Metal Organic Frameworks in Heterogeneous Catalysis: Recent Progress, New Trends and Future Perspectives

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Abstract

More than 95% (in volume) of all today's chemical products are manufactured through catalytic processes, making research into more efficient catalytic materials a thrilling and very dynamic research field. In this regard, Metal Organic Frameworks (MOFs) offer great opportunities for the rational design of new catalytic solids, as highlighted by the unprecedented number of publications appearing over the last decade. In this review, the recent advances in the application of MOFs in heterogeneous catalysis are discussed. MOFs with intrinsic thermo-catalytic activity, as hosts for the incorporation of metal nanoparticles, as precursors for the manufacture of composite catalysts and those active in photo and electrocatalytic processes are critically reviewed. The review is wrapped up with our personal view on future research directions.

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1. Introduction

A catalyst is a substance that increases the rate of a chemical reaction towards equilibrium without being appreciably consumed. The word “catalysis” stems from Greek: “κατα” that means “down” and “λυσις” that means “loosening”. In the eastern culture, the Chinese characters for catalyst refer to a marriage broker.¹ By using the adequate catalyst, one or a set of desired reactions proceed with a higher rate and selectivity at relatively mild conditions.

Catalysis is, and has been, a central piece in human development. Catalytic processes were already used by the ancient Egyptian civilization to produce alcohol for beverages and conservational uses. In the following centuries, catalysis was used by the Greek, Roman and Islamic empires and was later the main driving force for the agriculture revolution through the controlled synthesis of ammonia. Catalytic processes were again responsible, to a large extent, for the industrial revolution through the large-scale production of base chemicals (i.e. sulphuric acid).² Thanks to environmental catalysis we are still able to breathe (relatively) healthy air in spite of our society being powered by combustion engines. Nowadays, catalysts (especially solid ones) are used globally in the manufacture of over 10000 products worth over \$10 trillion per year, accounting for 15% of the world GDP. More than 95% (in volume) of all today’s chemical products are manufactured through catalytic processes, with a total market size of industrial catalyst manufacture close to \$16 billion.³

Considering these figures, it is not difficult to understand why catalysis research is at the forefront of chemistry, materials science and chemical engineering. It is also easy to understand that, after Metal Organic Frameworks became a hot topic in materials science, it was only a matter of a few

Figure 1. Assembly of a functional MOF with catalytically active sites by direct assembly or Post-Synthetic Modification (PSM) of a linker (a) or a metal node (b), nanoparticle encapsulation (c) or MOF utilization as a carbon support (d).

years until the first publications reporting catalytic properties of MOFs appeared.⁴⁻⁷ As of today, we estimate that in the order of 8000 journal articles and over a hundred patents have been published on the application of MOFs in catalysis.

Several features make MOFs, at least on paper, excellent candidates as heterogeneous catalysts: (i) an unprecedented structural diversity, (ii) the intrinsic hybrid organic-inorganic nature, (iii) the presence of uncoordinated metal sites and ready accessible organic struts, (iv) the potential for rational design and, last but not least, (v) a well defined porosity. Indeed, these properties

appear at the top of the wish list of every researcher engaged in catalysis engineering. At the same time, it is also fair to admit that it has taken a while until MOFs have found their place in the catalysis world and that, still nowadays, MOF catalysis raises important questions over its applicability in the real world. Yet, as the topic matures, it is clearer now where MOFs can make a difference in catalysis.

As depicted in Figure 1, several structural features of MOFs can be harvested for catalytic applications: (1) by using the metal nodes of the material when coordination vacancies are available; (2) by using the linker as organo-catalytic site; (3) by using the optoelectronic properties of the hybrid material and ligand to metal charge transfer to trigger photocatalytic processes; (4) as hosts for the encapsulation of additional catalytic sites such as nanoparticles, enzymes or other moieties; (5) *via* post-synthetic modification of the MOF scaffold; (6) as precursors for the formation of nanoparticle or single site catalysts *via* controlled decomposition and (6) by combining several of the above features.

In line with the large number of publications on MOF catalysis that we have witnessed over the last decade, a very large number of excellent reviews has been published, specially over the last few years.⁸⁻¹⁵ Therefore, in order to avoid excessive repetition and overlapping with those already existing reviews, here we focus on the most recent developments on MOF catalysis with emphasis on new approaches and applications, specially (but not constraint to) energy and environmental applications. In doing so, we critically review the most relevant publications of the 2017-2019 period while giving credit to earlier, pioneering, work. Because of space constraints and very recent reviews on those subjects, we deliberately left aside enzyme encapsulation¹⁶ and photocatalytically driven organic transformations.^{17,18} The interested reader is referred to those recent reviews for further information.

The article is structured in five main paragraphs that can be read independently and deal with (i) MOFs with intrinsic catalytic activity, (ii) the use of MOFs as supports for metal

nanoparticles, (iii) MOF mediated materials, (iv) electrocatalytic applications and (v) photocatalysis for environmental and energy applications. We finalize the text with our personal view on challenges to be addressed and potential future research directions. Overall, we hope that this article will be equally useful to those entering the thrilling MOF catalysis world and those already into the topic.

2 MOFs with intrinsic catalytic activity

Since their discovery, MOFs have been regarded by the catalysis community as ideal platforms for the heterogenization of homogeneous catalysts. Indeed, to a large extent, MOFs can be understood as molecules arranged in a crystalline lattice and, as such, through crystal engineering, a given homogenous catalyst could be extended through such a crystalline lattice, leading to solids with intrinsic catalytic activity. In this spirit, many as-synthesized MOFs can be regarded as single site catalysts.^{8,15,19,20} To date, mostly three different approaches have been proposed to achieve intrinsic catalytic activity (Figure 2): (i) through the introduction of open metal sites (coordinatively unsaturated sites), (ii) through the creation of defects and (iii) by using the organic linker as catalyst, be it through direct or indirect (post-synthetic modification) incorporation of such sites.

Figure 2. Potential sites to generate MOFs with intrinsic catalytic activity.

Following this classification, in the next sections we summarize recent reports on the field. It should be noted that, in this period, the MOF community has strongly focused on the use of robust MOFs based on tri and tetravalent metals along with extending the scope of catalytic reactions in which MOFs are active. Although in most cases MOFs do not display better catalytic activity than the state of the art for these reactions, we believe this is an important development in the field because it fades away doubts about stability under reaction conditions.

2.1 Catalysis on open metal sites and non-decorated frameworks

In 2017, Tu et al.²¹ reported on a new MOF series – multicomponent frameworks made from the trinuclear Cu-based pyrazolates $[\text{Cu}_3(\text{HPyC})_3]$ and $[\text{Cu}_3(\mu\text{-OH})(\text{HPyC})_3]^{2+}$ as metalloligands and zinc-based secondary building units (SBU). The one-pot synthesis approach allowed for the inclusion of multiple functionalized inorganic units into one framework and therefore enabled modulation of the MOFs' electronic properties. Five MOFs, denoted as FDM-3—7, were obtained by combining different building blocks and were tested as catalysts in carbon monoxide oxidation, hydrogen peroxide decomposition and benzyl

alcohol oxidation.²¹ The classic Cu(I)/Cu(II) reversible redox transformation of the trinuclear copper sites was inherited by the MOFs and further contributed to their catalytic activity. The MOFs' catalytic performance was highly dependant on the nature of the FDMs, demonstrating electronic modulation. Also remarkable is the fact that the use of pyrazole ligands highly improves MOF stability. Nikseresht et al.²² used a simple ultrasound-assisted synthesis to prepare tacrine analogues in the presence of $[\text{Cu}_3(\text{BTC})_2]$ as a catalyst. This framework was employed in the Friedländer reaction between 5-amino-4-cyano-2-phenyl-1,3-oxazole and appropriately substituted carbonyl derivatives under ultrasonic irradiation. The results showed that the active sites in $[\text{Cu}_3(\text{BTC})_2]$ were mainly copper atoms and that the role of the ligand was negligible. Dhakshinamoorthy et al.²³ suggested that $\text{Cu}_3(\text{BTC})_2$ was an active catalyst for the synthesis of borasiloxanes from silanes and pinacolboranes. Anbu and Dhakshinamoorthy²⁴ described the activity of $\text{Cu}_3(\text{BTC})_2$ in the Friedel-Crafts alkylation of indole with β -nitrostyrene. Surprisingly, in neither of these cases stability of CuBTC seemed to be an issue.

Nagarjun and Dhakshinamoorthy²⁵ showed that $\text{Fe}(\text{BTC})$ was an active catalyst for the aerobic oxidation of cyclooctane and linear hydrocarbons, without using radical initiators or peroxides. Han et al.²⁶ reported on the solvent- and HF-free synthesis of MIL-100(Fe), which exhibited good catalytic performance in the acetalization of benzaldehyde with methanol, yielding 93% benzaldehyde dimethyl acetal and maintaining its initial activity after five catalytic runs. Later, the same group extended this approach towards MIL-101(Cr), which was tested in the oxidation of benzyl alcohol, showing a 35% benzaldehyde yield.¹² Wang et al.²⁷ described the efficiency of MIL-100(Fe) towards catalytic ozone removal. MIL-100(Fe) exhibited a long-lasting ozone conversion efficiency of 100 % for over 100 h under the conditions of a relative humidity of 45 % and space velocity of $1.9 \times 10^5 \text{ h}^{-1}$ at room temperature. Huang et al.²⁸ explored MIL-100(Fe)'s catalytic activity in the transformation of hexose sugars into lactic acid. A yield of 32% was obtained for the case of fructose in H_2O at

190 °C. For the elucidation of the active site, the catalytic activities of Cu-BTC and MIL-100(Cr) were also tested and compared with the Fe one. Both materials were less active than MIL-100(Fe) since the concentration of Lewis acid centres in MIL-100(Fe) was found to be higher than that of the other two materials. Rostamnia and Alamgholiloo²⁹ employed mixed-valence OMS-MIL-100(Fe) Fe₂₊/ Fe₃₊ as a catalyst for the aza-Michael addition of various amines with α,β -unsaturated compounds. Open metal sites (OMS) were introduced by the treatment of as-synthesized MIL-100 under vacuum at 250 °C. OMS-MIL-100(Fe) showed product yields of up to 93% in the absence of any additive and was recycled with no apparent loss of activity. MIL-100(Fe), evacuated at different temperatures, was also used as a catalyst for selective ethylene tetramerization by Han et al.³⁰ Depending on the evacuation temperature, both the surface area and content of coordinatively unsaturated sites changed and were found to be the main factors affecting the oligomerization performance. When evacuated at 250 °C, MIL-100(Fe), with an intact pore structure and high concentration of Fe₂₊ sites, reached the maximal catalytic activity of $1.26 \times 10^5 \text{ g mol}_{\text{Fe}}^{-1} \cdot \text{h}^{-1}$, and more than 80% of the products were branched and ringed C₈ alkanes. The alkylaluminium cocatalysts presented a clear influence on the oligomerization performance, not only via scavenging but also by creating additional open sites. Again, the same approach was extended towards MIL-100(Cr),³¹ which showed moderate catalytic activities for ethylene oligomerization, but high selectivities towards the low-carbon olefins C₆, C₈, and C₁₀. Moreover, the oligomer distribution was different, depending on the evacuation temperature. The XPS results showed the reduction of some Cr₃₊ active sites to Cr₂₊, which was responsible for the polymerization. The MIL-100(Cr) catalyst evacuated at 250 °C exhibited the highest oligomerization and polymerization activities of up to $9.27 \times 10^5 \text{ g mol}_{\text{Cr}}^{-1} \cdot \text{h}^{-1}$ and $0.99 \times 10^5 \text{ g mol}_{\text{Cr}}^{-1} \cdot \text{h}^{-1}$, respectively. The oligomerization selectivity towards the low-carbon olefins C₆, C₈, and C₁₀ was approximately 99%. However, no analysis of the solid for the potential presence of large oligomers (a normal issue in case of

oligomerization reactions) was presented. Rivera-Torrente et al.³² studied the same catalytic system but with diethylaluminum chloride as a cocatalyst. The catalytic performances of MIL-100 and MIL-101 were then compared. In contrast to the penultimate work, here, MIL-100(Cr) was unable to reach significant activity since it showed a high stability towards the cocatalyst, while MIL-101 showed catalytic activity. However, diethylaluminum chloride changed the MOF's structure, and the nature of the catalyst's active site after introduction of the cocatalyst remained unclear. Santiago-Portillo et al.³³ directly prepared six isostructural MIL-101(Cr)-X (X = H, NO₂, SO₃H, Cl, CH₃, and NH₂) materials by reaction with Cr^{III} salts and corresponding terephthalic acid or by post-synthetic treatments of the pre-formed MIL-101(Cr). The MIL-101(Cr) materials were tested as heterogeneous catalysts for epoxide ring opening by methanol, benzaldehyde acetalization by methanol, and Prins coupling. The clear influence of the substituent followed a linear relationship with the Hammett meta constant of the substituent: the catalytic activity increased with the electron-withdrawing ability of the substituent. Yu et al.³⁴ explored four benign iron-based MOFs for the catalytic ozonation reaction. All Fe-MOFs had high catalytic performances, with MIL-53(Fe) demonstrating the highest catalytic activity because of it had the highest amount of LAS and it had a suitable porosity-derived mass transfer property.³⁴

Islamoglu et al.³⁵ employed a Ce-BDC framework for catalytic hydrolysis of the nerve agent simulant dimethyl 4-nitrophenyl phosphate (DMNP) and the nerve agent soman. The hydrolysis was found to be faster (8 min) than in the case of the previously reported UiO-66 (19 min).³⁶ In 2019, the same group employed NU-901 as a catalyst for fast DMNP hydrolysis. The system showed a <2 min half-life in the presence of bases with low and high molecular weight.³⁷

In 2017, Shaabani et al.³⁸ reported on using UiO-66 as a Lewis-acid solid catalyst for the synthesis of nitrogen-containing heterocycle scaffolds. The performance of UiO-66 was

compared to the performances of other catalysts (*e.g.*, RuCl₃·3H₂O, choline chloride/urea, cerium(IV) carboxymethylcellulose, *etc.*) in the one-pot synthesis of pyridine, quinoxaline and imidazopyridines derivatives under solvent-free conditions. The UiO-66 catalyst, due to its high density of active sites, displayed a higher yield while being tested at lower temperatures and was recycled three times with no change in activity nor in its structure. Zhang et al.³⁹ exploited the Lewis acid sites of UiO-66 as a catalyst for oxidative desulfurization (ODS). Under the optimal reaction conditions, the ODS conversion of dibenzothiophene reached 100%, though the recyclability was found to be insufficient. Dalapati et al.⁴⁰ in 2017 reported on a Ce(III)- and Ce(IV)-based MOF with a UiO-66 topology employing 3,4-dimethylthien[2,3-*b*] thiophene-2,5-dicarboxylic acid as a ligand. Owing to the presence of mixed-valence cerium ions, the activated MOF was able to oxidize the chromogenic peroxidase substrate—3,3',5,5'-tetramethylbenzidine (TMB) or 2,2'-azinobi(3-ethylbenzothiazoline-6-sulfonic acid)—using molecular oxygen. The MOF could be reused several times. Rojas-Buzo et al.⁴¹ demonstrated that Hf-based UiO-66-NH₂ and MOF-808 exhibited high catalytic activities in the Meerwein–Ponndorf–Verley reaction toward the formation of alcohols in high yields from biomass-based carbonyl compounds by direct hydrogen transfer. The catalytic performance of Hf-based MOFs was compared with that of the related Zr counterparts, and a higher efficiency was found for the former. As a side note, the reader will realize that there is a strong preference for the use of highly stable MOFs based on tri and tetra valent metals.

MOF catalysis can be based on not only open metal sites but also the linker bearing a functional group. For example, the classic and important Knoevenagel condensation reaction (Scheme 2) requires the presence of basic sites, which can be pyridyl, amide, *etc.*

Scheme 2. Knoevenagel condensation reaction

Mistry et al.⁴² prepared two MOFs by a room-temperature slow diffusion reaction. The compounds were formed by Cd-sulfoisophthalate layers that were cross-linked by bipyridyl linkers, forming three-dimensional structures. These species possessed Lewis acidic sites (*i.e.*, Cd metal centres) as well as basic sites (*i.e.*, azine, free pyridine, and uncoordinated sulfo oxygens), and they exhibited good catalytic activities for one-pot tandem deacetalization–Knoevenagel condensation reactions, both in the presence of a solvent and under solvent-free conditions. Zhang et al.⁴³ prepared ultrathin Ni-MOF nanosheets *via* a polyvinylpyrrolidone-assisted route, which also showed activity towards the Knoevenagel condensation reaction. Abdollahi and Morsali⁴⁴ synthesized $[\text{Zn}_2(\text{BDC})_{1.5}(\text{L})(\text{DMF})] \cdot 1.5\text{DMF}$ (L = pyridine 4-carboxylic acid), denoted as TMU-41. Removing the coordinated DMF molecules created OMS, which acted as a Lewis acid catalyst for the Knoevenagel condensation reaction.

2.2 Catalysis on defects

Defects in MOFs arise from the removal of either a linker, a cluster or a coordinated solvent (*e.g.*, water) molecule.⁴⁵ Defects lead to non-stoichiometric metal to linker ratios. Missing linkers are often seen being compensated by formates, oxygen, hydroxyl groups, water and/or chloride, however, due to the non-periodicity of defects, a comprehensive structural information is difficult to achieve and molecular simulations play a key role in better understanding the nature of these catalytic sites.^{15,46} Experimentally, defects can be directly quantified by elemental analysis and specially by thermogravimetric decomposition.⁴⁷ For instance, in case of UiO-66, in the presence of air, at temperatures over 200 °C dehydroxylation of the framework starts, giving rise to $\text{Zr}_6\text{O}_6(\text{ATA})_6$ followed by a second weight drop at around 400 °C that corresponds to the destruction of the MOF. The decomposition of an ideal sample leaves an amount of oxide corresponding to the stoichiometric ratio of the UiO structure, while decomposition of defected materials results in a higher amount of oxide than

the stoichiometrically predicted (as a consequence of the lower amount of organic linkers). This is the common technique used for quantification of defects, although hardly any chemical information can be extracted. To complement TGA and to gain structural and chemical information about the nature of defects, the presence of forbidden reflections in PXRD, UV-VIS, the presence of multiple O-H stretching bands in FTIR, the detection of modulation agents by NMR⁴⁸ and even direct observation of defects by high resolution TEM⁴⁹ have been applied. Recent publications on better understanding the nature of defects in MOF crystals are among the most exciting recent advances in the field.

When it comes to the consequences of defects, the catalytic activity of UiO-66 can be drastically increased by the introduction of defects since they have a significant impact on the porosity, mechanical properties and Lewis and Brønsted acidities.⁵⁰ The advantage of UiO-66 is that by tailoring the synthetic conditions or applying post-synthetic treatments, the chemical properties can be easily tuned.^{51,52} The presence of defects increases UiO-66's Lewis acidity since additional coordinatively unsaturated Zr ions are created; this feature has largely been deployed and reported.⁵³⁻⁵⁵

In 2017, Caratelli et al.⁵⁶ reported a comparison between hydrated and dehydrated linker-deficient UiO-66 and UiO-66-NH₂ for the Fischer esterification of carboxylic acids with methanol. Molecular modelling combined with experimental data on various defective hydrated and dehydrated materials unravelled the nature and role of the defective active sites and coordinated water molecules. The presence of coordinated water was revealed to provide extra Brønsted sites and to stabilize reaction intermediates through hydrogen bonds. As the role of the Zr Lewis acid centres was indispensable, the proposed reaction mechanism was based upon a dual Lewis/Brønsted catalytic function. The same year, Hajek et al.⁵⁷ theoretically investigated the Oppenauer oxidation of primary alcohols by defective UiO-66 using density functional theory (DFT) and the periodic approach. The studied defective UiO-66 was obtained

by terephthalic acid (BDC) linker removal, and thus, open active sites appeared on the Zr-*O*-Zr surface between coordinatively unsaturated Zr atoms. The catalytic activity was shown to spread all around the Zr-*O*-Zr site, with a Lewis acid centre at the under-coordinated Zr atoms and a Brønsted acid site on the μ_3 -oxygen. Both hydrated and dehydrated materials were tested in the aforementioned reaction of prenol with furfural, and the hydrated materials were found to be more active due to the presence of stronger basic sites, in agreement with the theoretical prediction. This work showed that not solely the Lewis acidity of the coordinatively unsaturated sites but also the interplay between the Lewis acid and the Brønsted base sites (oxo-atoms) played an important catalytic role.

