_2MIL101(Al)/PTA_{imp}$; and (b) Mannich pathway of acetaldehyde condensation with $NH_2MIL101(Al)$. Reprinted with permission from Ref. [148]. Copyright 2015, Elsevier.

alization of benzaldehyde with ethanediol [34].

In another report [149], the cooperative effect between Cu^{2+} as Lewis acid sites in HKUST-1 crystals and weak Brønsted acid sites of mesoporous silicas (MMS) support was realized in the Henry condensation between 4-nitrobenzaldehydes with methane as the liquid phase. Results showed that the use of a water medium could facilitate the synergy of the multi-sites and result in a dramatic increase in total yield (91%). This result was significantly superior when compared with 44% in nitromethane or 42% in propan-2-ol. MMS acted as the structure-directing agent (SDA) to assist the formation of small (4–8 nm) and evenly dispersed HKUST-1 crystals, and it also functioned as a matrix to support the MOF. Thus, MMS could provide the appropriate shaping of catalysts and facilitate the recovery of catalysts in the liquid phase. However, it should be noted that there was a significant decrease in the catalyst activity after the second cycle, which was attributed to the confinement effect of the matrix that inhibited the transportation of bulky β -nitroalcohol from the channels to the reaction system.

CONCLUSION AND OUTLOOKS

H-MOFs have stood out from the microporous MOFs in the field of heterogeneous catalysis due to their unique hierarchical porosity. Hierarchically porous structure is essential as it can reduce the mass transfer resistance and improve the mass transfer of guest molecules (caused by the nano-sized interconnection of mesoscale channels and mesopore walls). The accessibility of the reactant molecules to the micropores that contained important functional groups and active sites can be improved due to the controllable mesopores and macropores to tailor a specific catalytic process. Furthermore, these controllable mesopores and macropores can help to ensure the sufficient diffusion of product molecules, which in turn enhances the catalytic performance of the material (especially when large molecules are involved). The architectural design utilizes versatile and manufacturable porous crystals. Thus, the utilization of hierarchical structure can enable the further modification of catalyst using catalytic species, such as loading of MNPs or encapsulating active POM into the porous channels. These opportunities to advance catalyst development can provide unprecedented possibilities in the field of heterogeneous catalysis. In particular, the pore confinement effect can limit the growth of guest species and facilitate the synthesis of ultrafine nanoparticles.

Considering the achievements in microporous MOF and mesoporous MOF engineering, H-MOFs have grown to be a strong prospect as heterogeneous catalysts for structural design and multifunctional applications. This is because (i) the established chemical construction of H-MOFs allows the explicit assessment of structure-activity relationships and the catalytic mechanism towards a required process; (ii) the properties of hierarchical channels, e.g., shape/aperture/length/dimensionality, can be retro-designed at the atomic or molecular level based on the correlations among the framework structure, functionality, and practical application; (iii) currently, many technologies have emerged as effective tools for the construction of hierarchical structures, mainly employing large building units and fabricating large pores as crystal defects. Consequently, they provide a crucial technical basis for the continuous enrichment and optimization of H-MOF series; (iv) in H-MOFs, the open metal nodes and functional linkers, as well as grafted or

encapsulated guest species can serve as catalytic active sites. More importantly, the multiple catalytic centers can be easily designed and prepared *via* direct syntheses or post-synthesis modifications, and the resultant synergistic catalytic effect has attracted increasing attention from researchers.

This review summarized the recent advances and developments of H-MOFs in heterogeneous catalysis, focusing on three critical catalytic reactions, i.e., oxidation, hydrogenation, and condensation reactions. For a specific catalytic system, it is essential to select and modify H-MOF catalysts based on the reaction characteristics and properties of the substrates. For example, operating under harsh reaction conditions will require highly stable catalysts to ensure adequate catalytic reactivity and catalytic efficiency; a catalyst containing hydrophobic groups will be preferably used for an organic conversion process with a hydrophobic matrix. However, the actual industrial catalytic environment is far more complex than that created in the laboratory, which urges the further development of H-MOFs in terms of structure, composition, and performance. Ideally, the catalyst should be designed with the following considerations: non-toxicity/low toxicity, rich and effective active centers, hydrophilicity/hydrophobicity, high encapsulation capacity without leaching, high thermal/chemical stability, excellent catalytic selectivity, high catalytic efficiency even without co-catalysts, and good recyclability or regeneration capacity. However, it has been found that H-MOFs reported in previous studies for heterogeneous catalysis mainly emphasized catalytic performances, such as conversion, selectivity, and yield. Often, other performance metrics of H-MOFs are neglected, which can reduce their practical appeal as commercial catalysts. It is worth mentioning that stability is a fundamental issue during heterogeneous catalysis, especially under harsh conditions (high temperature or high pressure), and it is related to the catalyst lifetime and recyclability. The ability to mass-produce H-MOFs with excellent stability would imply their unlimited potential in commercial applications. However, the commercialization of H-MOFs is still largely hampered by their relatively low thermal stability and critical bottleneck caused by the low packing density due to mesoporosity. To overcome these limitations, more heat-resistant H-MOFs, such as UiO, MIL, ZIF series, or their derivatives, such as carbon materials or metal oxides, could be developed as candidates to achieve greater industrial applicability. Also, the shaping of H-MOF into a monolithic state is a necessary route to accelerate its industrialization process to overcome the limitations of powdered MOF during industrial engineering, such as clogging or the pressure drop generated by the packing process. Industrial-scale production of H-MOFs provides enough material for specific and necessary industrial prototype tests, which are an essential step preceding possible industrial applications, yet often overlooked at the laboratory scale. Batch synthesis under mild and green environment is advocated, and a balance has to be found between the product quality, space-time yields (STYs), cost, and environmental impact. Furthermore, it is also worthwhile to explore more possibilities of operating at mild catalytic conditions to protect the catalysts and yield more significant economic benefits. Based on the current state, it is believed that the attention on H-MOFs regarding their catalytic rate is still far from satisfactory (as shown in TOF values summarized from some representative studies in Table 1). Hence, future research in H-MOFs should consider the industrial demand and applicability, so that they

Table 1 Reaction conditions and catalytic performances of some previously reported H-MOF systems

Item	H-MOF catalyst	Substrate(s)	Target product	Reaction conditions	Conversion (%) ^a	Selectivity (%) ^a	Yield (%) ^a	TOF (h ⁻¹) ^a	Reusability (cycles) ^b	Ref.
A: Oxidation reaction (oxygenation/oxygenation-dehydrogenation reaction)										
1	Fe-MIL-101	Cyclohexane	Cyclohexanone	TBHP, air (1 atm), 70°C, 8 h	36	81			5	[54]
2	Cr-MIL-101				38	24			5	
3	Au-Pd@MIL-101	Cyclohexane	Cyclohexanone	Au: Pd = 1:1, O ₂ (1 MPa), 150°C, 4 h	21.3	80.8			4	[37]
4	Au/Zn-MOF	Cyclohexene	2-Cyclohexen-1-one	100°C, O ₂ (1 MPa), 8 h	82	98			4	[61]
5	Au/Cu-MOF				77	97			4	
6	MIL-101(Cr)@POM	cis-cyclooctene	1,2-Epoxyoctane	75°C, H ₂ O ₂ , 10 min	100		98	1922	3	[40]
7	HKUST-1/PANI-shp	Styrene	Benzaldehyde	TBHP, 80°C, 12 h	92	63			3	[150]
		cis-cyclooctene	1,2-Epoxyoctane		>99	>99		31.02	5	
		Cyclopentene	Cyclopentene oxide		>99	82		27.06		
8	Co(II)@Cr-MIL-101-P2I	Cyclohexene	Cyclohexene oxide	Isobutyraldehyde, acetonitrile, 35°C, air, 5 h	>99	74		24.42		[59]
		Bicyclo[2.2.1]hept-2-one	3-Oxatricyclo[3.2.1.0 ^{2,4}]-octane		>99	>99		33		
		Benzyl alcohol	Benzaldehyde	TEMPO, DME, 75°C, 3 h	100	>99			4	
9	Cu ₃ (BTC) ₂	2-Nitrobenzyl alcohol	2-Nitrobenzaldehyde	TEMPO, DME, 75°C, 10 h			>99			[30]
		4-Methylbenzyl alcohol	4-Methylbenzaldehyde	TEMPO, DME, 75°C, 7 h			>99			
		2-Propen-1-ol	2-Propenal	TEMPO, DME, 75°C, 6 h			>99			
		Cinnamic alcohol	Cinnamaldehyde	TEMPO, Na ₂ CO ₃ , 75°C, 2 h, O ₂	100		62		4	
10	Cu ₃ (BTC) ₂	Benzyl alcohol	Benzaldehyde	TEMPO, Na ₂ CO ₃ , 75°C, 6 h, O ₂	100		89			[151]
		4-Methylbenzyl alcohol	4-Methylbenzaldehyde	TEMPO, Na ₂ CO ₃ , 75°C, 18 h, O ₂	91		65			
11	(py3tren)Co ₂ @NU-1000	Benzyl alcohol	Benzaldehyde	TBHP, CD ₃ CN, 80°C, 2 h	56.0±1.4			490±20	3	[42]
12	V-Zr-NU-1200				78				3	
13	V-Th-NU-1200	4-Methoxybenzyl alcohol	4-Methylbenzaldehyde	TEA, O ₂ , 105°C, 5 h	58				3	[67]
14	V-Hf-NU-1200				51				3	
15	V-Ce-NU-1200				7				3	
16	Co-POM@MOF-199@MCM-41			80°C, O ₂ , 500 rmp, 180 min	99.1			52.1	3	[71]
17	Cs-POM@MOF-199@MCM-41				99.6				10	[72]
18	SRL-POM@MOF-199@MCM-41	Dibenzothiophene	Dibenzothiophene sulfone	60°C, 500 rmp, O ₂ , 150 min	100			56.1	14	[73]
19	C-POM@MOF-199@MCM-41			50°C, 500 rmp, O ₂ , 90 min	100				10	[74]
20	H ₃ PW ₁₂ O ₄₀ @POM	2-Chloroethyl ethyl sulfide	CEES	H ₂ O ₂ , 45 °C, 20 min	100	57			3	[75]
21	H ₅ PV ₂ Mo ₁₀ O ₄₀ @POM	2-Chloroethyl ethyl sulfide	CEES with CEESO ₂	O ₂ , 70°C, 45 min	100				3	[78]