In 2017, Cai and Jiang reported on a modulator-induced defect formation strategy for the synthesis of hierarchical pore (HP) MOFs, where a monocarboxylic acid modulator and an insufficient amount of organic linker were used.⁵⁸ The modulator played a dual role: the carboxylic acid coordinated to the metal ion for the formation of metal-oxo clusters, while the alkyl chain created structural defects and additional pore space. The approach worked for a range of MOFs – MIL-53, DUT-5, MOF-808, UiO-67 and UiO-66. The latter species was tested as a catalyst in the [3+3] cycloaddition reactions between 1,3-cyclohexanedione and various α,β -unsaturated aldehydes of different sizes (Scheme 1). In the case of the larger substrates, HP-UiO-66 presented a higher activity than that of the conventional UiO-66. Although the authors

Scheme 1. Cycloaddition reactions between 1,3-cyclohexanedione and α,β -unsaturated aldehydes

did not claim defects as the active sites, defect formation benefited the catalysis through the enhanced transport of large substrates. The same year Dissegna et al.⁵⁹ used water adsorption measurements as a key tool to study the generated defects in acetic-acid- and trifluoroacetic-acid-modulated UiO-66 frameworks. The authors revealed that increasing the amount of modulator caused increases in the surface area, total water uptake and hydrophilicity. The modulated framework was tested as a catalyst in the cyanosilylation of benzaldehyde, which is a reaction that exploits Lewis acid sites (here, generated by missing linker defects). The modulated UiO-66 showed a higher activity than that of the pristine framework. Ye et al.⁶⁰ successfully synthesized UiO-66 with increased defects, in the absence of a modulator and solvent, *via* mechanosynthesis using a mortar. The number of missing linkers per $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6$ in this material reached 2.16, which was substantially higher than that in UiO-66 prepared by the conventional method. As a result, this material exhibited enhanced catalytic activities in a series of catalytic oxidative reactions, including the oxidative desulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene and the oxidation of benzyl alcohol. In 2017, Kuwahara et al.⁶¹ demonstrated that sulfonic-acid-functionalized UiO-66 acted as an active heterogeneous catalyst for the hydrogenation transfer reaction of biomass-derived levulinic acid and its esters to produce γ -valerolactone (GVL) using alcohols as H-donors. Higher GVL yields were attained by increasing the content of sulfoterephthalic acid linkers (with a maximum GVL yield of 85% over UiO-66-S₆₀ at 140 °C), which far outperformed those of other MOFs embedding different metallic centres, bulk ZrO_2 , and pristine UiO-66 for a broad scope of substrates and alcohols. This result was due to the synergistic effect between Lewis basic Zr oxo clusters and Brønsted acidic $-\text{SO}_3\text{H}$ groups, which were uniformly arranged in the confined nanospace of UiO-66. UiO-66-S₆₀ was reusable for at least four successive cycles without a significant loss of catalytic activity.

In 2018, Yang et al.⁶² studied the chemistry of Zr₆O₈ nodes in UiO-66 and UiO-67 *via* infrared and nuclear magnetic resonance spectroscopies. The researchers elucidated the catalytic properties of the nodes for ethanol dehydration, which selectively made diethyl ether but not ethylene at 473–523 K. DFT calculations showed that the key to the selective catalysis was the breaking of the node-linker bonds (or the accidental adjacency of open/defect sites) that allowed catalytically fruitful bonding of the ethanol reactant to neighbouring sites on the nodes, facilitating ether formation through the S_N2 mechanism.

In 2017, Zwoliński and Chmielewski⁶³ reported on a series of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO)-appended UiO-66 and UiO-67 containing different amounts of TEMPO. The frameworks were studied as catalysts in the aerobic oxidation of alcohols. The materials were obtained using a relatively low-temperature, HCl-modulated *de novo* method developed by Katz et al.,⁶⁴ which incorporated a ligand mixture, and were shown to contain an abundance of missing cluster defects. The method yielded highly defective materials, with significantly larger pores and higher surface areas than those of the parent framework. In this study, the defects themselves were not the sole active sites, but they still benefited the catalysis. Large voids due to missing clusters and linkers allowed these materials to accommodate bulky TEMPO substituents in quantities of up to twice that theoretically predicted for the idealized structures – 33% instead of 17% in the case of UiO-66-TEMPO and 100% instead of 67% in the case of UiO-67-TEMPO. The most active framework–UiO-67-TEMPO with 38% TEMPO ligand – showed a high activity even at ambient and low (0 °C) temperatures. The catalyst was recycled three times; however, after the first run, the nature of the active sites was partially changed into a mixture of free radicals and oxidized oxoammonium cations, which could be easily reduced back by the addition of excess alcohol. The activity decreased after the second run, which was attributed to the partial amorphization of the framework. In 2018, Zhuang et al.⁶⁵ also reported on the synthesis of a robust TEMPO-

radical-functionalized UiO-68-TEMPO with varied missing linker defects, which was prepared with the H₂tpdc-TEMPO ligand (Figure 3). The researchers revealed that a synergistic effect between the TEMPO radicals and the hydrophilic and defective Zr-nodes affected the catalytic activity of UiO-68-TEMPO in the same reaction.⁶⁵ The missing linker defects were controlled by using different amounts of a benzoic acid (BA) modulator – a higher BA concentration resulted in a single-crystalline UiO-68-TEMPO with fewer defects, while a lower concentration led to highly defective microcrystals. The latter showed higher catalytic activity, as it possessed more Zr-node defects than did the single-crystalline UiO-68-TEMPO. The revealed synergy was confirmed by DFT – it was suggested that the ligated H₂O on the defects of the Zr-node facilitated the formation of benzyloxide species; as a result, the abstraction of an α -hydrogen from the benzyloxide species by TEMPO oxoammonium yielded benzaldehyde, which is a more efficient route than directly oxidizing benzyl alcohol.

Figure 3. (a) Chemical structure of H₂tpdc-TEMPO; (b) X-ray crystallographic structure of UiO-68-TEMPO; (c) Zr-node contains one missing linker defect. Reproduced with permission from reference ⁶⁵. Copyright 2019 American Chemical Society.

Zhao et al.⁶⁶ reported on MIL-101(Cr), with a stable hierarchical structure, which was produced by using phenylphosphonic acid (PPOA) as a modulator, *via* hydrothermal synthesis.

The presence of phenylphosphonic acid created structural defects and generated larger mesopores. The synthesized hierarchical MIL-101(Cr) possessed a relatively good porosity, and the larger mesopores exhibited widths of 4–10 nm. The framework showed a significant improvement in catalytic activity for the oxidation of indene. In 2018, Epp et al.⁶⁷ synthesized three MOFs (MOF-525, PCN-222 and PCN-224), based on the Zr-oxo-cluster node and a porphyrin linker, exhibiting different linker connectivities of 12, 8 and 6, as well as their porphyrin-linker metallated analogues. The frameworks were tested as catalysts in the cycloaddition of CO₂ and propylene oxide to propylene carbonate. The authors found that the catalytic activity correlated with the connectivity of the Zr-oxo nodes – within this series, the least connected PCN-224 (6-fold) exhibited a superior catalytic activity, while the more connected PCN-222 (8-fold) and MOF-525 (12-fold) were less active. However, the catalytic activity of the high-connectivity MOFs significantly depended on the defects, *i.e.*, the 12-fold MOF-525, exhibiting 16% missing linker defects, was more active than the 8-fold PCN-222 with fewer defects. Metallation of the porphyrin linkers with Mn(III) and Zn(II) centers increased the catalytic activity. Metallated centers acted as additional Lewis acid sites; in this case the higher activity was achieved with the metallated MOFs with higher connectivity. The disappearance of the correlation between the connectivity and catalytic performance with metallated MOFs comes from different linker/node ratios. PCN-222 has 2 linkers and MOF-525 has 6 linkers more per Zr₆-node than PCN-224. Mousavi et al.⁶⁸ also studied the CO₂ cycloaddition reaction in the absence of any solvent or co-catalyst using MOFs as catalysts. Four different M-DABCO MOFs (M=Zn, Co, Ni, Cu; DABCO stands for 1,4-diazabicyclo[2.2.2]octane) were synthesized by using a solvothermal method. Of the prepared MOFs, Zn-DABCO showed a superb activity and virtually 100% selectivity. Moreover, Zn-DABCO exhibited a significant activity comparable to or better than that of previously reported MOF catalysts for this reaction. The metal nodes in the ideal M-DABCO MOFs were

coordinatively saturated, so it was suggested that the catalysis took place at the structural and/or surface defects. The uncoordinated DABCO ligands played the role of co-catalyst, as they were present as basic sites. Chen et al.⁶⁹ reported the synthesis of a highly stable Ce-MOF (BIT-58). The particle size of BIT-58 was well tuned over a large size range by the coordination modulation method.⁶⁹ By decreasing the particle size from micrometres to nanometres, the mesopore volume increased about seven times ($0.35 \text{ cm}^3 \text{ g}^{-1}$ vs. $0.05 \text{ cm}^3 \text{ g}^{-1}$). Considering that most of this mesopore volume is located in the interparticle space, the available external area should be responsible for the observed increase in catalytic performance. In addition the defects of nano-BIT-58 became increasingly exposed (*i.e.*, ten times the total acid site amount), and the catalytic activity for the benzaldehyde to 2-benzylidenemalononitril transformation was largely increased (up to a 14-times increase in conversion efficiency) over that of BIT-58. The catalytic activity of ZIF-8 in the ring-opening polymerization of L-lactide without solvents or cocatalysts was reported by Luo et al.⁷⁰ Two different synthetic strategies were applied for synthesizing ZIF-8, the solvothermal approach and the spray-drying process. The catalytic activities were found to correlate with the presence of open active sites – structural defects that afforded active acidic and basic sites. The ZIF-8 assembled by the spray-drying technique displayed a superior catalytic activity at 160°C , leading to the formation of high-molecular-weight cyclic polylactides. The catalyst could be recycled and reused without any significant loss in activity. Chaemchuen et al.⁷¹ studied the creation and quantitative assessment of defects in ZIF-8, Zn-DABCO and MOF-5, obtained by different well-known synthesis procedures. The authors associated the crystallization rate with the structural arrangement and defect creation. The defect structures were found to enhance the catalytic activity of MOFs in different chemical reactions – the ring-opening polymerization of L-lactide and the Knoevenagel condensation. The defective MOFs showed high catalytic activities, which were explained by the presence of numerous acidic and basic sites originating from the defects. In the last two

cases, the authors did not comment on the pore size of ZIF-8 material, and, therefore, it is unclear whether the catalytic reactions took place inside the MOF's pores or on its surface.

2.3 Catalysis on decorated MOFs (de novo synthesis or post treatment)

In addition to the use of pristine and defective MOFs as catalysts, considerable efforts have been dedicated to the post-synthetic modification of these materials for catalytic applications.^{72,73}

For example, Cao et al.⁷⁴ provided an illustrative example of multivariate functionalities installed in a MOF (Figure 4). Typically, a multivariate MOF is a framework that contains two or more different functionalities; this can be achieved via mixed-linker one pot synthesis or by postsynthetic modification. In this study, LIFM-80 partook in the dynamic installation and uninstallation of functional secondary and ternary ligands in the primitive LIFM-28 as well as in metal-chelation and covalent-postmodification processes. Multiple active catalytic systems for oxidation, Knoevenagel condensation, click chemistry and other reactions were obtained. Another interesting example was reported recently by Zhou et al.⁷⁵ The authors described an isorecticular family of catalysts based on the multicomponent metal-organic framework MUF-77. The microenvironment around an active site was tuned by introducing functional groups (modulators) to the organic linkers at sites away from the catalytic unit. The catalysts produced in this way exhibited several unique features, including simultaneous enhancements in both reactivity and stereochemical selectivity for aldol reactions, the ability to catalyse Henry reactions that cannot be accomplished by homogeneous analogues, and a discrimination between different reaction pathways (Henry *vs.* aldol) that compete for a common substrate.

Figure 4. Generation of multivariate MOF catalysts *via* the dynamic spacer installation approach using proto-LIFM-28 and the resultant interconversions for different catalytic purposes. The molecular structures of the inserted functional spacers are illustrated for the crystal structures, in which the $-\text{ArSO}_3\text{H}$ group is simplified as an orange ball and Zr_6 -clusters are shown as purple polyhedrons. H and F are omitted for clarity. Reproduced with permission from reference 74. Copyright 2019 American Chemical Society.

In the following paragraphs we have divided additional works on post-synthetically modified frameworks into those focusing on CO_2 activation, C-H activation and other catalytic applications.

2.3.1 CO_2 conversion

The coupling of CO_2 with epoxides to produce cyclic carbonates is one of the most studied reactions in MOF catalysis (Scheme 3). Though polycarbonates can be formed as by-product, five-membered ring cyclic carbonate is the thermodynamic product of the reaction. The

reaction requires a cocatalyst, typically a tetraalkylammonium halide. The cocatalyst is believed to play the role in the formation of halo-alkoxide intermediate via nucleophilic attack on the activated by catalyst epoxide. This intermediate undergoes cycloaddition with carbon dioxide, resulting in the formation of a cyclic carbonate and co-catalyst regeneration.

Scheme 3. Carbon dioxide epoxidation reaction.

To achieve a high activity, many researchers have focused on improving the MOF CO₂ sorption capacity. Imidazoles and/or ionic liquids, which are known for their high carbon dioxide solubility and capture, have largely served to provide interesting solutions.⁷⁶ Bhin et al.⁷⁷ explored the catalytic prospective of chloro-functionalized ZIF-95 in capturing and coupling CO₂ *via* its cycloaddition with epoxides under solvent-free conditions. Though the framework alone was active at high temperatures, the addition of a quaternary ammonium co-catalyst was found to be crucial in providing a synergistic effect, thus, allowing for higher conversions at lower temperatures. The solvent-free coupling of CO₂ with epoxides was also reported by Demir et al.⁷⁸ The Zr-based MOF-53, with the *fcu* topology of UiO-67, was post-metallated with vanadium chlorides to produce MOF-53-VCl₃ and MOF-53-VCl₄. These frameworks were obtained from ZrCl₄, biphenyl-4,4'-dicarboxylic acid, and 2,2'-bipyridine-5,5'-dicarboxylic acid, which provided Lewis basic sites for the post-metalation and CO₂ activation, and from formic acid to prevent the coordination of biphenyl to Zr(IV) ions *in situ*, acting as a ligand. MOF-53 showed a BET surface area of 1821 m² g⁻¹, which decreased to 1343 and 1263 m² g⁻¹ after post-metalation for MOF-53-VCl₃ and MOF-53-VCl₄. When MOF-53 was used as a catalyst with 4-dimethylamino pyridine (DMAP) as a co-catalyst, a yield of 79.6%

was obtained, which was higher than that for ZrCl_4 (70.1%), UiO-67 (64.3%), UiO-67 (58.6%), as well as MOF-53- VCl_4 (49.9) and MOF-53- VCl_3 (40.5). Metallated MOFs showed a lower activity due to the decreased surface area and pore volume. Additionally, the yield gradually decreased after several catalytic runs, due to the active site poisoning by the product. A bifunctional imidazolium-functionalized MOF was reported by Liang et al.⁷⁹ (I-)Meim-UiO-66 (Zr) was prepared from the imidazole-containing Im-UiO-66 *via* the isorecticular synthesis and post-synthetic modification method by stirring and refluxing the reactant in a CH_3CN suspension of methyl iodide. The framework, containing Brønsted acid sites and iodide ions, acted efficiently in the same reaction for a broad range of substrates and without the addition of a co-catalyst. The same group also implemented imidazole moieties within so-called FJI-C10 — a chromium-based MOF with acidic Cr^{3+} sites and free halogen ions — *via* a mixed-ligand strategy.⁸⁰ Ding et al.⁸¹ decorated UiO-67 with an ionic liquid *via* the solvothermal assembly of the imidazolium-decorated biphenyl ligand and Zr^{4+} ions. Because of this functionalization, the framework exhibited adsorption of carbon dioxide that was highly selective over methane and nitrogen and was proven to be an active catalyst for CO_2 cycloaddition. Kurisingal et al.⁸² modified the pores of UiO-66- NH_2 with methylimidazolium- and methylbenzimidazolium-based IL units through a condensation reaction to generate ILA@U6N and ILB@U6N catalysts. Ding and Jiang⁸³ incorporated imidazolium-based poly(ionic liquid)s into a MIL-101 *via* the in situ polymerization of encapsulated monomers.

Aguila et al.⁸⁴ inserted a linear ionic polymer into MIL-101(Cr) to form MIL-101(Cr)-IP. The composite catalysed the fixation of carbon dioxide into epoxides at 50 °C, outperforming the individual counterparts and a physical mixture under the same reaction conditions. The enhanced performance of MIL-101(Cr)-IP was attributed to the cooperative catalysis between closely located halide ions on the linear polymer and the Cr^{III} Lewis-acid sites of MIL-101(Cr). In 2017, Gao et al.⁸⁵ developed an ultrastable zirconium-phosphonate

framework, Zr(H₄L), as a bifunctional catalyst with a co-catalyst of tetrabutylammonium bromide (TBAB) for the same CO₂ transformation. The non-porous framework, with embedded Lewis acid and Brønsted acid sites, consisted of infinite one-dimensional [Zr-O-P-O] chains and tetraphenylsilane tetrakis-4-phosphonic (H₄L) anions. The MOF's high activity was explained by the electron-withdrawing effect of the phenoxymethyl group facilitating the nucleophilic attack during the ring opening of the epoxide. Tang et al.⁸⁶ developed a new heterobimetallic system – Au/Zn-MOF – of regular hexahedral (RH) and rhombic dodecahedral (RD) MOF nanocages. The nanocages provided a high surface area (1129 m² g⁻¹), multiple highly dispersed active sites, an ordered porous MOF shell, and a controllable morphology and shell thickness. The Au/Zn-MOF was employed to catalyse the cycloaddition of CO₂ and epoxides under mild temperature and pressure conditions. The high catalytic performance of the catalyst was rationalized by the synergetic effect of the two metallic components and the unique hollow structures.⁸⁶ A plethora of other CO₂ cycloaddition MOF-based systems have been developed, *e.g.*, the zinc-based ZIF-23,⁸⁷ the solvent-free amine-functionalized solvothermal (s)- or microwave (m)-assisted NH₂-MIL-101(Al),⁸⁸ the zirconium-based VPI-100 (Cu) and VPI-100 (Ni),⁸⁹ and flexible Zn-based MOFs,⁹⁰ as well as the mononuclear Cu^{II} MOF⁹¹ and Cd^{II} MOF.⁹² The catalytic systems for CO₂ insertion into epoxides are summarized in the Table 1, where decorated, *de novo* synthesized, and pristine MOF-based catalysts are included.

Table 1. MOFs as catalysts for the CO₂-epoxide coupling reaction.