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Item	H-MOF catalyst	Substrate(s)	Target product	Reaction conditions	Conversion (%) ^a	Selectivity (%) ^a	Yield (%) ^a	TOF (h ⁻¹) ^a	Reusability (cycles) ^b	Ref.
22	V-containing Cr-MIL-101	Methyl phenyl sulfide	Methyl phenyl sulfone	H ₂ O ₂ , EtOH, RT, 1 h			98	1.63	7	[152]
		Dibutyl sulfide	Dibutyl sulphoxide	H ₂ O ₂ , EtOH, RT			98	6.54		
		Dibenzothiophene	Dibenzothiophene sulfone	H ₂ O ₂ , CH ₃ CN, RT			98	1.23		
		Dibenzothiophene	Dibenzothiophene sulfone	<i>n</i> -dodecane, O ₂ , 140°C, 2 h	40				5	
23	MUV-2	Dibenzothiophene	Dibenzothiophene sulfone	<i>n</i> -octane, O ₂ , 50°C	91.76–93.76				9	[154]
24	CNTs@MOF-199	Thiophene	Thiophene sulfone with thiophene sulfoxide						3	[155]
25	MIL-125 (Ti)	Dibenzothiophene	Dibenzothiophene sulfone	TBHP, 80°C, 30 min	~50			~7.5		
B: Dehydrogenation reaction										
1	Pt ₆ Pd ₁₅ /MM-MIL-53(Al)	2-Octanol	2-Octanone				62.4	64	5	[83]
		2-Hexanol	2-Hexanone				58.6	60		
		2-Pentanol	2-Pentanone				46.3	48		
		2-Heptanol	2-Heptanone	144°C, 48 h			47.1	49		
		4-Heptanol	4-Heptanone				49.8	51		
		Cyclooctanol	Cyclooctanone				57.6	59		
		Cyclohexanol	Cyclohexanone				63.7	66		
		Diphenylmethanol	Benzophenone	130°C, 60 h, 600 rpm	~75				5	
		Acetophenone	1-Phenylethanol	50°C, 30 bar H ₂ , 20 h, 600 rpm	~70				5	
		Benzophenone	Diphenylmethanol	140°C, 30 bar H ₂ , 5 h, 600 rpm	~66				5	
		1-Phenylethanol	1-Acetyl-1,3-cyclohexadiene		98	97				
		1-(4-Methoxyphenyl)ethanol	4'-Methoxyacetophenone		96	97				
		1-(2-Methoxyphenyl)ethanol	2'-Methoxyacetophenone	90°C, 24 h	93	92				
		Benzyl alcohol	Phenylacetaldehyde		96	58				
2	Pd/TiO ₂ @MIL-101	1-(4-Methylphenyl)ethanol	4'-Methylacetophenone		98	>99				[81]
		1-(2-Methylphenyl)ethanol	2'-Methylacetophenone		94	>99				
		1-Phenyl-1-propanol	Propiophenone	90°C, 40 h	95	>99				
		4-Methylbenzyl alcohol	4-Methylbenzaldehyde		97	67				
		1-(4-Fluorophenyl)ethanol	4'-Fluoroacetophenone		91	>99				
		1-Phenyl-1-pentanol	Valerophenone	90°C, 48 h	91	>99				
		Propane	Propene	200°C	~3	~55		1.02		
		Formic acid	H ₂	32°C, 3 h	~6	~31		0.54		
							123 μmol mL ⁻¹	214		
3	Co-ALM+NU-1000									[38]
4	Co-SIM+NU-1000									
5	NH ₂ -MIL-125/Pd									[90]

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Item	H-MOF catalyst	Substrate(s)	Target product	Reaction conditions	Conversion (%) ^a	Selectivity (%) ^a	Yield (%) ^a	TOF (h ⁻¹) ^a	Reusability (cycles) ^b	Ref.
6	AgPd@MIL-100(Fe) core-shell NPs	Formic acid	H ₂	25°C, 2 h			178.5 mL M ⁻¹	58	5	[89]
7	Pt@MIL-101	Ammonia borane	H ₂	RT, 4 min			~26 mL mg ⁻¹		5	[29]
C: Hydrogenation reaction										
1	Ni@MesMOF-1	Nitrobenzene	Aniline	H ₂ (1 atm), MeOH	99 (<4 h)				3	[92]
2	Pt/FT-U10-66	Styrene	Phenylethane	NaBH ₄ , MeOH	99 (<15 min)					
3	MIL-101(Cr)@Pt@MIL-101(Fe) _{2,9}	<i>n</i> -hexene	<i>n</i> -hexane	1 bar, 35°C	96.43				3	[96]
4	MIL-101@Pt@FePCMPsponge	Cinnamaldehyde	Cinnamyl alcohol	RT, 3 MPa H ₂	99.80	95.60		16.9	5	[94]
5	Pt/MIL-101	Cinnamaldehyde	Cinnamyl alcohol	RT, 3 MPa H ₂ , 15 min	97.60	97.30		1516		[41]
6	Pd/MIL-101	Styrene	Phenylethane	H ₂ , 35°C, 24 h	>99				3	[26]
7	Pt/MIL-101	Phenol	Cyclohexanone	0.1 MPa H ₂ , 25°C, 11 h	>99.9	>99.9			5	[56]
8	Pd/MIL-101	Octene	Octane	1.5 bar H ₂ , 35°C, 5 h	>99					[156]
		Benzylamine	Dibenzylamine	20 bar H ₂ , 35°C, 5 h	>60				6	
		Nitrobenzene	Aniline	DMF, 120°C, 6 h, 0.6 MPa H ₂	100	>99				[93]
			Dicyclohexylamine	<i>n</i> -hexane, 120°C, 8 h, 0.6 MPa H ₂	100	99.1			6	
D: CO ₂ Cycloaddition reaction										
1	FJI-C10	Epichlorohydrin	4-(Chloromethyl)-1,3-dioxolan-2-one	1 bar, 80°C, 12 h			87	247	6	
		Allyl glycidyl ether	4-(Prop-2-enoxymethyl)-1,3-dioxolan-2-one	1 bar, 80°C, 24 h			93	265		[106]
		Styrene oxide	4-Phenyl-1,3-dioxolan-2-one	1 bar, 80°C, 48 h			48	136		
		Phenyl glycidyl ether	4-Phenoxymethyl-1,3-dioxolan-2-one	1 bar, 80°C, 48 h			38	109		
2	Zn-BDC	Propylene oxide	Propylene carbonate	80°C, 2 h			97.4		3	[101]
		Propylene oxide	Propylene carbonate		90	>99	90		5	
		Epichlorohydrin	4-(Chloromethyl)-1,3-dioxolan-2-one		78	>99	78			
3	UMCM-1-NH ₂	Allyl glycidyl ether	4-(Prop-2-enoxymethyl)-1,3-dioxolan-2-one	1.2 MPa, RT, 24 h	55	>99	55			[102]
		Styrene oxide	4-Phenyl-1,3-dioxolan-2-one		53	>99	53			
		Cyclohexene oxide	Hexahydro-1,3-benzodioxol-2-one		10	>99	10			
4	ZIF-8/CN	Epichlorohydrin	Chloropropylene carbonate		100	100			4	[157]