MOF	Substrate	Yield / %	Cocatalyst	Temperature / °C	CO ₂ pressure / atm	Time / h	Reference
ZIF-95	propylene oxide	91	TBAB	120	11.8	24	⁷⁷
MOF-53(Zr)	epichlorohydrin	98	DMAP	100	15.8	2	⁷⁸

(I ⁻)Meim-UiO-66	allyl glycidyl ether	74	No	120	1	24	79
(I ⁻)Meim-UiO-66	epichlorohydrin	93	no	120	1	24	79
(I ⁻)Meim-UiO-66	styrene oxide	33	no	120	1	24	79
FJI-C10(Cr)	epichlorohydrin	87	no	60	1	24	80
UiO-67-IL	epichlorohydrin	99	TBAB	90	1	3	81
UiO-67-IL	epichlorohydrin	75	no	90	1	3	81
ILA@U6N	epichlorohydrin	94	no	80	11.8	4	82
polyILs@MIL-101	epibromohydrin	85	no	70	1	24	83
polyILs@MIL-101	1,2-epoxyhexane	89	no	70	1	24	83
polyILs@MIL-101	1-butene oxide	94	no	45	1	48	83
MIL-101(Cr)-IP	epichlorohydrin	99	no	50	1	68	84
Zr(H ₄ L)	styrene oxide	95	TBAB	100	9.8	12	85
Zr(H ₄ L)	epichlorohydrin	>99	TBAB	100	9.8	10	85
RH-Au/Zn-MOF nanocages	propylene oxide	56	no	r.t.	1	6	86
RH-Au/Zn-MOF nanocages	propylene oxide	98	no	70	30	6	86
RD-Au/Zn-MOF nanocages	propylene oxide	96	no	70	30	6	86
ZIF-23(Zn)	propylene oxide	70.3	no	100	29.6	24	87
ZIF-23(Zn)	propylene oxide	49.1	TBAB	60	11.8	6	87
s-NH ₂ -MIL101(Al)	styrene oxide	96	TBAB	120	18	6	88
m-NH ₂ -MIL101(Al)	styrene oxide	95	TBAB	120	18	6	88
s-NH ₂ -MIL101(Al)	styrene oxide	14	no	120	18	6	88
m-NH ₂ -MIL101(Al)	styrene oxide	11	no	120	18	6	88

VPI-100(Ni)	epichlorohydrin	98	<i>n</i> -Bu ₄ NBr	90	10	6	89
VPI-100(Cu)	epichlorohydrin	95	<i>n</i> -Bu ₄ NBr	90	10	6	89
VPI-100(Ni)	1,2-epoxyhexane	20	<i>n</i> -Bu ₄ NBr	90	10	6	89
VPI-100(Cu)	1,2-epoxyhexane	18	<i>n</i> -Bu ₄ NBr	90	10	6	89
Zn-MOF	epichlorohydrin	>99	TBAB	RT	bubbling	<i>n.a.</i>	90
Cu MOF	epichlorohydrin	99	TBABr	80	19.7	4	91
Cd ^{II} MOF (HL-7)	propylene oxide	75.5	TBAB	RT	1	<i>n.a.</i>	92

In 2017, Xiong et al.⁹³ reported on two cluster-based MOFs assembled from multinuclear Gd- and Cu-clusters. The MOFs [Gd₃Cu₁₂I₁₂(IN)₉(DMF)₄]_{*n*}.*n*DMF] and [Gd₄Cu₄I₃(CO₃)₂(IN)₉(HIN)_{0.5}(DMF)(H₂O)]_{*n*}.*n*DMF.*n*H₂O] (HIN stands for isonicotinic acid; denoted as MOF I and II, respectively) were tested as catalysts for CO₂ carboxylation with 14 kinds of terminal alkynes at 1 atm and 80-100 °C. Both MOFs showed high thermo- and solvo-stabilities and a high catalytic activity – for all 14 substrates, with either electron-withdrawing or electron-donating groups, and the yields of the corresponding esters were found to be higher than 52% or 65% for MOFs I and II, respectively. The multinuclear building blocks [Cu₁₂I₁₂] and [Cu₃I₂], from which these MOFs were assembled, were also believed to be the catalytic centres. MOFs I and II were able to capture 11.8 and 17.3 cm³ g⁻¹ of CO₂ at 273 K and 1 atm, respectively. These adsorption processes possibly enhanced the concentration of CO₂ around the [Cu_{*x*}I_{*y*}] clusters, which would account for the divergence in the catalytic activities of the two MOFs – MOF II had a higher capacity and therefore higher conversion. Zhou et al.⁹⁴ reported on a porous silver coordination polymer as a catalyst for the same reaction. The active silver(I) ions endowed a specific alkynophilicity to activate the C≡C bonds of alkyne-containing molecules *via* π activation. The catalyst provided yields above 92% for the cyclization of a broad range of propargylic alcohols with CO₂ when triphenylphosphine was used as a co-catalyst. Ji et al.⁹⁵ anchored single Ru atoms and triatomic Ru₃ clusters on ZIF-8.

The authors discovered a high catalytic activity toward the semi-hydrogenation of alkynes. Interestingly, the ZIF-8 shell served as a molecular sieve for olefins to achieve absolute regioselectivity of the catalysing terminal alkynes but not internal alkynes. Propargylic alcohol carboxylation was also studied by Hou et al.⁹⁶ The researchers employed $[(\text{NH}_2\text{C}_2\text{H}_6)_{0.75}[\text{Cu}_4\text{I}_4(\text{L})_3-(\text{In})_{0.75}]\cdot\text{DMF}\cdot\text{H}_2\text{O}]$ (L = isonicotinic acid) cluster-based heterometallic MOFs and obtained yields above 90% for a broad range of substrates. Another approach for CO_2 utilization focuses on its fixation into poly(alkylene carbonates), as was reported by Padmanaban et al.⁹⁷ The authors enhanced the activity of a zinc glutarate MOF by etching its surface with HCl and preparing nanosized MOF particles. Kang et al.⁹⁸ prepared three new 3D MOFs $[[\text{M}_2(\text{XN})_2(\text{IPA})_2]\cdot 2\text{H}_2\text{O}]_n$ ($\text{M}=\text{Co}$ (1), Mn (2), Ni (3)) by the solvothermal method. All three compounds served as efficient heterogeneous catalysts for the cycloaddition of aziridine and CO_2 under mild conditions, while compound 1 could be reused at least five times without any significant decrease in catalytic activity. Zhang et al.⁹⁹ performed successful CO_2 hydrosilylation over UiO-68 that contained metal-free N-heterocyclic carbene moieties, which were installed by a post-synthetic ligand exchange.

Over the last two years, to the best of our knowledge, only a few works have been dedicated to MOF single-site-based catalysts for carbon dioxide conversion to oxygenates. In 2017, An et al.¹⁰⁰ immobilized molecular iridium complexes into a UiO-type MOF *via* refluxing with $\text{IrCl}_3\cdot 3\text{H}_2\text{O}$ in mixture of THF and DMF. The catalytic hydrogenation of CO_2 to form formic acid/formate was performed by placing the MOF catalyst in a Soxhlet-type reflux-condensing system. Droplets of hot water seeped through the MOF catalyst to create dynamic gas/liquid interfaces, which maximized contact between the CO_2 , H_2 , and H_2O and the catalyst to achieve a high turnover frequency of 410 h^{-1} at atmospheric pressure and $85\text{ }^\circ\text{C}$. Li et al.¹⁰¹ encapsulated the ruthenium complex $(\text{tBuPNP})\text{Ru}(\text{CO})\text{HCl}$ (tBuPNP = 2,6-bis((di-tert-butylphosphino)methyl)pyridine) in UiO-66 *via* an aperture-opening process resulting from

dissociative linker exchange (Figure 5). The resulting encapsulated complex, [Ru]@UiO-66, was a very active catalyst for the hydrogenation of CO₂ to formate in DMF/*l*,8-diazabicyclo(5.4.0)undec-7-ene (DBU) mixtures. Unlike the analogous homogeneous catalyst, [Ru]@UiO-66 could be recycled five times, showed no evidence for molecular catalyst decomposition, and was less prone to catalyst poisoning.

Figure 5. Catalysis with MOFs using aperture-opening encapsulation. Reproduced with permission from reference 101. Copyright 2018 American Chemical Society.

2.3.2 C-H bond activation

C-H bond activation is another group of reactions that is very popular among MOF researchers.¹⁰²

Wang et al.¹⁰³ described how a Mn-based metal–organic framework (CPF-5) promoted the direct amination of C-H bonds with an unprecedented activity for a Mn-based system. Hoang et al.¹⁰⁴ employed Cu-CPO-27 as a recyclable heterogeneous catalyst for the direct C-H amination of quinoxalin-2(*1H*)-ones with amines to produce 3-aminoquinoxalin-2(*1H*)-ones. High yields (up to 89%) were achieved in the presence of molecular oxygen as the oxidant. Tran et al.¹⁰⁵ presented the synthesis of copper-based VNU-18, with the copper cluster

possessing three kinds of geometrical cluster units. This material was demonstrated as an active catalyst for the direct coupling of a wide range of carbonyls and N–H amines. Pham et al.¹⁰⁶ reported on the mixed-linker iron-based MOF VNU-20 [Fe₃(BTC)(NDC)₂·6.65H₂O] that was solvothermally synthesized from 1,3,5-benzenetricarboxylic acid, 2,6-naphthalenedicarboxylic acid and FeCl₂. VNU-20 was utilized as a recyclable catalyst for the functionalization of coumarins with *N,N*-dimethylanilines (yield 84%) *via* direct C–H bond activation. To et al.¹⁰⁷ synthesized VNU-21 [Fe₃(BTC)(EDB)₂·12.27H₂O] *via* a mixed-linker synthetic strategy using 1,3,5-benzenetricarboxylic acid, 4,4'-ethynylenedibenzoic acid, and FeCl₂. VNU-21 was consequently used as a recyclable heterogeneous catalyst in the one-pot synthesis of quinazolinones *via* two steps under an oxygen atmosphere. Xu et al.¹⁰⁸ developed an efficient route for the synthesis of diverse benzimidazoles from the 537-MOF [Cu₂(TPPB)₂](DMF)₆]-catalysed C–H functionalization of amidines. This process featured not only operation in air, instead of an O₂ atmosphere, but also a broad substrate scope and good functional-group compatibility, wherein challenging amidines derived from aryl nitriles without ortho-substituents afforded products in high yields.¹⁰⁸

In 2017, Ikuno et al.¹⁰⁹ reported on a first-generation MOF-based catalyst for the selective conversion of CH₄ to CH₃OH using a Cu-NU-1000 material. Cu-NU-1000 comprises Cu-oxo clusters that are deposited over zirconium-based nodes of NU-1000 *via* atomic layer deposition (ALD). Copper was present under ambient conditions as a mixture of ~15% Cu⁺ and ~85% Cu₂⁺, as shown by X-ray absorption spectroscopy (XAS). A combined extended X-ray absorption fine structure (EXAFS) and DFT study showed that the predominant cluster was likely to be a trimeric Cu-hydroxide-like structure that bridged two nodes across the c-pore of the MOF. Methane activation was performed at atmospheric pressure and temperatures of 150 °C and higher using a catalyst pre-activated in an O₂ flow. The obtained results showed that a significant fraction of the Cu atoms appeared to be spectators. Nevertheless, the active Cu

species deposited on NU-1000 converted methane to methanol and dimethyl ether with a 45–60% selectivity, with the remainder being CO₂. Extra CO₂ was reported to be produced during the first catalytic run – the result of partial linker decarboxylation. The installation of Cu active sites within a MOF for the same reaction was also reported by Baek et al.¹¹⁰ in 2018. The researchers were inspired by the particulate form of methane monooxygenase (pMMO) – an enzyme that is capable of oxidizing methane under mild conditions. MOF-808 was chosen as a scaffold for the catalyst design. The judicious choice of a framework with appropriate topology and chemical functionality allowed the post-synthetic installation of imidazole-bearing units for subsequent metalation with Cu(I) in the presence of O₂. The catalyst showed a high selectivity for methane oxidation to methanol under isothermal conditions at 150 °C. Spectroscopic analyses and DFT calculations suggested a bis(μ -oxo) dicopper species ligated to biologically relevant imidazole moieties – the same species as the inspirational pMMO contains – as probable active sites of the catalyst. In the same year, Osadchii et al.¹¹¹ reported on the selective C-H bond oxidation of CH₄ by MIL-53(Al), where isolated antiferromagnetically coupled high-spin Fe species were post synthetically integrated into the MOF's crystalline scaffold either by electrocatalytic or hydrothermal exchange. Similarly isolated Fe sites are found in soluble methane monooxygenase (sMMO, Figure 6a). The obtained MIL-53 (Al, Fe) catalysts were tested in the direct methane oxidation at 60 °C and 30 bar in aqueous media, using hydrogen peroxide as an oxidant. The catalysts prepared through an electrochemical protocol resulted in a multitude of isolated mono and dimeric Fe species and in the best catalytic performances, with *TOFs* on the order of 90 h⁻¹ and selectivities towards oxygenates of *ca.* 80% (Figure 6b). The suggested mechanism, based on the spectroscopic data and DFT calculations, is shown in Figure 6c. Firstly, H₂O₂ was activated by the dimeric Fe species, and a bridging hydroxyl group was formed and stabilized. Then, the bridging O site in Fe-(μ -O)-Fe homolytically cleaved the C-H bond, resulting in the formation

of a terminal Fe-OH species and CH₃ radical. Finally, the former recombined with the latter, and adsorbed methanol was formed.

Figure 6. MOF-mediated direct methane oxidation: (a) the structure of the sMMO enzyme, where each $\alpha_2\beta_2\gamma_2$ dimer contains two di-iron active sites (blue spheres and ball-and-stick representation); (b) the MIL-53(Al, Fe) catalyst, with a ball-and-stick representation of a site-isolated Fe within the MIL-53 octahedral [AlO₆] chain; and (c) the proposed mechanism for methane oxidation to methanol with H₂O₂ over the dimeric Fe site in MIL-53(Al, Fe). Reproduced with permission from reference 111. Copyright 2018 American Chemical Society.

2.3.3 Other reactions

In 2017, Pourkhosravani et al.¹¹² reported two post-synthetic strategies to covalently anchor oxovanadium(IV) complexes to the organic linkers of UiO-66(NH₂). In the first method, the available amino groups of UiO-66(NH₂) were treated with salicylaldehyde to form a modified UiO-66 (UiO-66-SI). The synthesized UiO-66-SI was then treated with [VO(acac)₂] to produce UiO-66-SI/VO(acac). In the second method, UiO-66(NH₂) was directly treated with [VO(acac)₂] to form UiO-66-N/VO(acac)₂. The catalytic performances of UiO-66-SI/VO(acac) and UiO-66-N/VO(acac)₂ were tested in the epoxidation of geraniol with tert-

butyl hydroperoxide. The results indicated 100% conversion with 100% selectivity towards 2,3-epoxygeraniol after 60 and 120 min of reaction time. The catalytic activity was attributed to the high dispersion of the catalytic sites on the MOF and to the proper pore size of UiO-66(NH₂). The structures of both catalysts remained intact after three catalytic runs. Zhang et al.¹¹³ metallated a UiO-67-like framework with an iridium(III) complex to obtain a methane borylation catalyst. The pristine framework was prepared *via* a mixed-linker “doping” method, where 1,10-phenanthroline-3,8-dicarboxylic acid was used to partially displace BPDC. The iridium complex [Ir(1,5-cyclooctadiene) μ -Cl)]₂ was used as the active site precursor. The catalyst exhibited a selectivity of >99% for monoborylated methane, with bis(pinacolborane) as the borylation reagent in dodecane, at 150 °C and 34 atm of methane. The preference for the monoborylated product was ascribed to the shape-selective effect of the MOF pore structures. Li et al.¹¹⁴ studied the size effect of active sites in UiO-66-supported nickel catalysts, synthesized *via* atomic layer deposition (ALD), on ethylene hydrogenation. The size was varied by applying a different number of ALD cycles; the largest clusters displayed the highest per-nickel-atom activity. Non-innocent catechol groups have been introduced into the backbones of UiO-68-like zirconium based MOFs by Zhang et al.¹¹⁵ The framework underwent metalation of the phenylcatechol groups with Cu(II) engenders Cu(I) species, and the final solid exhibited high catalytic activity for cyclohexene oxidation. The redox properties of the non-innocent catechol ligands were employed to alter the catalytic activity of the metallated MOFs by modifying the oxidation state of the active catalyst. Zhang et al.¹¹⁶ reported a urea-containing UiO-68 isorecticular PCN-56-UM with mixed terphenyldicarboxylate struts –H₂-mtpdc and H₂-utpdc, Figure 7, – by utilizing a microwave-assisted heating method. The solid worked as an efficient hydrogen-bond-donating heterogeneous catalyst for the Henry reactions of benzaldehydes and nitroalkanes. This mixed-strut MOF exhibited an improved catalytic activity compared to that of the analogue based purely on the urea-functionalized linker.

Elumalai et al.¹¹⁷ described a recyclable and highly active nickel catalyst immobilized on an azide-functionalized UiO-66 platform for the Suzuki–Miyaura coupling reaction, which operates under mild conditions. Prior to the nickel introduction, a series of bidentate ligands on the MOF surface were installed *via* an azide-alkyne “click” reaction. This mixed-ligand catalyst formed from a combination of 1 equivalent of MOF-immobilized ligand, 1 equivalent of nickel source, and 1 equivalent of PPh₃. High yields (up to 93%) were obtained for a broad range of substrates.

Figure 7. Rapid preparation of the mixed-strut MOF PCN-56-UM with TPDC linkers of 2',5'-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (denoted as H₂-mtpdc) and 2'-(3-(3,5-bis(trifluoromethyl)phenyl)ureido)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (denoted as H₂-utpdc) *via* a microwave method. Reproduced with permission from reference 116. Copyright 2019 Royal Society of Chemistry.

In 2017, Oozeerally et al.¹¹⁸ reported on the conversion of glucose into fructose and 5-hydroxymethylfurfural (HMF) using UiO-66-MSBDC. In this study, starting with pristine UiO-66, the organic linker was partially replaced by 2-monosulfo-benzene-1,4-dicarboxylate (MSBDC), used as an additional Brønsted site. The ratio between BDC and MSBDC linkers

was found to be crucial for the MOF's stability, where a high MSBDC content led to framework collapse. The catalyst with 20% of MSBDC showed a yield of 28% at 140 °C in water after 3 h of reaction time, while the pristine UiO-66 showed only a 10% yield. The recyclability test revealed only a slight loss in activity after the third catalytic run. A phosphate-modified NU-1000 was also tested in the same reaction, as was reported by Yabushita et al.¹¹⁹ The selective Lewis acid in the MOF was introduced *via* phosphate immobilization within the MOF by a simple impregnation method. The catalytic data demonstrated that partial phosphate modification was beneficial in terms of maximizing the HMF yield since the strong Lewis acid sites were poisoned by the oxo substituents of the grafted phosphate species, which would otherwise facilitate side reactions. In contrast, fully poisoning the Brønsted acid sites diminished the catalytic performance of the zirconia-cluster nodes.