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Item	H-MOF catalyst	Substrate(s)	Target product	Reaction conditions	Conversion (%) ^a	Selectivity (%) ^a	Yield (%) ^a	TOF (h ⁻¹) ^a	Reusability (cycles) ^b	Ref.
5	NU-1008	Styrene oxide	4-Phenyl-1,3-dioxolan-2-one	RT, 1 bar, TBAB	100		99.4			[158]
		Epichlorohydrin	4-(Chloromethyl)-1,3-dioxolan-2-one		95	>99			5	
		Propylene oxide	Propylene carbonate		94	>99				
6	MIL-88-NH ₂ (Fe)	Allyl glycidyl ether	4-(Prop-2-enoxymethyl)-1,3-dioxolan-2-one	0.1 MPa, 45°C, 12 h	72	>99				[103]
		Styrene oxide	4-Phenyl-1,3-dioxolan-2-one		40	>99				
		Cyclohexene oxide	Hexahydro-1,3-benzodioxol-2-one		11	>99				
7	MOF-74	Propylene epoxide	Propylene carbonate	23°C, 12 bar, 48 h			98	41	3	[159]
E: Esterification reaction										
1	ZIF-8	Oleic acid with glycerol	Monoglyceride	150°C, 20 h	57	100			3	[121]
2	HPW/UiO-66-NH ₂	1-Butene with acetic acid	sec-butyl acetate	110°C, 2 MPa	39.40	98			3	[119]
3	HPW/EDG-MIL-101	1-Butene with acetic acid	sec-butyl acetate		31.50%	97.50			3	[113]
4	IL/MIL-101(Cr)	Acetic acid with amyl alcohol	Amyl acetate	80°C, 1 h	>80%				6	[160]
5	MIL-101(Cr)-SO ₃ H	Acetic acid with methanol	Methyl acetate		>99	>98			5	
		Acetic acid with ethanol	Ethyl acetate		>99	>98				
		Propionic acid with ethanol	Ethyl propionate		>99	>98				
		Benzoic acid with methanol	Benzoic acid methyl ester	170°C, 8 h	>99	97.3				[114]
		Phthalic acid with methanol	Methyl hydrogen phthalate		>99	95				
6	MIL-101@POM	Acetic acid with <i>n</i> -butanol	Butyl acetate	383 K	~50				8	[112]
F: Alkylation reaction										
1	MIL-101 (Fe)	Benzene with ethanol	Ethylbenzene	150°C	72.9	43.6				[127]
2	MIL-88 (Fe)	Benzene with ethanol	Ethylbenzene	175°C	72.1	76.2				
3	MOF@polyHIPE	<i>p</i> -xylene with benzyl bromide	2,5-Dimethyldiphenylmethane	110°C, 2 h	99					[129]
4	MOF-5/SBA-15	Toluene with benzyl bromide	<i>p</i> -benzyltoluene	100°C	95.7				4	[130]
5	MOF-5/SBA-15	Toluene with benzyl bromide	<i>p</i> -benzyltoluene	80°C, 3 h	100				3	[131]
6	MIL-100(Sc ₆₀ Fe ₄₀)XS	Trifluoroacetaldehyde ethyl hemiacetal with 2-methylindole	1-(2-Methyl-1 <i>H</i> -indole-3-yl)-2,2,2-trifluoroethanol	RT, 6 h			95			[161]

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Item	H-MOF catalyst	Substrate(s)	Target product	Reaction conditions	Conversion (%) ^a	Selectivity (%) ^a	Yield (%) ^a	TOF (h ⁻¹) ^a	Reusability (cycles) ^b	Ref.
7	Zn-MOF	Toluene with <i>tert</i> -butyl chloride	<i>tert</i> -butylbenzene	170°C, 2 h, decane	99.6	99.3				[162]
8	Zn-MOF	Biphenyl with <i>tert</i> -butyl chloride	4- <i>tert</i> -butylbiphenyl		100	66.1				
G: Coupling reaction										
1	Palladium-CPI	Iodobenzene with phenylacet- ylene	Toluene	RT, 24 h			55		4	[135]
2	8 wt%Pd@MIL-101Cr-NH ₂	<i>p</i> -bromoanisole with organo- boron	Biphenyl compound	H ₂ O, 6 h			70–100		10	[136]
		Boronic acids or pinacolate esters with heteroaryl iodides (hetero)aromatic or vinyl- boronic acids with aryl iodides or aryl bromides	Biaryls	K ₂ CO ₃ , H ₂ O/EtOH (1:1)	80–100		48–98			
		Pyrazole with oxazole derived boronic acids			98–100		62–93			
		4-Iodoanisole with phenyl- boronic acid	4-Phenylanisole		50–100		41–96			
3	8 wt%Pd@MIL-101Cr-NH ₂	1-Iodo-4-methyl-benzene with phenylboronic acid	4-Phenyltoluene	K ₂ CO ₃ , H ₂ O/DMF, 1 h			97			[138]
		inter-nitroiodobenzene with phenylboronic acid	3-Nitrobiphenyl				83			
		Bromobenzene with phenyl- boronic acid	Biphenyl				>99			
		Iodobenzene with phenyl- boronic acid	Biphenyl	K ₂ CO ₃ , H ₂ O/DMF, 3 h			48			
		4-Bromobenzaldehyde with phenylboronic acid	4-Biphenylcarboxaldehyde				>99			
							96		5	
H: Knoevenagel condensation										
1	MIL-101@POM	Benzaldehyde with ethyl cyanoacetate	Ethyl 2-cyano-3-phenylprop-2- enoate	40°C, DMF			>90	656		[112]
2	CS-CA/Cu-MOF	Aromatic aldehydes with malononitrile	Benzylidenemalononitrile derivatives	25°C, 10 min	100	100			8	[147]
3	TSHM/s/Au	Benzaldehyde with ECA	α,β-unsaturated nitriles	RT, 1 atm, 12 h			59.6		3	[146]
4	MIL-101(Al/Fe)-NH ₂ (X)	Benzaldehyde dimethyl acetal with malononitrile	Benzylidenemalononitrile	90°C, 90 min	100		>99		5	[144]
5	UPC-101-Al	Benzaldehyde and malononitrile	Benzylmalononitrile	CH ₂ Cl ₂ , RT, 5 h			99.1			[145]

a) The data are based on the first cycle. TOF = (mole of molecular conversion)/(mole of surface atoms of catalyst × reaction time). b) The data are based on the catalytic activity without significant loss after being recycled. DMF = *N,N*-dimethylformamide; TEA = triethanolamine; RT = room temperature; ECA = ethyl cyanoacetate.

can be adopted industrially.

Overall, H-MOF is a key emerging material and various new opportunities have surfaced in both exploratory and user-oriented research. However, it is expected that this field will require further long-term studies to translate from the proof-of-concept phase to commercial breakthroughs in heterogeneous catalysis. We hope that this review can provide researchers with more new inspirations to stimulate the emergence of new concepts and broader applications for H-MOFs.

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Conflict of interest The authors declare no competing financial interest.

Chongxiong Duan received his PhD degree in chemical engineering from South China University of Technology in 2019. He is currently an associate professor at the School of Materials Science and Hydrogen Engineering, Foshan University. His research interests focus on the development of porous materials (MOFs, porous carbon, zeolites) and their application.

Hongxia Xi received her PhD degree in chemical engineering from South China University of Technology in 1996. She then worked as a post-doctor for two years at Sun Yat-sen University, as a visiting scholar for one year at Savoie University, France, and as a senior visiting scholar for six months at The State University of New Jersey, USA. She is currently a professor of chemical engineering at South China University of Technology. Her research interests focus on the development of porous materials and their application.

Yi Yu was born in 1996, Guangdong Province, China. She is studying at the School of Chemistry and Chemical Engineering, South China University of Technology in Guangzhou, China. She is now doing her research under the guidance of Prof. Hongxia Xi. Her current research is mainly focused on the synthesis of porous functional organic materials and their application in gas adsorption and heterogeneous catalysis.

多级孔金属-有机骨架材料在多相催化方面的研究进展

段崇雄^{1,4}, 梁宽¹, 林家辉¹, 李静静¹, 李理波², 康乐³, 余仪^{2*}, 奚红霞^{2*}

摘要 兼具微孔、介孔和大孔结构的多级孔金属-有机骨架(H-MOFs)是近年来发展迅猛的一类多孔晶体材料,在诸多领域尤其是多相催化方面具有广泛的应用前景。本文综述了近年来H-MOFs在多相催化领域的研究进展,包括氧化反应、加氢反应和缩合反应等。重点介绍了H-MOFs多级孔结构的多功能性,以及其工业适用性,如催化活性、选择性、稳定性等。最后展望了H-MOFs在多相催化领域的应用前景、面临的挑战以及待解决的问题。