The latter case and the aforementioned work by Ikuno et al.¹⁰⁹ are two of many examples where the NU-1000 framework played the role of a catalyst scaffold. NU-1000 has largely been explored as a platform for catalyst development.¹²⁰ Its structure can be visualized as a trihexagonal tiling, built using eight connected $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{H}_2\text{O})_4(\text{OH})_4$ nodes at each vertex and tetratopic 1,3,6,8-(*p*-benzoate)pyrene linkers positioned at each edge.¹²¹ The framework is highly stable, both chemically and thermally, due to the strong bonding between the zirconium nodes and the carboxylates of the linkers. The framework also possesses Lewis acidity on the Zr_6 nodes and exceptionally wide (31 Å) mesoporous channels that can facilitate mass transport, both important features for catalyst design.¹²² Kim et al.¹²³ installed single atoms and few-atom clusters of platinum at the zirconia nodes of NU-1000 *via* a targeted vapour-phase synthesis. The catalytic Pt clusters, site-isolated by organic linkers, exhibited a high catalytic activity for ethylene hydrogenation while being resistant to sintering up to 200 °C. Rimoldi et al.¹²⁴ also employed ALD, using tetramethoxysilane ($\text{Si}(\text{OMe})_4$) as a precursor, for NU-1000 post functionalization. This treatment led to the incorporation of silicon

oxide clusters composed of only a few silicon atoms in the framework's pores. The resulting material was found to be catalytically active, despite the inactivity of related bulk silicon dioxide, thus, demonstrating the positive effects of having nanosized clusters of SiO_x. Hydroxylated aluminium ions were installed within NU-1000 *via* ALD by Yang et al.¹²⁵ Single-site iridium diethylene complexes were anchored to the nodes of the modified and unmodified MOFs by reaction with Ir(C₂H₄)₂(acac) (acac = acetylacetonate) and then converted to Ir(CO)₂ complexes by treatment with CO. The infrared spectra of these supported complexes showed that the incorporation of Al weakened the electron donor tendency of the MOF and therefore increased the catalytic activity of the initial supported iridium complexes for ethylene hydrogenation, as did the selectivity for ethylene dimerization. Li et al.¹²⁶ dispersed few-atom cobalt oxide clusters on a NU-1000 *via* two distinct routes, namely, a solvothermal deposition on the MOF (SIM) and atomic layer deposition on the MOF (AIM), denoted as Co-SIM+NU-1000 and Co-AIM+NU-1000, respectively. Both frameworks were found to be active for the catalytic oxidative dehydrogenation (ODH) of propane to propene at reaction temperatures as low as ~200 °C. Cobalt was found to be the active species, with the initial catalyst activation (ligand loss + cobalt oxidation) being achieved by heating in O₂. Different catalytic activities, as well as selectivities, toward propene formation were observed under the same experimental conditions for these two materials. For the same conversions and conditions, the selectivity for Co-AIM+NU-1000 was higher than that for Co-SIM+NU-1000. This result was rationalized by the differing distributions of the Co sites in these two materials during catalysis. In the authors' other work, the effect of promoters was studied.¹²⁷ It was reported that a range of inorganic catalytic promoters – oxy clusters of Ni(II), Zn(II), Al(III), Ti(IV), and Mo(VI) – could be controllably introduced into a catalytic assembly comprising cobalt(II)oxo,hydroxo species (active-site precursors) on the zirconia-like nodes of NU-1000. While the weakly Lewis acidic promoters accelerated the cobalt-mediated propane ODH, the

strongly acidic metal oxides slowed the reaction. The observed catalytic activities for the metal-ion-promoted ODH of propane followed the order $\text{Ni(II)} > \text{Zn(II)} > \text{Al(III)} > \text{Ti(IV)} > \text{Mo(VI)}$. Later, a method allowing to redirect cobalt deposition to different sites in a well-ordered support was described. Naphthalene dicarboxylate linkers were incorporated into the MOF and were used to bridge between two adjacent nodes in NU-1000, inducing the cobalt ions to coordinate in previously unfavourable sites.¹²⁸ Otake et al.¹²⁹ reported the synthesis and oxidation catalytic activities of a single-atom-based vanadium oxide incorporated in NU-1000 and MOF-808(Hf). The vanadium moieties were introduced by a post synthetic metalation, and they were found to coordinate differently to the nodes of MOF-808 versus those of NU-1000. MOF-808-V revealed that the as-prepared material, while featuring only a single vanadium atom per node, employed three distinct vanadium binding sites. Heating changed the siting positions such that the vanadium ions would occupy essentially only a single site. The activity of the single-site version of the catalyst in the oxidation of 4-methoxybenzyl alcohol under an oxygen atmosphere was thrice that of the multisite version. Buru et al.¹³⁰ incorporated phosphotungstic acid (PTA) into NU-1000 *via* an impregnation method in aqueous media, which resulted in the hybrid material $\text{PW}_{12}\text{@NU-1000}$. The composite material presented the highest polyoxometalate (POM)/node loading synthesized by this method while still maintaining a high porosity. POM@NU-1000 was tested as a heterogeneous catalyst for the oxidation of 2-chloroethyl ethyl sulfide using hydrogen peroxide as the oxidant. The MOF showed a higher catalytic activity than that of either of the individual constituents alone. The difference between the heated and as-synthesized materials was attributed to the thermally induced POM migration.¹³¹ Ahn et al.¹³² used PTA encapsulated within NU-1000 as a catalyst for *o*-xylene isomerization. A maximal loading of ~ 1 POM per unit cell of NU-1000 appeared to stabilize the structures of both the PTA and NU-1000. When WO_x was installed by other methods, such as by the impregnation of tungsten amido complexes, isolated WO_x sites

appeared to be unreactive in this reaction. The POM@NU-1000 catalyst showed an atypical selectivity toward disproportionation that likely resulted from the particular pore structure of the MOF support, in which two Keggin units were stabilized in close proximity in the smaller side channels of the MOF. A molecular nickel catalyst for ethylene dimerization was also achieved with NU-1000 as a scaffold.¹³³ The molecular modifiers Facac- and Acac- were introduced to the MOF in an atomically precise fashion *via* an ALD-like, vapour-phase delivery mechanism; they consequently displaced node aqua and hydroxo ligands and bound to Zr(IV) in a chelating fashion. Compared with the modifier-free catalyst, the materials exhibited a low catalytic activity but good selectivity, with the exclusive formation of butenes and a strong preference for the 1-butene isomer. The same group later explored a related concept: the authors were able to tune the support/catalyst interactions and therefore the catalyst activity *via* the parallel installation of organic modifiers on the support itself.¹³⁴ In 2019, Goetjen et al.¹³⁵ supported chromium onto Zr₆ nodes *via* a solvothermal deposition – liquid-phase metalation. The obtained Cr-SIM-NU-1000 showed a conversion of 20% and *TOFs* of *ca.* 60 h⁻¹ in ethylene oligomerization, with the C₈-C₂₈ product range following the Schulz-Flory distribution; the results revealed that the Cr-based MOF possessed a catalytic activity superior to that of Cr₂O₃. The catalysis took place at the ambient temperature and 1 bar of ethylene with a minimal cocatalyst quantity. NU-1000 stabilized chromium against chemical deactivation and metal leaching from the heterogeneous system. Selective alkyne semihydrogenation to *E*-alkenes was achieved when heterobimetallic active sites, comprising Rh as an active metal and Ga as a promoter, were preassembled and delivered onto NU-1000.¹³⁶ High selectivity was achieved by engineering close proximity between Ga and Rh. The obtained Rh-Ga site was found to be responsible for both the chemoselective hydrogenation of alkynes (over alkenes) and the stereoselective alkene isomerization to acyclic *E*-alkenes.

In 2017, Metzger et al.^{137,138} reported the use of a cation-exchanged MFU-4l (MFU-4l = $\text{Zn}_5\text{Cl}_4(\text{BTDD})_3$, H_2BTDD = bis(*IH*-1,2,3-triazolo[4,5-*b*],[4',5'-*i*])dibenzo[1,4]dioxin). Although the direct solvothermal synthesis of a nickel-doped MFU-4l from mixtures of Ni^{2+} and Zn^{2+} starting materials was unsuccessful, a simple exchange of the parent zinc framework, obtained by soaking in an *N,N*-dimethylformamide (DMF) solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, led to the nickel-substituted materials, where the Ni content could be tuned by varying the soaking time and temperature. Exchanging Zn^{2+} ions for Ni^{2+} did not affect the structural integrity or the porosity of the framework. Ni-MFU-4l displayed a high activity for ethylene dimerization, using methylaluminoxane (MAO) as a cocatalyst, due to the creation of well-defined and site-isolated Ni(II) active sites bearing a close structural homology to molecular tris-pyrazolylborate complexes. In propylene dimerization, the catalyst showed a high selectivity towards branched hexenes.¹³⁹ Another interesting example of the MOF-based catalytic platform is the primary-amide-functionalized metal organic framework, $[\text{Zn}_2(2\text{-BQBG})(\text{BDC})_2] \cdot 10\text{H}_2\text{O}]_n$ (2-BQBG = 2,2'-(butane-1,4-diylbis((quinolin-2-ylmethyl)azanediyl))diacetamide), which was reported to be a highly efficient hydrogen-bond-donating heterogeneous catalyst for the Friedel–Crafts alkylation of indole and β -nitrostyrenes under mild reaction conditions.¹⁴⁰

Ji et al.¹⁴¹ showed that the $\text{Ti}_8(\mu_2\text{-OH})_4$ node of MIL-125 could be used as a support for a single-site Co^{II} -hydride catalyst for arene hydrogenation. Upon deprotonation, the Ti-oxo clusters coordinated to Co^{II} centres as a tetradentate ligand to afford MIL-125- CoCl without forming multi-Co oligomers due to the MOF site isolation effect. The treatment of MIL-125- CoCl with NaBEt_3H led to the partial reduction of the Ti-oxo support to form $\text{Ti}^{\text{III}}_2\text{Ti}^{\text{IV}}_6\text{-BDC-Co}^{\text{II}}\text{H}$, which featured electron-rich high-spin Co^{II} centres with electron-donating Ti^{III} -oxo ligands. The corresponding oxidized MOF $\text{Ti}^{\text{IV}}_8\text{-BDC-Co}^{\text{II}}\text{H}$ was totally inactive, suggesting the crucial role of Ti-oxo cluster reduction on the catalytic activity.

Lewis pairs (LP), stabilized within a MOF, gain stability upon recycling due to the sterically favourable environment that MOFs can offer. LP were installed within MIL-101(Cr) *via a* stepwise anchoring strategy by Niu et al.¹⁴² First, 1,4-diazabicyclo[2.2.2]octane (DABCO) was coordinated to Cr³⁺ open metal sites. Second, B(C₆F₅)₃ was introduced to form MIL-101(Cr)-LP. The strong coordination between MIL-101 and the LP stabilized the latter, therefore, preventing its leaching. The MIL-101(Cr)-LP composites were tested in the catalytic reduction of imines, showing a steady activity for at least seven cycles. LP, stabilized within UiO-67-NBF₂ were reported by Li et al.¹⁴³ The obtained catalyst showed activity toward the direct hydrogenation of carbon monoxide to formaldehyde. Shyshkanov et al.¹⁴⁴ synthesized SION-105, a water-stable MOF with a boron-based ligand, that provided the Lewis acidic sites for the *in situ* formation of LP upon the addition of a basic component. The system was tested as a catalyst for the non-metal-mediated and LP-mediated production of benzimidazoles from CO₂ and diamines, where the latter acted as a Lewis base.

Functionalized MIL-101(Cr)-SO₃H was employed by Sun et al.^{145,146} to support Ag or Cu catalysts. Both catalysts showed high activities for the solvent-free syntheses of propargylamines through A₃ coupling. Surprisingly, the Cu-based catalyst outperformed the Ag-based one – *TOFs* of 680000 h⁻¹ and 6600 h⁻¹, respectively. Huxley et al.¹⁴⁷ metallated a Mn^{II}-based MOF **1** (**1** = [Mn₃(L)₂(L')]), where H₂L = bis(4-(4-carboxyphenyl)-1H-3,5-dimethylpyrazolyl)methane and L' possesses a non-coordinated bis(3,5-dimethylpyrazol-1-yl)methane moiety) with [Mn(CO)₅Br].¹⁴⁷ The authors further anchored azide species to the Mn sites, following the introduction of a dialkyne for the “click” [3 + 2] cycloaddition reaction. The final liberation of the “click” products from the porous material was achieved by N-alkylation with MeBr, which regenerated the starting framework and organic product (Figure 8).

Figure 8. Graphical depiction of the site-isolation strategy using a dialkyne substrate, showing the introduction of the dialkyne, its “click” conversion, and then liberation by alkylation with MeBr to produce the desired *N*-methyl alkynyl triazole. Reproduced with permission from reference 147. Copyright 2018 American Chemical Society.

In addition, Crabtree’s catalyst was encapsulated inside the pores of the sulfonated MIL-101(Cr) *via* cation exchange by Grigoropoulos et al.¹⁴⁸ This hybrid catalyst was active for the heterogeneous hydrogenation of non-functionalized alkenes, either in solution or in the gas phase. The encapsulation enhanced the catalyst’s stability and selectivity towards hydrogenation over isomerization for substrates bearing ligating functionalities.¹⁴⁸ Porphyrin moieties were introduced into MOFs by Pereira et al.¹⁴⁹ The researchers used 5,10,15,20-tetrakis(*p*-phenylphosphonic acid)porphyrin (H₁₀TPPA) as a linker in the preparation of porphyrin-based Por-MOFs through coordination to lanthanides cations. The resulting materials, formulated as [M(H₉TPPA)(H₂O)_x]Cl₂·yH₂O [*x* + *y* = 7; M₃₊ = La³⁺, Yb³⁺, and Y³⁺], prepared using the hydrothermal synthesis, were evaluated as heterogeneous catalysts for the oxidation of thioanisole by H₂O₂. Nano-Por-MOFs proved to be effective catalysts, with Por-MOF (La) exhibiting the best catalytic performance with a conversion of thioanisole of 89% in the first cycle and with a high selectivity for the sulfoxide derivative (90%). The catalyst maintained a roughly constant activity for three consecutive runs.¹⁴⁹ Jiang et al.¹⁵⁰ synthesized

a 4-fold interpenetrated $[\text{Cd}_3(\text{tipp})(\text{bpdc})_2] \cdot \text{DMA} \cdot 9\text{H}_2\text{O}$ ($1 \cdot \text{Cd}$; $\text{H}_2\text{tipp} = 5,10,15,20$ -tetrakis(4-(imidazol-1-yl)phenyl)porphyrin). The present Cd and carboxylate oxygen afforded rich Lewis acidic and basic sites. The framework featured a high catalytic performance and recyclability for the cyanosilylation of various aldehydes with trimethylsilyl cyanide (TMSCN) and for the Knoevenagel condensation reactions of several aldehydes with malononitrile. Wang et al.¹⁵¹ incorporated an iridium-porphyrin complex, $\text{Ir}(\text{T CPP})\text{Cl}$ (T CPP = tetrakis(4-carboxyphenyl)porphyrin), into a MOF to generate Ir-PMOF-1(Hf) as a molecular nanoreactor for Si–H insertion reactions. Ir-PMOF-1(Hf) showed the highest selectivity for the most inert primary silanes, with an inverted selectivity order – primary > secondary > tertiary. Lv et al.¹⁵² reported a base-resistant porphyrin PCN-602 that was constructed with a 12-fold $[\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2\text{Pyrazolate}_{12}]$ cluster and the pyrazolate-based porphyrin ligand 5,10,15,20-tetrakis(4-(pyrazolate-4-yl)phenyl)porphyrin. Apart from its robustness in hydroxide solution, PCN-602 also showed a high stability in aqueous solutions of F^- , CO_3^{2-} , and PO_4^{3-} ions. The Mn^{3+} -porphyrinic PCN-602, as a recyclable MOF catalyst, presented a high catalytic activity for the C–H bond halogenation reaction (Scheme 4) in a basic system, significantly outperforming its homogeneous counterpart.

Scheme 4. C-H bond halogenation reaction catalysed by PCN-602

Castro et al.¹⁵³ synthesized a MOF material from the reaction of 5,10,15,20-tetrakis[2,3,5,6-tetrafluoro-4-(4-pyridylsulfanyl)phenyl]porphyrin with copper(II) acetate. The material showed a higher heterogeneous catalytic activity than did the homogeneous porphyrin–copper(II) complex for the oxidation of catechol into ortho-benzoquinone in the presence of air or H_2O_2 . MOFs are also allowed to heterogenize powerful pincer complexes. Burgess et al.¹⁵⁴ constructed a $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{L-PdX})_3$ metal organic framework (1-X) from Pd

diphosphinite pincer complexes ($[L-PdX]_4 = [2,6-(OPAr_2)_2C_6H_3]PdX]_4$, Ar = *p*-C₆H₄CO₂-, X = Cl, I) (Figure 9). The reaction of 1-X with $PhI(O_2CCF_3)_2$ facilitated the I-/ CF₃CO₂- ligand exchange to generate 1-TFA and I₂, as a soluble by-product. 1-TFA was found to be an active and recyclable catalyst (yields up to 89%) for the transfer hydrogenation of benzaldehydes using formic acid as a hydrogen source. In contrast, the homogeneous analogue *t*Bu(L-PdTFA) is an ineffective catalyst owing to the decomposition under the catalytic conditions, highlighting the beneficial effects of immobilization.¹⁵⁴ This approach was extended towards Pt and Pd PNP pincer complexes, and the framework denoted as 2-PdX showed a catalytic activity towards the hydroamination of *o*-alkynyl aniline providing a 77% yield of the desired product.¹⁵⁵ The catalyst, though, suffered from poor recyclability due to the consumption of the TFA- counteranions. When I-/ BF₄- was used in the ligand exchange instead of I-/ CF₃CO₂-, the catalyst showed higher Lewis acid catalytic activity and recyclability. The difference was attributed to the weaker coordinating nature of BF₄- and its lower propensity to undergo deleterious side reactions with the substrate.¹⁵⁶ Zhang et al.¹⁵⁷ designed and utilized a tritopic terpyridine-based linker to construct a mesoporous PCN-308 with β-crystobalite topology. Due to the direct one-pot synthesis, the terpyridine-based chelating sites were evenly distributed across the scaffold and could easily be accessed by post-synthetic metalation of redox-active metal ions under mild conditions. The scaffolded MOF materials Fe@PCN-308 and Co@PCN-308 contained high loadings of catalytic centres and turned out to be efficient catalysts for alkene epoxidation and arene borylation, respectively. Furthermore, another promising pincer-unit-containing MOF was synthesized, but its catalytic activity was not tested.¹⁵⁸

Figure 9. Synthesis and framework structure of 1-PdX. Reproduced with permission from reference 154. Copyright 2016 American Chemical Society.

Chen et al.¹⁵⁹ reported on the application of three porous chiral MOFs with the framework formula [Mn₂L(H₂O)₂] prepared from enantiopure phosphocarboxylate ligands of *1,1'*-biphenol that were functionalized with 3,5-bis(trifluoromethyl)-, bismethyl-, and bisfluoro-phenyl substituents at the 3,3'-position. The former MOF exhibited an enhanced tolerance to water, weak acids, and bases compared with that for the MOFs with -F and -Me groups. Under both batch and flow reaction systems, the CF₃-containing MOF demonstrated high yields and enantioselectivities for the alkylation of indoles and pyrrole with a range of ketoesters or nitroalkenes. In contrast, the corresponding homogeneous catalysts presented low enantioselectivity in the tested reactions. Later, the same group developed a broad library of 16 isostructural MOFs based on an enantiopure phosphocarboxylate ligand of *1,1'*-biphenol with pendant tert-butyl group at the 3,3'-position.¹⁶⁰ The series of MOF materials (Mg²⁺, Ca²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Pd²⁺, Pb²⁺, Cr³⁺, Fe³⁺, Al³⁺, Ga³⁺, Zr⁴⁺, Ti⁴⁺, and Sn⁴⁺) showed a regular variation in the Lewis acidity found to be able to catalyze four types of asymmetric organic transformations – asymmetric allylboration, propargylation, Friedel–Crafts alkylation and sulfoxidation – with an activity higher than that of the corresponding homogeneous systems. The number of MOFs employed in asymmetric catalysis is scarce. The reason behind

is current limitations in designing a MOF that has channels of a several nanometres in size. In order to achieve high enantioselectivity, the substrates (relatively large molecules) should be able to enter a chiral environment, and a product should be able to leave. Catalysis that happens on the surface decreases the chiral selectivity.

As of 2019, high-throughput computational screening can be a particularly appealing method to reduce the time-to-discovery of MOFs with desirable physical and chemical properties. *e.g.*, Rosen et al.¹⁶¹ tried a fully automated, high-throughput periodic density functional theory (DFT) workflow for screening promising MOF candidates was developed and benchmarked, with a specific focus on applications in catalysis. Considering the immense number of existing and potential MOFs, such a screening approach will become a very useful tool.

3 MOFs as supports for metal nanoparticles

Metal nanoparticles (MNPs) are among the most important catalytic sites. A large number of very relevant industrial processes rely on the use of metal nanoparticles. Of special interest for the application of MOFs are those in which catalytic performance in terms of selectivity is highly related with the size of the metal nanoparticle employed, the so-called structure sensitive reactions. In these cases, the objective of the catalyst engineer is to achieve a particle size distribution close to that of the optimal particle size for the reaction so that both activity and selectivity are maximized. The use of MOFs as hosts for metal nanoparticles has been explored since the early days of MOF catalysis,¹⁶²⁻¹⁶⁵ but probably only over the last few years real advances and improvements in performance over the state of the art catalysts have been reported. As comprehensively discussed above, MOFs' catalytic centres are either metal ions, which can act as Lewis acids, and/or organic linkers. Both of these centres can be tuned or modified, *e.g.*, it is relatively feasible to realize different dangling functional groups (such as –

NH₂, -SH, -SO₃H, -OH, *etc.*) on the linkers that should improve metal-support interactions¹⁶⁶⁻¹⁶⁸ and call for the use of MOFs as supports for nanoparticles. While a large body of papers claims that a synergistic effect between MOF and MNPs exists, this phenomenon varies in nature and is still poorly understood. However, this synergy has undoubtedly proven its importance in enhancing catalytic processes. These resulting composites often show a better performance in catalysis than do MNPs immobilized on conventional supports, *e.g.*, metal oxide, carbon-based and zeolite materials. A high dispersion of nanoparticles within the pores and easy access to active sites for substrates are typical for such composites since the support is highly porous and crystalline (ordered).

MOFs play different roles in these composites: they (i) stabilize MNPs within pores and control the uniform small particle size and distribution; (ii) assist in the selectivity of the reaction, *e.g.*, by sieving small substrate molecules and/or blocking oversized molecules from catalytic interactions; (iii) alter the electronic properties of MNPs by controlling their electronic density and the electron charge transfer between the MOF and an MNP; (iv) catalyse one-pot tandem reactions in which both the MOF and MNPs act as separate active sites in their respective reactions. MNPs within MOF structures should be thoroughly characterized, as it is crucial to assess the link between their environment and performance. Inductively Coupled Plasma (ICP), infrared and UV-vis spectroscopy, nuclear magnetic resonance are common tools to determine NPs' composition. XRD analysis is used to study the particle's size and whether the MOF's stability is good enough to be used for the chosen catalytic process. XPS allows to determine the oxidation state of the metal embedded within a MOF and investigate electron transfer between a NP and a MOF. TEM and SEM are powerful tools to study NPs' morphology and their dispersion. Last but not least, nitrogen physisorption is used to quantify porosity prior and after nanoparticle deposition.

In this chapter of the review, we discuss the main approaches for the synthesis of MNP@MOF (MNPs mainly located within the pores of MOFs) and MOF@MNP (MNPs on the external surface of MOFs) composite materials, *e.g.*, “ship in a bottle”, colloidal deposition, ‘bottle around the ship’, *etc* (Figure 10). Afterwards, we describe the recent progress in heterogeneous catalysis by using MNP/MOF systems (composite materials with MNPs within the MOF and/or on the external surface of the MOF).

Figure 10. Different strategies followed for the formation of nanoparticle – MOF composites.

3.1 Synthesis

The composite synthetic route plays an important role since it can affect the subsequent catalytic performance, as many MNP-catalysed reactions are structure sensitive. Ning et al.¹⁶⁹ synthesized five Au NP@UiO-66 catalysts by various methods: impregnation-reduction-H₂ (**I-H**), impregnation-reduction-NaBH₄ (**I-S**), deposition–precipitation-carbonization (**D-C**), deposition–precipitation-H₂ (**D-H**) and colloid-immobilization (**C-I**). The authors showed that **I-H** delivered the best result among those of the other catalysts prepared *via* other synthetic approaches in the oxidative valorization of furfural (FUR). As shown in the TEM images of the Au@UiO-66 prepared by the **I-S**, **D-C** and **D-H** methods, Au nanoparticles of a large size (*ca.* 10-25 nm) and uneven dispersion were observed (Figure 8A (b)–(d)). Methods **C-I** and **I-H** yielded Au nanoparticles that were within the range of 2–3 nm and uniform in size (Figure

10A(a) and (e)). It is worth mentioning that the crystal structure of UiO-66 remained intact during synthesis while using the **I-H** and **C-I** methods, whereas the other methods led to framework collapse (Figure 10B (a)–(g)). The catalytic performances of Au@UiO-66 synthesized by the **I-H** and **C-I** methods were attributed to the small size of the Au nanoparticles and the well-preserved pore structure of UiO-66. The TEM images and XRD of the used **I-H** Au@UiO-66 catalyst revealed that after 5 catalytic cycles, no Au particle agglomerations could be observed, and UiO-66 retained its crystalline structure (Figure 11A (f) and Figure 11B (h)). Another example that highlights the importance of the synthetic method was shown by Butson et al.¹⁷⁰ The researchers demonstrated that MOFs featuring the pore breathing effect could possibly exhibit a preferential phase behaviour for nanoparticles obtained by different reduction methods. This effect was shown with MIL-53(Al), which is known for its breathing phenomenon. Pd(NO₃)₂ was dissolved in acetonitrile and added to a pre-activated MOF. The authors further investigated two reduction methods: electrodeposition and gas-phase reduction. The former method yielded nanoparticles between 0.5 - 0.8 nm, while the latter produced larger nanoparticles of 0.9 – 1.1 nm. While TEM showed that both methods yielded Pd nanoparticles embedded within the pores of Al-MIL-53, the host material adapted a different configuration in each case, as suggested by TEM, XRD and PDF analyses.

Figure 11. (A) TEM images of Au@UiO-66 catalysts synthesized *via* different methods: (a) I-H, (b) I-S, (c) D-C, (d) D-H, and (e) C-I. (f) The Au@UiO-66 catalyst synthesized using the I-H method. (B) XRD patterns of the Au@UiO-66 catalysts synthesized by different methods:

(a) a simulated pattern of UiO-66, (b) as-synthesized UiO-66, (c) I-H, (d) D-C, (e) I-S, (f) D-H, and (g) C-I. (h) The Au@UiO-66 catalyst synthesized *via* the I-H method. Reproduced with permission from reference ¹⁶⁹. Copyright 2018 Elsevier.

3.1.1 “Ship in a bottle” MNP/MOF

Assembling the active species within the pores of a pre-formed support is known as “*ship in bottle*” synthesis. This approach is supposed to prevent MNPs from aggregation and to limit their growth to the pore size of the host material. However, the task remains challenging due to many factors, such as the wettability of the internal MOF’s surface; the interactions between the metal precursor and pore environment; the thermal, chemical and mechanical stabilities of the framework; *etc.* The most common techniques to introduce metal precursors into MOFs include chemical vapour deposition, solution impregnation, double-solvent impregnation, and one-pot synthesis.

3.1.1.1 CVD. Usually, an activated MOF is placed together with a volatile metal precursor in the same vial under vacuum. During the evacuation, the metal precursor diffuses into the MOF channels but also remains on the external surface. After the subsequent reduction or thermal treatment, the precursor turns into nanoparticles. The particle size distribution fluctuates largely when such a protocol is employed.

Hermes et al.¹⁷¹ reported the pioneering work whereby MOF-5 was used as a host and the volatile complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]$, $[(\eta^5\text{-C}_5\text{H}_5)\text{Cu}(\text{PMe}_3)]$, and $[(\text{CH}_3)\text{Au}(\text{PMe}_3)]$ were used as guest inclusion compounds. Eventually, Pd/Au/Cu@MOF composites were obtained by the reduction of the respective guests. The gold particles were sized in a range from 5 to 20 nm; however, for palladium and copper, the average size ranged from 1 to 2 nm.

Currently, this method is rarely used for the preparation MNP@MOF composite materials for catalysis.¹⁷² Although this method allows for the synthesis of very small particles

within MOFs, it requires a synthesis incorporating expensive and volatile complexes and high precision during the impregnation process to avoid MNP agglomeration on the external surface of the support.

3.1.1.2 Solid grinding. Solid grinding, as follows from its name, involves the grinding of MOF powder together with a volatile metal precursor. The latter penetrates into MOF channels and undergoes the subsequent reduction that leads to the formation of the composite material.

Ishida et al.¹⁷³ were the first who showed the deposition of a metal precursor on an MOF by the solid grinding method. The authors tested several MOFs with different pore sizes: CPL-1(4x6 Å²), CPL-2(6x8 Å²), Al-MIL-53(8.5x8.5 Å²), MOF-5(15x15 Å²), and Cu-BTC (17 x 17 Å²) with the volatile complex Me₂Au(acac) as the gold precursor. The grinding of the mixture of MOFs and Au salt for 20 minutes in an agate mortar at RT was followed by heating in a stream of 10% H₂/N₂ at 120 °C for 2 h to obtain MNPs with size <2 nm. The small size of the MNPs was attributed to the highly ordered nature of the porous frameworks, porous structures, pore size of MOFs and potential hydrogen binding between Me₂Au(acac) and uncoordinated carboxylic groups what also prevent particles from aggregation.

The restrictions for this method are the same as those for MOCVD: the precursors are expensive and should be volatile, and the formation of nanoparticles on the external surface of the MOF is unavoidable.

3.1.1.3 Solution impregnation. The solution impregnation method is based on dispersing and mixing a pre-synthesised MOF powder with dissolved metal precursors. The MOFs pores become filled with the metal precursor solution because of the capillary effect. Again, the precursor's reduction step is required to form MNPs. The main disadvantage of this method is the lack of precursor location control and therefore the poor particle distribution on both the interior and exterior surfaces of MOFs.

Sabo et al.¹⁷⁴ showed the first successful attempt to apply the solution impregnation technique to form MNPs within MOFs. The guest-free MOF-5 was vigorously stirred with a CHCl_3 solution of $\text{Pd}(\text{acac})_2$, followed by the slow solution evaporation under an argon atmosphere and by the solid activation under vacuum. The resulting yellowish powder of $\text{Pd}(\text{acac})_2$ included in the MOF-5 was then placed in a reducing H_2 atmosphere and heated to 200 °C for 1 hour, leading to the reduction of Pd^{2+} to Pd. However, even at room temperature, the obtained catalyst was not stable in air due to the low hydrothermal stability of the MOF-5 support. The decoration of the pores with $-\text{NH}_2$ or $-\text{bpy}$ moieties overcame this issue – the metal precursor tended to preferentially coordinate to these functional groups, allowing for greater location control. Hwang et al.¹⁷⁵ applied this approach for the first time with MIL-101(Cr). MIL-101 is known for its ability to create coordinatively unsaturated metal sites by the thermal removal of the terminal water molecules of the metal clusters. The water molecules were replaced by ethylenediamine (ED) molecules coordinated to clusters. ED-MIL-101 stabilized metal precursors by the interaction between positively charged ammonium groups and anionic metal precursors, such as $[\text{PdCl}_4]^{2-}$, $[\text{PtCl}_6]^{2-}$, and $[\text{AuCl}_4]^-$. The further reduction by NaBH_4 led to the formation of nanoparticles with an average size of 2-4 nm, which are substantially smaller than the particles within the unmodified MIL-100 (>20 nm). Goswami et al.¹⁷⁶ obtained Au NPs by first installing 4-carboxy-phenylacetylene (PA) species into a MOF that are capable of organometallic bond formation with Au(I). The installation of PA to the eight-fold hexa-zirconium(IV)-aqua,hydroxo,oxo nodes of NU-1000 was conducted by solvent-assisted ligand installation (SALI). Afterwards, the proton of acetylene was replaced with a monometallic $\text{Au}(\text{I})\text{PEt}_3^+$ ion (PEt_3 = triethylphosphine). Finally, the Au(I) sites were reduced to Au(0) by NaBH_4 . This reduction was accompanied by the release of gold atoms from grafted phenylacetylides, diffusion of the gold atoms through the framework, and assemblage of atoms into two types of triethylphosphine-coated NPs of *ca.* 1.5 and 3.7 nm.¹⁷⁶

The choice of the solvent plays an important role in determining the MNPs size. Rivera-Torrente et al.¹⁷⁷ showed that the internal surface of MIL-100 showed different wettability values for H₂O and CHCl₃. The wetting of the hydrophilic surface of MIL-100 was limited by hydrophobic Pd(acac)₂ solution in CHCl₃. This effect led to the different sizes of the reduced Pd nanoparticles – ca. 15 nm in the case of CHCl₃, while with the aqueous solution of Na₂PdCl₄, particles with sizes of up to 60 nm were formed on the surface of the MOF.

Recently, Yang et al.¹⁷⁸ synthesized Ni-Fe bimetallic NPs supported on Ce_xO located on the MOF surface. Pre-activated MIL-101(Cr) was immersed in water and mixed with precursor aqueous solutions of NiCl₂·6H₂O, FeSO₄·7H₂O, and Ce(NO₃)₃·6H₂O in a 3:3:1 ratio. After 10 minutes of stirring at room temperature and the further reduction by NaBH₄, Ni-Fe/Ce_xO particles were obtained with an average size of 10.3 nm. Furthermore, the particles' size was greater than the MOF pore size; thus, the particles were located on the surface of the MOF, rather than in the pore space. To show the advantages of using cerium oxide, bare Ni-Fe NPs supported on MIL-101 were synthesized. The lack of cerium led to the formation of particles with an average size of 30 nm. At the same time, the lack of MOF support led to a worse distribution of Ni-Fe-Ce_xO particles, yet as smaller particles (9.5 nm).¹⁷⁸

3.1.1.4 Double solvent approach. One of the main disadvantages of the other methods is the formation of MNPs on the external surface. However, the double solvent approach (DSA) is a rational way for the synthesis of MNP@MOF composites. This method allows the conducting of the precise deposition of NPs on the internal surface of the pores. The driving force of this approach is the capillary effect, which limits the deposition of metal salts onto the outer space of frameworks. Usually MOF powder is dispersed in a hydrophobic solvent, *e.g.*, hexane. Subsequently, a small amount of the aqueous solution of the metal precursor salt is added to a vigorously stirred dispersion. After the reduction process, the small metal clusters are encapsulated within the MOF matrix.

Aijaz et al.¹⁷⁹ applied the DSA for the first time in the synthesis of well-dispersed and size-controlled MNPs inside the pores of an MOF. Activated MIL-101(Cr) was suspended in *n*-hexane, which played the role of a hydrophobic solvent. After sonication, the aqueous solution of H₂PtCl₆ was added dropwise under constant stirring. After the reduction with H₂, well-distributed Pt nanoparticles were obtained inside of the pores with an average size of 1.8 nm. Recently, Sun et al.¹⁸⁰ applied the DSA for the preparation of a non-noble trimetallic system (Cu@Co@Ni) with an average particle size of ~3.3 nm embedded within MIL-101(Cr). During the reduction process by ammonia borane, Cu ions were the first to be reduced to form Cu NPs as a core, and the formed intermediate species (Cu–H) promoted the subsequent reduction of Co²⁺, prior to Ni²⁺, for the deposition of a Co middle-shell on the NPs. Similarly, the generated Co–H species acted as a strong reducing agent for the reduction of Ni²⁺ to give the NPs a Ni exterior shell. This system showed activity for the tandem hydrogenation of nitroarenes by the hydrogen from ammonia borane dehydrogenation and CO oxidation.

Lately, a few works were published with using the DSA as a preparation method for MNP@MOF composite materials.¹⁸¹⁻¹⁸³

3.1.1.5 One-pot synthesis. The previously described synthetic methods require multiple steps to obtain composites. A one-pot synthesis typically requires the mixing of MOFs and metal precursors in one batch with mild reduction agents. The addition of polyvinylpyrrolidone (PVP) prevents the nanoparticles from agglomerating, and there exist scenarios where additional functional groups (*i.e.*, bipyridine) in an organic linker are required for binding the metal salt.¹⁸⁴

Liu et al.¹⁸⁵ described the one-pot synthesis of hollow Cu₂O/Au@HKUST-1 particles. In a typical experiment, ethanoic solutions of H₃BTC and HAuCl₄ and the dimethylacetamide solution of Cu₂O were mixed, shaken and left for 5 to 25 min. The driving force of the reaction is the galvanic replacement reaction. Depending on the time of the reaction, particles with

different HKUST-1 thicknesses were obtained with Au nanoparticles size of several nanometres captured inside (Figure 12).

Figure 12. TEM images of underdeveloped $\text{Cu}_2\text{O}/\text{Au}@\text{HKUST-1}$ hollow nanostructures obtained at 1 min (a), 5 min (b), 10 min (c), 15 min (d), 20 min (e) and 25 min (f). Reproduced with permission from reference 185. Copyright 2019 Elsevier.

3.1.2 Colloidal deposition

The colloidal deposition technique is the preferred technique for particles to be deposited on the external surface of the MOF. In this case, the MOF and MNPs are synthesized individually, following mixing by stirring in a solvent. When the NPs' size allows for its penetration into a MOF, the particles are distributed on both external and internal surfaces. When this is not the case, the NPs are attached solely to the external surface due to physical adsorption and/or electrostatic interactions. It is worth noting that some MOFs, due to the lack of electrostatic interactions, cannot preserve particles from detachment during catalytic experiments.

Recently, Ning et al.¹⁶⁹ deposited Au particles on UiO-66. To the aqueous solution of PVP with HAuCl₄ (with a PVP/Au weight ratio 1.2) that was stirred for 1 hour, a solution of NaBH₄ was added rapidly followed by UiO-66 addition and overnight stirring. After centrifugation, washing, drying under vacuum and calcination, the Au@UiO-66 composites were obtained. The catalyst showed a 92.1% of conversion with 100% selectivity towards the oxidative valorization of furfural with methanol. The catalytic activity was almost the same as that for the catalyst obtained by the solution impregnation method (100% conversion and 100% selectivity).

3.1.3 “Bottle around ship” or “templated synthesis”

This method consists of the introduction of presynthesized MNPs into the MOF precursor solution for the subsequent growth of the framework around the particles. To prevent MNPs from agglomerating, surfactants are frequently used, *e.g.*, PVP, cetyltrimethylammonium bromide (CTAB) and other surfactants. The main problem with this method is that binders are difficult to wash away from the framework completely and these binders limit the access to MNPs, thus, the catalytic performance decreases. However, this method allows for MNP@MOF growth with controlled NP size and shape.¹⁸⁶ To deal with this problem, a sacrificial template synthesis is used. Typically, presynthesized MNPs coat the removable template shell. During the synthesis, the MOF covers the templated particles, and after the selective removal of the template, a yolk-shell structure is formed. Li et al.¹⁸⁷ synthesized Cu₂O@ZIF-8 by protecting unstable Cu₂O NP with a size of 140 nm, by a SiO₂ shell with a 25 nm thickness during ZIF formation. After SiO₂ etching with NaOH, a yolk-shell material with a good stability for multiple catalytic cycles in the hydrogenation of nitroarenes was obtained.

3.1.4 Thermal decomposition

In contrast to MOF pyrolysis (the method is discussed below), the partial thermal decomposition of MOFs allows for the capturing of small metal or metal oxide particles inside hierarchical pores while maintaining the framework's backbone and crystallinity.

Feng et al.¹⁸⁸ reported a partial delignation process on multivariate MOFs (MTV-MOF) – frameworks that contain more than two functional groups within their structure. The authors found that UiO-66-NH₂ and UiO-66 demonstrated different thermal stabilities.¹⁸⁸ Aminoterephthalic ligands could be removed at 350°C, whereas terephthalic ones were stable up to 480°C. By varying the heating temperature and the ratio between these two linkers from 0 to 41 %, the size of the newly formed mesopores could be tuned from 0.8 to 15 nm. Thermolysis was also found to lead to the formation of ultrasmall 1-3 nm sized ZrO₂ particles dispersed within the framework (Figure 13). In comparison with the pristine MOF, the delignated MOF demonstrated a high catalytic activity in the Meerwein-Ponndorf-Verley reaction, which was attributed to a strong Lewis acidity. Moreover, it is possible to precipitate an additional metal salt prior to the partial MOF decomposition to synthesize bimetallic particles. Choi and Oh¹⁸⁹ synthesized bimetallic Pd-Co MNPs supported on hollow ZIF-67 by the partial thermal decomposition of a polystyrene@ZIF-67/Pd₂₊ material. First, carboxylic-acid-functionalized polystyrene microspheres were immersed into a Co(NO₃)₂ and 2-methylimidazole methanolic solution. The mixture was heated at 70 °C while being ultrasonically dispersed to form polystyrene@ZIF-67. Afterwards, the polystyrene@ZIF-67 was then immersed in a methanolic solution of Na₂PdCl₄ for 10 min to load Pd₂₊ into the micropores of the ZIF-67 shell. The resulting polystyrene @ZIF-67/Pd₂₊ was pyrolysed at 400°C, and the polystyrene core spheres were removed together with the partial decomposition of the framework. This action resulted in the formation of bimetallic Pd-Co with an average size of 2.7±0.7 nm embedded within the hollow ZIF-67 structure. It is worth mentioning that

the calcination at 400 °C did not alter the crystalline structure of ZIF-67, while further temperature increases led to the framework decomposition.

Figure 13. Mechanism for hierarchically porous structure formation. (a) The amino-functionalized linker tends to undergo a decarboxylation process at relatively low temperatures, and the resulting terminal ligand could be further removed through thermal or chemical treatments. (b) $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$ clusters are transformed into decarboxylated Zr_6O_6 clusters after linker thermolysis, and they tend to aggregate with the assistance of oxygen species, eventually forming ultrasmall MO nanoparticles. (c) Overall, the microporous MTV-MOF, UiO-66-NH₂-R%, is converted into ultrasmall MO@HP-MOF composites through controlled linker thermolysis. Reproduced with permission from reference 188. Copyright 2018 American Chemical Society.

3.1.5 Spray drying

Recently, a spray-drying process was applied for the synthesis and modification of MOFs.^{190,191} In this method, MOF nanocrystals are agglomerated to form spherical particles by the rapid

evaporation of a solvent containing the organic ligand and metal ions from the sprayed droplet. This method allows for shaping MOF particles into spherical beads (average size = 3.4 ± 1.8 μm) while keeping the initial size of included nanoparticles. This approach was also applied to obtain MNP@MOF composite materials.

Yazdi et al.¹⁹² synthesized Au@CeO₂ supported within UiO-66 beads. The synthesized core-shell Au@CeO₂ particles had an average size of 9.6 ± 2.0 nm with an Au core size of 4.2 ± 1.2 nm. The particles were functionalized with PVP and dispersed in DMF, and after the addition of terephthalic acid and Zr(OPr_n)₄, the mixture was placed in a spray-drying device. After the thermal removal of PVP, it was found that the Au@CeO₂ particle size did not alter within the beads. The catalyst demonstrated a good catalytic activity towards CO oxidation – among the best results for other MNP@MOF compounds. Kubo et al.¹⁹³ applied this method to obtain Fe₃O₄/HKUST-1 and (Fe₃O₄, TiO₂)/HKUST-1. In a typical experiment, different amount of presynthesized particles of Fe₃O₄ and/or TiO₂ were added to the solution of Cu(NO₃)₂ and trimesic acid. After spray drying, the HKUST-1 particles agglomerated into bigger particles with a geometric mean diameter (GMD) of 1.55 μm , consisting of pristine MOF particles with a GMD of *ca.* 240 nm. Both Fe₃O₄ and TiO₂ particles were located inside the HKUST-1 particles and remained the same size as before the spray drying.¹⁹³

3.1.6 Other methods

Yang et al.¹⁹⁴ described a combined surfactant-free spray-assisted technique for the preparation of Pt NPs with an average size of 2.6 ± 0.3 nm and the colloidal deposition of MNP on MOF and MOF+¹⁹⁵ technique to obtain the deposited-on material Co-MOF-74@(Pt@Fe₂O₃). The MOF+ technique consisted of the deposition of Fe₂O₃ (that played a role in the hydrogenation of cinnamaldehyde) on the surface of MOFs with a phenol moiety in the linker structure. The resulting material Co-MOF-74@(Pt@Fe₂O₃) was synthesized by an immersion of the pristine

Co-MOF-74 into the solution of pre-synthesized Pt NPs and FeCl₃ salt. The catalyst showed a 63% conversion with 100 % selectivity for the hydrogenation of cinnamaldehyde to cinnamyl alcohol within 1 h.

The Cu₂O@HKUST-1@Au hybrid material was synthesized by Zhan et al.¹⁹⁶ by using the utilization of the galvanic replacement between Cu₂O and HAuCl₄. First, Cu₂O@HKUST-1 was synthesized by mixing ethanolic solutions of H₃BTC with presynthesized Cu₂O. Due to the difference in the standard reduction potentials of AuCl₄⁻/Au (0.99 V. *vs.* (SHE)) and Cu₂⁺/Cu₂O (0.20 V. *vs.* SHE), the galvanic replacement reaction was assumed to be feasible. Gold nanoparticles, with an average size of 31 ± 5 nm (without PVP) and 13 ± 3 nm (with the addition of PVP), were synthesized by mixing solutions of Cu₂O@HKUST-1 and HAuCl₄ at pH=4.

3.2 Catalysis

The catalytic performance of MNP@MOF composites is known to cover a wide range of reactions, from the reduction of nitroarenes to organic coupling reactions. The MIL, UiO and ZIF families are by far the most widely used MOF supports. In this part of the review we focus on the application of MNP@MOF in heterogeneous catalysis. The application of these composite materials in photocatalysis and electrocatalysis can be found in the other parts of this review.

3.2.1 CO related chemistry

Catalytic CO oxidation to CO₂ is not only a commonly used catalytic process for practical applications but also a model reaction for testing the activity of heterogeneous catalysts.¹⁹⁷

Recently, Tsumori et al.¹⁹⁸ prepared a so-called “Quasi-MOF” which is a deligated Cr-MIL-101 with a strong interaction between the inorganic node and the included gold

nanoparticles. This interaction led to a fascinating boost in the catalytic activity. After the inclusion of gold nanoparticles (3 nm) by a solution impregnation technique, it was found that 573 K is the temperature at which Cr-MIL-101 partial framework decomposition occurs and is accompanied by the release of CO₂ and the formation of Cr-O sites, which are important for the adsorption and activation of O₂ species in the CO oxidation reaction. Au@Cr-MIL-101 with 11.6 wt % of Au catalyst was tested in CO oxidation in the temperature range from 193 to 523 K. At temperatures from 193 to 298 K, the catalyst showed 100% CO conversion but exhibiting different lifetimes – up to 6500 min (Figure 14).

Figure 14. Catalytic Activity in CO Oxidation. (a) The catalytic performances of Au/MIL-101, 11.6 wt % Au/MIL-101(x) prepared by calcination for 1 hr, MIL-101(573), and Au/Cr₂O₃(573) towards CO oxidation at 298 K. (b) The catalytic performance of 11.6 wt % Au/MIL-101(573) prepared at various calcination durations (i.e., 5, 15, 30, 60, and 180 min) towards CO oxidation at 298 K. (c) The conversion of CO to CO₂ as a function of the reaction temperature over Au/MIL-101(573) calcined for 30 min with different amounts of catalyst (i.e., 0.025, 0.05, and

0.1 g) at a reaction gas flow rate of 33 mL/min. (d) CO oxidation at various temperatures catalysed by Au/MIL-101(573) calcined for 30 min. Reproduced with permission from reference 198. Copyright 2018 Cell Press.

The deposition of NPs on the external surface is commonly undesired. Yet, Tong et al.¹⁹⁹ claimed that they were the first to specifically study the use of MOFs as classical support for nanoparticles. For this purpose the authors synthesized composites of ZIFs covered with MNPs (M = Au, Pd, Pt) by the solution impregnation method. The average size of the metal nanoparticles was 3.3 nm. Both ZIF-8 and ZIF-67 did not show any catalytic activity up to 200°C. However, both ZIF(Co/Zn)@M (M = Au, Pd, Pt) started showing activity at 30, 43, and 53 °C for the cobalt material and 72, 73, and 74°C for the zinc MOF. The order of the catalytic activities for both MOFs followed the trend Pd>Pt>Au. The CO conversion reached 100% at 120, 190, and 220 °C for ZIF-67 and at 190, 230 and 270°C for ZIF-8. It was found by TEM that the supported NPs mostly exposed their (111) planes. DFT calculations revealed that the most stable configuration occurred when the (111) plane, which has a negative charge in MOF composites, bonded with the two nitrogen atoms of imidazole ligands, which donated electrons to metals. This donation led to different CO adsorption properties for ZIF(Co/Zn)@M materials, which further led to different catalytic activities. The same trends in catalytic activity were observed for benzyl aldehyde oxidation.

Wang et al.²⁰⁰ reported CO oxidation over Cu_xO@UiO-66. The composite catalyst was prepared with the spray-drying method with an average size for Cu_xO particles of 0.8 nm. Due to the exothermal nature of the oxidation of CO to CO₂, even under the operational temperature T = 220 °C, some spots at the interface of CuO NP and UiO-66 were overheated to *ca.* 346 °C. It is worth to noting that 346°C is lower than the expected temperature of decomposition of UiO-66 and lower than the synthesis temperature of Cu_xO@UiO-66 (400°C). This local

overheating initiated the thermal decomposition of UiO-66. As a result, the MOF served as a template for the formation of ZrO_2 distributed among Cu_xO . This new material exhibited highly active Cu–Zr–O interfaces, and ultimately, it was $\text{Cu}_x\text{O}/\text{ZrO}_2$ that catalysed CO oxidation during the 2nd and 3rd cycles. The MOF composite catalyst reached 97% CO conversion at 220°C, which outperformed the commercially available CuO (30-50 nm) and unsupported Cu_xO . Additionally, the stability test showed that the catalyst preserved the same activity over three runs.

Vico-Solano et al.²⁰¹ studied the application of Pd@MIL-88B-NH₂(Cr/Fe) for carbonyl compound syntheses, *i.e.*, amides, esters, carboxylic acids, and α -ketones. The catalysts were prepared by the solution impregnation method. By varying the reaction conditions, high selectivities and yields were achieved for the carbonylation of aryl halides in the presence of various nucleophiles. The catalytic results were comparable to those of the commercial Pd/C. However, both Pd/C and Pd@MIL-88B-NH₂ suffered from Pd leaching. Starting from 8-9 wt % of Pd, after the first, run only 0.6-0.8 wt % Pd remained, and the framework changed its structure. However, this newly formed phase remained the same after subsequent catalytic cycles with the same activity.

3.2.2 CO₂ utilization

The reverse water gas shift (RWGS) reaction, the transformation of CO₂ into CO, is regarded as a powerful step in the valorization of carbon dioxide because the main product, CO, can be further transformed into valuable chemicals and fuels through well-known and established Fischer-Tropsch chemistry. Han et al.²⁰² synthesized different composite materials Au@Pd@MOF-74, Pt@MOF-74, and Pt/Au@Pd@MOF-74 based on MOF-74(Zn). Pt@MOF-74 showed the best catalytic performance with a 1:1 ratio of H₂/CO₂ at 400 °C and 2 MPa of CO₂. The same material also revealed some activity and very good selectivity for the

photoreduction of CO₂ to CO. Similarly, Pt/Au nanoparticles encapsulated in UiO-66²⁰³ and the novel [Co₂(oba)₄(3-BPDH)₂].4H₂O²⁰⁴ (oba = 4,4'-oxybis(benzoic acid); 3-BPDH = N,N'-bis-(1-pyridine-3-yl-ethylidene)-hydrazine) were studied under similar conditions. In both cases, the reaction at such a temperature and the formation of water resulted in framework decomposition, highlighting the main issue in the application of MOFs as supports in high-temperature catalysis.

CO₂ methanation is a relatively facile reaction that requires low temperatures and is normally carried out in the presence of Ni catalysts. Zhao et al.²⁰⁵ reported a Ni@UiO-66 catalyst for the reduction of CO₂ to CH₄. The catalyst was synthesized by the solution impregnation of different amounts of Ni(NO₃)₂ and the subsequent reduction with H₂, yielding Ni NPs with a size of *ca.* 2 nm. The catalytic tests were performed under 1 MPa of H₂/CO₂ (molar ratio of 3) in a temperature range from 200 to 340 °C. The catalyst showed a superior performance over that of conventional systems such as Ni/ZrO₂ and Ni/SiO₂ and a good stability (>100 h) at 300 °C.

Carboxylation is another potential application of CO₂. Dutta et al.²⁰⁶ published the carboxylation of terminal alkynes by using a new MOF assembled from 5,10,15,20-tetrakis(4-pyridyl)porphyrin, 1,2-diamino-3,6-bis(4-carboxyphenyl)benzene and Zn²⁺ salt at 100 °C under solvothermal conditions and Ag nanoparticles. The Ag@MOF composite was synthesized by solution impregnation and reduction by NaBH₄, with the average size of Ag nanoparticles being 3.07 nm. The catalytic experiments were performed under mild conditions – 1 atm and 60 °C. Afterwards, the reaction catalyst could be recovered and used again with an average 10% loss in yield for every further catalytic run.

3.2.3 Dehydrogenation

Hydrogen production from hydrogen-rich solid compounds, such as hydrazine, hydrazine borane, and ammonia borane, is a promising approach for effective hydrogen storage. The solid nature, stability, safe use at room temperature and high hydrogen content of these compounds have attracted the attention of research groups. Supported nanoparticles on an MOF were tested as perspective catalysts for on-demand hydrogen generation from these compounds.^{178,180,207,208}

Li et al.²⁰⁹ prepared immobilized $\text{Ni}_{0.5}\text{Fe}_{0.5}\text{-CeO}_x$ particles, with an average particles size of 10.3 nm, on the surface of MIL-101 (Cr). The catalytic test showed that $\text{Ni}_{0.5}\text{Fe}_{0.5}\text{-CeO}_x/\text{MIL-101}$ demonstrated 100% conversion and 100% H_2 with a *TOF* of 351.3 h^{-1} , better than the performance of $\text{Ni}_{0.5}\text{Fe}_{0.5}\text{MIL-101}$ (Figure 15). The catalyst also showed good catalytic stability throughout 5 cycles, and the conversion remained at 100%. Furthermore, $\text{Ni}_{0.5}\text{Fe}_{0.5}\text{-CeO}_x/\text{ZIF-67}$, ZIF-8, and UiO-66 were tested and showed complete decomposition with TOF values of 361.5, 192.3 and 300 h^{-1} , respectively.

Figure 15. a) Time-course plots for the molar ratio of $\text{nH}_2+\text{N}_2/\text{nN}_2\text{H}_4\text{BH}_3$ from the decomposition of HB (0.5 m, 2 mL) catalysed by $\text{Ni}_{0.5}\text{Fe}_{0.5}\text{-CeO}_x/\text{MIL-101}$, $\text{Ni}_{0.5}\text{Fe}_{0.5}/\text{MIL-101}$, $\text{Ni}_{0.5}\text{Fe}_{0.5}\text{-}$

CeO_x, Ni_{0.5}Fe_{0.5}, pure MIL-101, and CeO_x. b) The mass spectrum of the gases released from the complete decomposition of HB catalysed by the Ni_{0.5}Fe_{0.5}–CeO_x/MIL-101 nanocatalyst in argon at 343 K. c) Time-course plots for the molar ratio of n_{H₂+N₂}/n_{N₂H₄BH₃} and the total reaction time catalysed by NiFe–CeO_x/MIL-101 with different Fe contents. d) Time-course plots for the decomposition of HB (0.5 m, 2 mL) by catalysed by Ni_{0.5}Fe_{0.5}–CeO_x/MIL-101 at different temperatures and e) the related Arrhenius plots. f) The recycling test for the Ni_{0.5}Fe_{0.5}–CeO_x/MIL-101 nanocatalyst toward the decomposition of HB at 343 K under the ambient atmosphere. (n_{NiFe} = 0.2 mmol, 14 mol% Ce.). Reproduced with permission from reference 209. Copyright 2018 John Wiley & Sons.

3.2.4 Hydrogenation reactions

Redfern et al.²¹⁰ synthesized copper nanoparticles embedded inside a Zr-based NU-1000 MOF. Copper NPs with sizes of <1 and *ca.* 4 nm were synthesized by the solution impregnation method of a Cu precursor and subsequent reduction by H₂. For acetylene hydrogenation to ethylene, in comparison with Cu/ZrO₂ yielding a *TOF* of 45±1 h⁻¹ with a 1:1 H₂/C₂H₂ ratio, Cu@NU-1000 showed a *TOF* of 100±20 h⁻¹. Ethane, 1-butene, and 1,3-butadiene were observed as by-products. A high acetylene conversion (95 %) led to the increase in the amount of C₄ up to 15 mol % with <2% of ethane present in the mixture. However, when the catalyst was tested with the industrially used mixture of 97% ethylene and 3% acetylene, the complete consumption of acetylene was observed with 99.5% selectivity towards ethylene and less than 0.5 mol % of ethane, and C₄ products were also observed.

The reduction of olefins has been studied over different MNP/MOF composite materials.^{181,211} Meng et al.²¹² synthesized a Pt@UIO-66-NH₂ catalyst by impregnation and a subsequent annealing at 250°C to fabricate a mesoporous MOF (Pt@UiO-66-NH₂-2h). Due to

the increased diffusion rate of the reagents, an increase in the turnover frequency of more than 30 times was observed for the mesoporous solid.

Chen et al.²¹³ synthesized MOF140-AA by using Ni^{2+} as a metal source and squaric acid as the organic ligand with the addition of PVP and acetic acid at 140°C. Pd was further introduced by solution impregnation. The catalyst was tested for phenol hydrogenation and compared with Pd/SBA-15, Pd/ZrO₂, Pd/Al₂O₃, and Pd/SiO₂, with the MOF showing the best performance.

The reduction of nitroarenes, in addition to being an industrially important reaction, is also a model hydrogenation reaction.^{176,183,187,214-219} Choi et al.¹⁸⁹ synthesized 5.5 wt. % - PdCo nanoparticles supported on hollow ZIF structures with a remarkable catalytic activity. However, as in many other cases, the authors claimed full re-usability of the catalysts by performing recycling experiments at 100 % conversion, therefore, not much can be said about the long-term stability of this system. The possibility of cascade reactions was demonstrated by Zheng et al.²⁰³ The authors stepwise introduced C₆₀ and Pd NP into UiO-67 to obtain a C₆₀Pd_n@UiO-67 composite and conduct a cascade synthesis of arylamines through the hydrogenation of nitrobenzene and the subsequent reductive amination of benzaldehyde. According to HRTEM, C₆₀Pd_n particles, with an average size of 5 nm, were evenly distributed within the MOF particles. The catalysts showed a higher activity and selectivity than did the core-shell Pd@UiO-67, bare C₆₀Pd_n particles and commercial Pd/C.

The selective reduction of C=O moieties is another interesting process^{220,221} in which NP@MOF composites have been tested. The selective reduction of the C=O bonds of α,β -unsaturated carbonyl compounds is challenging because C=C bond reduction is preferable both thermodynamically and kinetically.¹⁹⁴ Yuan et al.²²² synthesized MIL-101@Pt@FeP-CMP with an MOF, NPs, micro- and mesoporous polymers and an iron(III) porphyrin (FeP-CMPs). This catalyst showed a high catalytic activity for the selective reduction of C=O bond in the

hydrogenation of cinnamaldehyde. In comparison with the unmodified hydrophilic MIL-101, FeP-CMP was used to form a hydrophobic porous shell that resulted in an increased adsorption capacity for cinnamaldehyde. In addition, the Fe porphyrin was also claimed to participate in the hydrogenation reaction.

Lin et al.²²³ deposited Ru NPs on the surface of MIL-101-SO₃H to conduct the tandem conversion of methyl levulinate (ML) to methyl-3-hydroxyvalerate (MHV) and of MHV to γ -valerolactone (GVL). In this case, the utilization of a sulfonated linker allowed for a better Ru dispersion and higher catalytic activity.

3.2.5 Oxidation of alcohols and carbonyl compounds

Zhan et al.¹⁹⁶ synthesized Cu₂O@HKUST@Au by galvanic replacement. The average sizes of the gold particles were *ca.* 13 nm and 31 nm, with and without addition of PVP, respectively. Cu₂O@HKUST@Au, having 13 nm Au particles, presented a good catalytic activity towards alcohol oxidation using *tert*-butyl hydroperoxide as an oxidant. As expected, Cu₂O@HKUST@Au with an Au particle size of 31 nm showed a lower conversion. The authors suggested that HKUST-1 acted as an active site and the Au NPs (1.6 wt. %) activated *tert*-butyl hydroperoxide *via* forming *t*-butoxyl radicals for further oxidation.

Jiang et al.²²⁴ studied the Guerbet reaction for upgrading ethanol to *n*-butanol, which is a four-step process involving dehydrogenation, aldol condensation, dehydration and hydrogenation steps (Scheme 5). Pd@UiO-66 was synthesized by the impregnation method with Pd NP highly dispersed within the framework with an average Pd particle size of 2.2 nm. The combination of acidity from the framework and Pd resulted in a highly active catalyst that was fully reusable, with no aggregation being observed. In line with the comments above, ethanol dehydrogenation and crotonaldehyde hydrogenation occur at the Pd sites, while

unsaturated Zr sites were active in the aldol condensation of acetaldehyde and promoted the dehydration of 3-hydroxybutyraldehyde.

Scheme 5. Guerbet reaction pathway. Reproduced with permission from reference ²²⁴. Copyright 2018 American Chemical Society.

3.2.6 Organic coupling reactions

NP@MOF catalysts were used in Suzuki-Miyaura coupling, an important reaction in synthetic organic chemistry.²²⁵ Xiong et al.²²⁶ synthesized a novel MOF-based catalyst in multiple steps. First, the novel MOF composite was synthesized by mixing La salts, H₂bdc-NH₂ and a suspension of pre-synthesized Fe₃O₄ nanoparticles. Afterwards, a Schiff base was formed post-synthetically by mixing pyridine-2-carboxyaldehyde and Fe₃O₄@La-MOF, with dangling amino groups, in ethanol. Finally, PdCl₂ was coordinated to the newly formed chelated NN moiety. In the reaction of 2-bromobenzene and phenylboronic acid the catalyst showed a *TOF* of 42886 h⁻¹. This result was superior to that of any other MOF-based catalyst for Suzuki coupling, with the *TOF* being the second best among any Suzuki reaction catalysts. The recycling test showed that the catalyst could be reused at least 12 times without a significant yield loss. However, it must be stressed that ppms of Pd in solution might have already

promoted the Suzuki coupling, making this family of reactions a difficult one to demonstrate the heterogeneous nature of a given solid catalyst.

Tan and Zeng²²⁷ synthesized a series of Pd/M-HKUST-1-R (M = Ce³⁺, Co²⁺, Ni²⁺, Cu²⁺, Mg²⁺, Li⁺, Na⁺, K⁺), where the Lewis basicity could be easily tuned by varying M. Pd nanoparticles with an average size of 4 nm were synthesized *via* the reduction of Pd(acac)₂ by ethanol. These particles were supported on the ring-like defective anionic HKUST-1-R with uncoordinated carboxylic groups. The Pd NPs were found to donate electrons to the framework and result in the carboxylates to act as Lewis basic sites – varying metal cations with different electron affinities allowed either maintaining basicity or switching to acidity. The Pd NPs catalysed the oxidation of benzyl alcohol to benzyl aldehyde and acted as a co-catalyst for the Knoevenagel condensation. While Lewis basic sites catalyse the Knoevenagel condensation to form ethyl cyanoacetate, the presence of ethanol in the reaction mixture allowed Lewis acid sites to catalyse the acetalization between benzyl aldehyde and ethanol.

Ning et al.¹⁶⁹ synthesized a series of Au@UiO-66-X (X = -H, -NH₃, -NO₂, -COOH, -NH₃Cl) catalysts for the oxidative valorization of furfural (FUR) with ethanol and methanol. Au NPs prepared by the solution impregnation method showed the best catalytic performance among that of the others, *i.e.*, the ones prepared *via* colloidal immobilization and deposition precipitation with a subsequent reduction or calcination. For the transformation of FUR with ethanol, Au@UiO-66 with different functional groups were tested. Au@UiO-66-COOH showed the best result.

4 MOF-mediated materials in heterogeneous catalysis

One of the most important challenges that heterogeneous catalysis faces currently is to develop materials with uniform well-defined active sites that deliver high selectivity and prevent deactivation.^{228,229} For this purpose, the combination of computational methods to anticipate

the catalyst activity coupled with novel synthesis approaches to develop the desired structure are currently the standard in catalyst research. However, going from material design to an actual catalyst is not always straight forward. For instance, in case of nano-particle based catalysis, achieving high metal loadings and controlled particle size while avoiding the tendency of nanoparticles to grow into larger crystallites with time *via* sintering is not an easy task.

Recently, the use of metal–organic frameworks as sacrificial templates for the preparation of heterogamous catalysts has attracted a great deal of attention.^{14,230} Although originally highly criticised by both MOF researchers and by the more traditional catalysis community, a large number of papers in this topic demonstrates that the controlled decomposition of MOFs opens the door to the manufacture of materials that cannot be synthesized following traditional approaches. MOFs can be converted to considerably more stable materials by simple post treatments, which commonly involve pyrolysis. These MOF-mediated structures (MOFMSs) retain most of the unique properties of the parent MOF, such as the high porosity, tuneable composition and high metal loading, making these new structures ideal materials for heterogamous catalytic applications and frequently outperforming their conventional catalyst counterparts.^{14,231,232} Moreover, this new generation of MOFMSs offer almost endless degrees of freedom to tune-up catalyst performance. As a consequence of these impressive features, MOFMSs are gaining in popularity among researchers. We refer the interested reader to some recent reviews on the topic.^{14,230,233-237} In this section, we focus on the most recent applications of MOFMSs for heterogeneous catalysis, presenting first a comprehensive and systematic introduction of the different strategies to obtain MOF-mediated materials.

4.1 Synthesis routes for MOF-mediated catalysts

The transformation of MOFs or their derived nanostructures is based on the collapse of the framework at high temperatures. The final properties of this new nanostructure can be tuned by selecting the proper atmosphere or/and the reaction temperature. Further post-treatments are sometimes needed to achieve the desired material. In Figure 16, we summarize the different common approaches to synthesize these MOF-mediated materials. We grouped all possible outcomes into three main groups: i) nanoparticles embedded in a carbon matrix, ii) metal oxides and iii) nanostructured carbons.

Figure 16. Different strategies to synthesize these MOF-mediated materials: i) nanoparticles embedded in a carbon matrix, ii) metal oxides, iii) nanostructured carbons.

The synthesis of metal nanoparticles embedded in a carbon matrix usually proceeds through a direct carbonization of the parent MOF in an inert atmosphere (*i.e.*, Ar or N₂), leading to highly dispersed nanoparticles encapsulated in a porous carbon matrix. Multiple MOFs have

been carbonized to synthesize these metal-carbon structures, including MOFs based on Fe,^{231,238-240} Zn,²⁴¹⁻²⁴³ Co,²⁴⁴⁻²⁴⁸ and Cu,^{237,243,249-252} with all of them sharing similar carbonization mechanisms. During the initial stages of the pyrolysis part, the organic ligand decomposes and evaporates to the gas phase, while the remaining fraction forms a porous carbonaceous matrix at higher temperatures. The final pyrolysis temperature and the metal reduction potential determine the metal species formed (*i.e.*, metal, metal oxide, or carbide). Das et al.²⁵³ studied a wide range of metal and metal oxide nanoparticles from MOFs (Cu/CuO, Co/Co₃O₄, ZnO, Mn₂O₃, MgO and CdS/CdO) and observed that the metal ions with a reduction potential of -0.27 volts or higher always form pure metal nanoparticles during carburization in N₂; whereas metal ions with a reduction potential lower than -0.27 volts tend to form metal oxide nanoparticles during pyrolysis in N₂.

The Tamman temperature of the metallic species needs to be considered as well to control the size of the resulting nanoparticles. In this matter, Wezendonk et al.²⁵⁴ combined in situ XAFS, DRIFTS, and Mössbauer spectroscopy to investigate the structural changes in Fe during pyrolysis of the iron MOF Basolite F-300. These authors showed that, the carbonization temperature governed the final size, phase, and porosity of the final Fe/C nanostructure. In particular, the pyrolysis of Basolite F-300 at 400 °C favoured the formation of highly dispersed epsilon carbides with a particle size of 2.5 nm; while for pyrolysis at a temperature of 600 °C, Hagg carbide particles of 6.0 nm were formed. Above these temperatures, extensive carburization and sintering was reported, with particle sizes above 28 nm (see Figure 17).

Figure 17. (a) Fe phase transformation during the pyrolysis of Fe-BTC towards Fe@C. (b) The Fe phase distribution after pyrolysis at different temperatures. Adapted from reference 254. Copyright 2016 American Chemical Society.

Additionally, the organic linker can play a very important role in the properties of the final catalyst. For instance, Chen et al.²⁵⁵ reported the formation of cobalt-embedded in N-doped porous carbons from ZIF-67, taking advantage of its high porosity, high nitrogen content, and rich content of cobalt ions. Due to the hierarchical porous carbon structure, the N-doping effect and the homogeneous cobalt dispersion, their composite exhibited the best electrocatalytic activities towards both the ORR and OER. Furthermore, secondary metals could also be incorporated into the final structure to promote the selectivity for the desired fraction. In this regard, Ramirez et al.²³¹ studied the addition of 14 different secondary metals (Fe, Cu, Mo, Li, Na, K, Mg, Ca, Zn, Ni, Co, Mn, Pt, and Rh) to the original Fe@C MOFMS for the production of light olefins *via* CO₂ hydrogenation. The authors concluded that the

catalytic performance could be tuned to produce the desired fraction depending on the metal loaded into the Fe MOFMS.

The second type of structure that can be obtained thorough MOFs is porous metal oxides. The preparation of metal oxides from MOFs is carried out in a similar way to the formation of the above discussed nanoparticles embedded in the carbonaceous matrix, only the pyrolysis atmosphere is changed from an inert gas to air/oxygen. Therefore, once the MOF structure collapses at the decomposition temperature, the remaining carbonaceous structure is burned, leading to the carbon-free metal oxide. Many porous metal oxide nanostructures have already been synthesized by this approach, such as zinc oxides,^{241,242,256,257} cobalt oxide,²⁵⁸⁻²⁶² iron oxides,²⁶³⁻²⁶⁵ copper oxides,²⁶⁶⁻²⁶⁸ *etc.* For instance, Zhang et al.²⁶⁷ synthesized CuO/Cu₂O porous composites with adjustable compositions and various morphologies, including cubes, octahedra, rods and wires from Cu-based MOFs. Furthermore, bimetallic metal oxides can be easily prepared as. Wu et al.²⁶⁹ prepared porous Zn_xCo_{3-x}O₄ hollow polyhedral metal oxides *via* ZIF templating. Their approach involved the bottom-up formation of a heterobimetallic ZIF template by the coprecipitation of Zn and Co ions in the presence of 2-methylimidazolate and by the subsequent thermal decomposition of the template (see Figure 18).

Figure 18. Schematic illustration for the preparation of bimetallic ZIFS and their conversion to spinel Zn_xCo_{3-x}O₄ hollow polyhedra. Reproduced with permission from reference 269.

Copyright 2014 American Chemical Society

The third class of structures presented in Figure 16 are MOF-mediated porous carbons.²⁷⁰⁻²⁷² The preparation of porous carbon materials from MOFs can be carried out by two different methods. The first one is based on the direct carbonization of the MOF at sufficiently high temperatures to vaporize the metal clusters, leading only to the carbon matrix. This MOF-based carbonaceous structure can also be achieved at moderate temperatures with the addition of further post treatments to remove the metal nanoparticles. For example, Li et al.²⁷³ reported the preparation of rod-like 3D porous metal free carbons *via* the carbonization of well-defined nanorod zinc MOFs. The removal of the metal was achieved during a high-temperature carbonization, obtaining carbons with a highly specific surface area of 1700 m² g⁻¹.

Another way to prepare the nanostructured carbon materials involves the incorporation of an additional carbon source (*i.e.*, glucose) and using the MOF as a sacrificial template. Liu et al.²⁷⁴ reported for the first time the preparation of these kinds of MOF-based carbons. They

used an MOF-5 framework as the template and FA as the carbon precursor. The carbonization of the PFA/MOF-5 composite was performed at 1000 °C for 8 hours with an Ar flow, yielding porous carbon with a BET surface area and pore volume of 2872 m² g⁻¹ and 2.06 cm³ g⁻¹, respectively.

Finally, all of these structures can be completely redesigned by incorporating secondary external metal precursors, giving endless tuning possibilities. For instance, Ji et al.²⁷⁵ reported a novel MOF (ZIF)-mediated approach to synthesize atomically dispersed Ru clusters *via* Ru precursor (Ru₃(CO)₁₂) incorporation in the ZIF MOF and the subsequent pyrolysis treatment. After the thermal treatment, uniform Ru₃ clusters were obtained. In the same way, Yang et al.²⁷⁶ prepared several monometallic or bimetallic nanoparticles confined within hollow nitrogen-doped porous carbon capsules. These composites were obtained from the pyrolysis of ZIF-8 nanocrystals decorated with Pt nanoparticles and then coated with a tannic acid coordination polymer or metal-impregnated RF polymer (see Figure 19). In a clever manner, the tannic polymer shell coated on the ZIF-8 nanocrystal employed by the authors underwent thermal decomposition at a low temperature, providing a template for the porous nitrogen-doped graphitic carbon that subsequently emanated from the pyrolysis of the ZIF. Hollow capsules were then produced with a shape and size that was defined by the ZIF crystal. The Pt nanoparticles that were enveloped between the ZIF crystal and the shell layer served as nucleation points for the supported bimetallic nanoparticles. The resulting alloyed Pt/Co nanoparticles were highly active and selective for the hydrogenation of nitroarenes to anilines.

Figure 19. (a) Synthesis of ZIF-8/Pt@M-TA core-shell composites and their pyrolysis to produce NHPC_1, Pt@NHPC_1, and PtCo@NHPC_1 capsules. TEM images of (b) Pt@NHPC_1, (c) ZIF-8/Pt@Co-TA, and (d) PtCo@NHPC_1. (e) An HRTEM image showing an individual PtCo bimetallic nanoparticle; (f) A STEM image of PtCo@NHPC_1. (j-m) Elemental mapping images of PtCo@NHPC_1. Adapted from reference 276. Copyright 2016 American Chemical Society.

4.2 Catalytic applications of MOF-mediated catalysts

The unique structures described in the previous section demonstrate that MOFs can be ideal precursors for the construction of heterogeneous catalysts. The exceptional features of MOFMSs have driven researchers to apply these structures to multiple catalytic reactions, and generally, these MOF-mediated catalysts have yielded performances superior to that of their conventional counterpart. An overview of the different applications of MOFMSs for heterogeneous catalysis is summarized in Table 2. We can observe that a great variety of MOFs have already been studied, including ZIFs,^{244,248,259,277-289} Fe,^{231,232,239,240,254,285,290-293} Cu^{243,250,266,267,294-300} and Ce MOFs.^{268,289,301-303} Additionally, among all possible reactions, nitro-compounds hydrogenations,^{244,263,276,280,281,285,304-307} alcohols oxidations,^{247,293,297} CO oxidation^{250,259,264-268,277-279,289,294-296,301,308} and Fischer-Tropsch^{232,246,254,285,290-292,309,310} are the

most studied applications, with CO₂ conversion gaining increasing momentum.^{231,239,311-314} As already mentioned above, excellent reviews already exist in the field.^{14,233,235,315} Therefore, in this chapter, we focus on the most recent implementation of MOFMSs for heterogeneous catalysis.

Table 2. Summary of the different applications of MOFMSs for heterogeneous catalysis.

Catalytic reaction	MOF
CO oxidation	Cu-BTC, ^{250,266,267,294-296} Ce-UiO-66, ²⁸⁹ ZIF-67, ^{259,277-279} MIL-100, ^{264,265,308} Ce-BTC ^{268,301,303}
Fischer–Tropsch	Fe-BTC, ^{232,254,290-292,316} MIL-88, ²⁸⁵ Co-BTC ^{246,309,310}
Alcohol oxidation	MIL-88, ²⁹³ ZIF-8, ²⁷⁵ HKUST-1, ²⁹⁷ Zn/Co-ZIF ²⁴⁷
Nitro compound hydrogenation	ZIF-67, ^{244,280,281,306,307} ZIF-8, ²⁷⁶ MIL-88, ²⁶³ Co-Ni-BTC, ²⁸⁵ Ce-BTC, ³⁰⁴ Co-BTC ³⁰⁵
Styrene epoxidation	ZIF-67 ²⁸⁴
Biofuel upgrade	ZIF-8 ³¹⁷
Alcohol esterification	ZIF-67 ^{282,283}
NO reduction	Ce-ZIF-67 ³⁰²
Reverse water–gas shift	Zn–Cu–BTC ²⁴³
CO ₂ methanation	Ru–UiO-66, ³¹¹ ZIF-67, ³¹² Ni-BTC ³¹³
CO ₂ hydrogenation to methanol	Pd-ZIF-8 ³¹⁴
CO ₂ hydrogenation to olefins	Fe-BTC, ²³¹ MIL-88 ²³⁹
Dehydrogenation of ammonia borane	ZIF-67 ²⁸⁶
Reduction of Cr(VI)	ZIF-8 ²⁸⁷
Synthesis of aza-Heterocycles	HKUST-1 ³⁰⁰
Cycloaddition of CO ₂ into epoxides	Zn-Co-ZIF ³¹⁸
Depolymerization of lignin	ZIF-8/67 ²⁴⁸
Sonogashira cross-coupling	Cu-BTC ²⁹⁹
Propane dehydrogenation	Fe-BTC ²⁴⁰
Dehydrogenation of formic acid	UiO-66 ³¹⁹

Hydrogenation of dimethyl oxalate	HKUST-1 ²⁹⁸
Dehydration of glycerol	MIL-96 ³²⁰
Benzene hydrogenation	Ni-BTC ³²¹
CO ₂ fixation	ZIF-67, ²⁸⁸ ZIF-8 ²⁸⁹

Recently, Guo et al.³⁰¹ reported a series of CeO₂-CuO bimetallic metal oxides derived from a Ce-Cu-MOF and compared their catalytic activities toward CO oxidation. In particular, the authors prepare two types of bimetallic metal oxides: CeO₂-CuO, prepared from the thermal treatment of a Ce-MOF followed by CuO loading *via* the impregnation method, and Ce-Cu-Ox, achieved by the direct calcination of a bimetallic Ce(Cu)-MOF at 600 °C for 3 h. The catalytic activity was tested using a continuous flow fixed-bed micro-reactor at atmospheric pressure with a CO/O₂/N₂ mixture in a volume ratio of 1:10:89. The authors found the CeO₂-CuO exhibited a high catalytic activity in comparison to that of Ce-Cu-Ox; an almost 80% CO conversion for CeO₂-CuO at 250 °C and only 22% for Ce-Cu-Ox derived from the Ce(Cu)-MOF. The difference in performances was attributed to the interaction between Cu and CeO₂ species that determined the redox properties of the catalyst, as both CeO₂-CuO and Ce-Cu-Ox catalysts were derived from the same Ce-MOF, with no evident difference in crystal structure, surface area or size/morphology.

Zacho et al.²⁸⁶ explored the hydrolytic dehydrogenation of ammonia borane using Co nanoparticles supported on nanoporous nitrogen-doped carbon derived from a bimetallic Co/Zn ZIF-67 as the catalyst. The catalytic activity was tested in an automated gas burette system with 10-20 mg of the catalyst and a solution of 50 mg H₃NBH₃ in 10 mL H₂O. The highest catalytic activity was obtained from ZIF-67/8 with a molar ratio of Co/Zn = 1 and carbonized at 900 °C to remove Zn by evaporation. At room temperature, this catalyst resulted in a turnover frequency of 7.6 mol H₂/mol Co min⁻¹ and an apparent activation energy of E_a = 44.9 kJ mol⁻¹.

Zhao et al.³²² investigated PdCu nanoalloys immobilized in N-doped carbon/graphene nanosheets and explored their activity towards the catalytic reduction of the toxic Cr(VI). The researchers first synthesized N-doped carbon/graphene nanosheets (NCG) through the carbonization ZIF-8 and further loaded it with PdCu nanoalloys *via* a hydrazine-involved hydrothermal method. The reduction of Cr(VI) was carried out with formic acid (FA) in a standard quartz cell with a 2.5 mL solution volume. The catalyst suspension (containing 15.2 μg of the PdCu alloy) was injected into the solution containing 0.5 mL of $\text{K}_2\text{Cr}_2\text{O}_7$ (2.5 mM), 0.5 mL of FA (1.25 M) and 1.0 mL H_2O at 25 $^\circ\text{C}$, and time-course UV-vis absorption spectra were recorded in the wavelength range of 280–550 nm. The resulting PdCu/NCG material showed a high activity of 38.2 $\text{min}^{-1} \text{mg}^{-1}$ for the catalytic reduction of Cr(VI) by FA. DFT calculations showed that electrons immigrated from Cu to Pd atoms upon their alloying, altered the density of states of PdCu metals and upshifted their d-band centres. This facilitated the chemisorption and C–H breakage of formic acid to produce active H species on the catalyst.

Martín et al.³⁰⁰ reported a novel and simple solid-state mixing and calcination procedure for the preparation of active and robust supported metal oxide nanoparticles that catalyse C–C and C–N bond formations. The methodology presented by the authors was based on the solvent-free grinding and cocalcination of MOFs (HKUST-1 or MOF-5) with aluminosilicates (USY or MCM-41). This solid-state synthesis allowed for the generation of MOF-derived non-precious metal oxide nanoparticles, with a low metal content, in a porous aluminosilicate matrix. The synthesized catalyst outperformed state-of-the-art solid catalysts for the syntheses of various aza-heterocycles under mild and heterogeneous conditions, exhibiting the highest turnover frequencies (TOFs) ever reported. The authors attributed these excellent performances to the higher availability of the metal oxide sites when they were dispersed within the porous matrix with respect to the bulk metal oxide.

Zhong et al.²⁵² synthesized Pd–Cu alloys embedded in hollow octahedral N-doped porous carbon (Pd–Cu@HO-NPC) using HKUST-1 as a template (see Figure 20). First, the authors coated an imidazolium-based ionic polymer (ImIP) on the HKUST-1 MOF. Subsequently, the anion exchange generated hollow Pd–Cu@HO-ImIP, in which the HKUST-1 template was decomposed simultaneously during the anion exchange, as this MOF is water sensitive. Finally, the resultant material was pyrolysed at 500 °C in N₂ to yield the final Pd–Cu@HO-NPC structure. The authors tested this material in several oxidations of hydrocarbons, and it displayed high activities and selectivities. For instance, in the oxidation of indane using air as an oxidant in the presence of 0.2 mol% palladium, an 86% conversion of indane was achieved in 24 h with a selectivity towards 1-indanone of above 99%.

Figure 20. Schematic illustration of the synthesis of Pd–Cu@HO-NPC. Adapted from reference 252. Copyright 2018 Royal Society of Chemistry.

Chaemchuen et al.³¹⁸ reported metal nanoparticles encapsulated in a nitrogen-doped porous carbon material derived from the pyrolysis of bimetallic Zn/Co MOFs. Interestingly, the authors synthesized the bimetallic MOF using a spray-drying procedure to provide a synthesis method for large-scale production. The synthesized MOFMSs were applied to the solvent-free cycloaddition of CO₂ into an epoxide for producing carbonate compounds without a co-catalyst. Among all the conditions studied by Chaemchuen et al.,³¹⁸ the Zn/Co MOFs

pyrolysed under a reducing atmosphere (5% H₂/Ar) at 1000 °C exhibited the best catalytic performance, displaying a 93% yield. The authors related the higher catalytic performance with the increasing number basic sites obtained at high pyrolysis temperatures, resulting from the Zn elimination.

Lin et al.³¹³ presented a facile synthesis for Ni nanoparticles confined in carbon shells derived from Ni MOFs and applied them for low-temperature CO₂ methanation at ambient pressure. In particular, the Ni@C catalyst was prepared through the pyrolysis of Ni-MOF powders at 500 °C for 2 h with a heating rate of 1 °C min⁻¹ under a N₂ atmosphere. The catalytic performance of the catalysts was evaluated in a fixed-bed flow reactor under atmospheric pressure. Before the reaction the catalyst was first reduced at 250 °C in a H₂/He (10 vol%) stream to ensure metallic Ni in the Ni@C catalyst. The authors tested several temperatures and, when the reaction temperature was increased to 325 °C, a CO₂ conversion of 100% was achieved with a CH₄ selectivity of 99.9%, whereas only trace amounts of CO were detected.

Sun et al.²⁴⁸ explored cobalt nanoparticles embedded in porous carbon derived from the pyrolysis of bimetallic zeolitic imidazolate frameworks (BMZIFs) based on ZIF-8 and ZIF-67. The BMZIFs were carbonized at 900 °C for two hours under an argon atmosphere at a heating rate of 5 °C min⁻¹ to yield the final Co/C catalyst. The authors tested the Co/C structures in the selective oxidative depolymerization of lignin and observed that, when compared with the traditional supported catalyst, the MOF-derived catalyst improved the catalytic efficiency, obtaining yields of up to 65%. Moreover, the MOF-derived catalyst could be recovered and recycled with an external magnet without any loss of activity for at least five times.

Yin et al.³¹⁴ reported PdZn alloy catalysts derived from a Pd-impregnated zeolitic imidazolate framework-8 for the CO₂ hydrogenation to methanol. Different pyrolysis temperatures (350, 400 and 500 °C) were investigated to study their effect on the Pd particle size, Pd dispersion and state of surface oxygen. The catalytic tests were carried out on a fixed-

bed continuous-flow microreactor with a CO₂/H₂ mixture molar ratio of 1:3 and a pressure of 4.5 MPa. The PdZn catalyst prepared at 400 °C gave the highest methanol yield of 0.65 g g_{cat}⁻¹ h⁻¹ at 270 °C, with a *TOF* of 972 h⁻¹. These values ranked at the top of the already reported Pd-based catalysts. The authors attributed the excellent activity of the MOF-mediated catalyst to the high content of small-sized PdZn alloy particles coupled with the high content of oxygen defects on the ZnO surface.

Yang et al.³⁰⁶ reported MOF-derived cobalt phosphide/carbon nanocubes for the selective hydrogenation of nitroarenes to anilines. The authors used the help of a capping agent, cetyltrimethylammonium bromide (CTAB), to synthesize the uniform ZIF-67 nanocubes. Then, after mixing the nanocubes with porous red phosphorus, the Co₂P/CN_x composite was obtained through a simple pyrolysis step (see Figure 21). The resulting composite displayed an excellent performance in the hydrogenation of nitroarenes to anilines. In particular, a 99 % nitrobenzene conversion with 99 % selectivity for aniline was obtained for a reaction time of 6 h.

Figure 21. Top: Graphical presentation of the synthesis of Co₂P/CN_x nanocubes. Bottom: Bright-field TEM images of the ZIF-67 (a) and Co₂P /CN_x nanocubes (b). SEM images are shown in the inset (scale bar, 500 nm). The selected area electron diffraction pattern of Co₂P/CN_x nanocubes along with the simulated diffraction pattern of Co₂P (c). An HAADF-STEM image of a Co₂P/CN_x nanocube (d) and the corresponding EDX elemental maps for Co (e), P (f), C (g), and N (h). Adapted from reference 306. Copyright 2019 John Wiley & Sons.

Sarazen and Jones²⁴⁰ explored the application of Fe@C structures derived from the pyrolysis of Basolite F-300 for the propane dehydrogenation reaction. In agreement with the previous works of Wezendonk et al.,²⁵⁴ the authors found that the phase of the supported iron (metal, oxide or carbide) was affected by the temperature of pyrolysis. Pyrolysis at either 400 or 500 °C resulted in Fe₂O₃, while the samples pyrolysed at 600 and 700 °C yielded Fe₃C. Furthermore, the authors observed that propene selectivity increased with the pyrolysis

temperature for the same isoconversion, achieving a selectivity higher than 80% for the sample pyrolysed at 700 °C.

Zhang et al.³⁰⁴ prepared a porous CeO₂/Au/CeO₂ nanorod catalyst using Ce-MOF as a sacrificial template. The preparation involved several sequential steps: first, the authors synthesized the Ce-MOF, followed by anchoring Au onto the Ce-MOF with a chloroauric acid solution. Afterwards, they deposited CeO₂ particles on Ce-MOF/Au through a hydrothermal reaction, and finally, they pyrolysed the resulting material at 550 °C for 4 h to obtain the CeO₂/Au/CeO₂ catalyst. In comparison with the CeO₂/Au counterparts, the CeO₂/Au/CeO₂ catalyst exhibited a remarkably high catalytic activity toward the reduction of 4-nitrophenol to 4-aminophenol by NaBH₄, with a stable conversion of 87.9% for at least 3 additional cycles.

For a similar nitrophenol reduction reaction, Sheng et al.³⁰⁵ reported Co₄N supported on hollow porous nanocages (PNCs) through a direct nitridation of a Co-MOF. To synthesize the final composite the authors first prepared Co-MOF nanocubes of approximately 150 nm as the precursor and pyrolysed the material at 450 °C under N₂ for 1 h with a ramp rate of 10 °C/min. Interestingly, the authors observed that the hollow nanostructure was retained when the pyrolysis temperature was lower than 600 °C. Finally, to produce Co₄N@PNCs, a nitridation was carried out at 500 °C under an NH₃ atmosphere. The samples exhibited a high catalytic activity towards the nitrophenol reduction, with a TOF of 52.01×10^{20} molecule g⁻¹ min⁻¹.

Song et al.³¹⁹ reported monodispersed PdAg NPs immobilized on a ZrO₂/C/rGO support derived from UiO-66 MOF and evaluated their activities in the dehydrogenation of formic acid (FA), displaying a TOF as high as 4500 h⁻¹ at 333 K with 100% H₂ selectivity; these results were comparable to those of the most active heterogeneous catalysts reported to date. The excellent performance was attributed to the high dispersion of ultrafine PdAg NPs. To synthesize the PdAg@ZrO₂/C/rGO catalyst, UiO-66/GO was first prepared by

solvothermally treating the MOF precursor solution together with graphene oxide (GO). After the pyrolysis at 1073 K for 5 h under an Ar flow, the resultant solid was used as the catalyst support for the PdAg nanoparticles (see Figure 22).

Figure 22. Schematic illustration of the preparation of the PdAg@ZrO₂/C/rGO nanocatalyst.

Adapted from reference 319. Copyright 2018 John Wiley & Sons.

Wu et al.²⁹⁷ investigated Pt and Nickel supported on mesoporous carbon derived from a Cu-MOF (HKUST-1) for nitrophenol reduction and methanol oxidation reactions. The carbon materials, with hierarchical pores, employed as the support were prepared by the calcination of HKUST-1 at 550 °C for 6 h inside a furnace. Following which, the resulting powder was etched with HCl to remove metal species. Subsequently, a second pyrolysis was conducted at high temperatures to improve the crystalline degree. The reported materials showed an excellent activity for the catalytic reduction of nitrophenol with KBH₄ and an enhanced efficiency for the oxidation of CH₃OH compared to that of the commercially available Pt/C.

Chen et al.²⁴⁷ reported a facile route to synthesize yolk-shell Co@C-N nanoreactors by the direct thermolysis of a hollow Zn/Co-ZIF precursor and applied them towards the aerobic oxidation of alcohols. The preparation of these nanoreactors is summarized in Figure 23. First, the authors synthesized ZIF-67 nanocrystals coated with a ZIF-8 layer to obtain a core-shell ZIF-67@ZIF-8 structures. The ZIF-67@ZIF-8 was then treated with Co^{2+} in methanol at 120 °C for 4 h to generate the hollow Zn/Co-ZIF. Finally, this hollow Zn/Co-ZIF was placed in a tubular furnace and then heated at 800 °C for 3 h with a heating rate of 1 °C/min under Ar to yield the final yolk-shell Co@C-N nanoreactor (Figure 23). The authors also prepared two more MOFMs from pure ZIF-67@ZIF-8 and ZIF-67 for comparison purposes in the aerobic oxidation of alcohols. The yolk-shell Co@C-N nanoreactor showed a significantly enhanced catalytic activity for the oxidation of alcohols; the nanoreactor yielded a 99% conversion under atmospheric air and base-free conditions, significantly higher than that of the ZIF-67- and ZIF-67@ZIF-8-derived materials. Moreover, the yolk-shell Co@C-N nanoreactor was also more efficient than most of the previously reported non-noble catalysts.

Figure 23. (a) Schematic illustration of the synthesis of hollow yolk-shell Co@C-N nanoreactors. (b) Schematic illustration of the synthesis of solid Co-based nanocomposites by the direct pyrolysis of ZIF-67 nanocrystals. (c) Schematic illustration of the synthesis of solid core-shell Co-based nanocomposites by the pyrolysis of core-shell ZIF-67@ZIF-8 precursors. Adapted from reference 247. Copyright 2018 American Chemical Society

Ye et al.²⁹⁸ developed a MOF-derived preparation for a robust Cu/SiO₂ catalyst to be used in the hydrogenation of dimethyl oxalate (DMO) to ethylene glycol (EG). The Cu/SiO₂-MOF catalyst was prepared by the sol-gel method. HKUST-1 powder was dispersed in distilled water, and then, pure ethanol and TEOS were added to obtain a SiO₂/HKUST-1 composite. The solid product was calcined in static air at 350 °C for 5 h to remove the HKUST-1 organic part and to leave ultrafine copper species (3.3 nm) dispersed on the porous SiO₂ matrix. The catalytic performance test was performed in a fixed-bed reactor with a feed of a 20 wt % of DMO in CH₃OH and H₂, keeping a H₂/DMO molar ratio of 50. The Cu/SiO₂ catalyst

displayed a selectivity towards EG that was higher than 95.0% with a lifetime of 220 h. These results outperformed the ones obtained by conventional copper-silica catalysts, such as SBA-15 and MCM-41, as well as HMS-based copper catalysts.

Yang et al.³⁰⁷ reported MOF-derived Co₃S₄ supported on nitrogen-doped carbon (CN) hollow nanoboxes for the reduction of nitroarenes. The synthesis of Co₃S₄@CN nanoboxes involved three steps. First, zeolitic imidazolate framework (ZIF-67) nanocubes were prepared. Then, ZIF-67 was converted to Co₃S₄/CN hollow nanoboxes with a low crystallinity by adopting thioacetamide as the sulfur source. In the final step, a simple thermal treatment resulted in the formation of Co₃S₄/CN hollow nanoboxes. The catalyst provided high conversion efficiencies and selectivities for a variety of nitroarene substrates that contain electron-donating or electron-withdrawing substituents under mild reaction conditions (in methanol at 60 °C). Furthermore, the nanobox inhibited both dehalogenation and vinyl hydrogenation reactions, which are common limitations of state-of-the-art Pd-based catalysts. The Co₃S₄/CN catalyst exhibited a good stability and was readily reused over at least three cycles with nitrobenzene as substrate. Afterwards, the conversion decreased to 77 %, while the selectivity remained at >99 % for the aniline product due to a slight agglomeration of the smaller active particles and the unavoidable catalyst loss during the recycling procedure.

Huang et al.³²⁰ studied the dehydration of glycerol in acrolein with a MOD-derived γ -Al₂O₃. The Al MOF MIL-96 was heated to 650 °C for 12 h with a heating rate of 1 °C/min under air to obtain the final MOF-based Al₂O₃. Catalyst testing was performed with a weight hourly space velocity for glycerol of 2.4 h⁻¹ and with a glycerol/H₂O weight ratio of 1:9. The catalytic data showed that the stability and selectivity obtained over the MOF-mediated Al₂O₃ catalyst were superior to the ones obtained by standard alumina samples. In particular, the selectivity towards acrolein was maintained with a conversion of 80% for almost 200 h.

Finally, Wezendonk et al.²⁹⁰ continued their previous work with the Fischer-Tropsch reaction by investigating the formation of iron carbides through a MOF-mediated approach. The authors' preparation of Fe@C catalysts *via* MOF-mediated synthesis allowed them to control the active phase formation. The reduction of the pyrolysed MOF, followed by a low-temperature Fischer-Tropsch treatment, resulted in the formation of the ϵ' -Fe_{2.2}C. On the other hand, direct carburization *via* the high-temperature Fischer-Tropsch resulted in the formation of χ -Fe₅C₂. The authors also observed that the Fe nanoparticles formed in the MOF pyrolysis were extremely prone to oxidation, with a conversion of the reduced iron phase into maghemite (γ -Fe₂O₃) of over 92%. Additionally, the authors found that both carbides displayed similar conversions, with a higher methane selectivity and lower C₅⁺ selectivity for the ϵ' -Fe_{2.2}C phase.

5 Electrocatalysis on MOFs

Figure 24. (a) Strategies of employing MOFs as electrocatalysts

5.1 MOFs as electrocatalysts

Most research in electrocatalysis currently focuses on the reactions related to the production of artificial fuels through water splitting (consisting of the H₂ and O₂ evolution reactions (HER and OER, respectively)) and CO₂ reduction,³²³⁻³²⁵ as well as the utilization of the product fuels through the reverse fuel cell reactions (especially the O₂ reduction reaction, ORR).^{325,326} The development of economical and effective catalysts for these reactions is critical to answering the ultimate energy and environmental challenge that besets the world today – how to limit and reduce the amount of CO₂ in the atmosphere caused by the mass exploitation of fossil fuels. MOFs can in principle be directly utilized as electrocatalysts to maximize catalytic surface area and to precision-tune active sites. However, the widespread development of such MOFs has been hampered by the poor conductivity, diffusion limitations due to pore size, debatable stability of the MOFs under electrocatalytic conditions, and the generally poor performance of MOF electrocatalysts compared to that of other reported materials.

5.1.1 O₂ evolution

The OER specifically refers to the electrochemical oxidation of water to produce O₂ gas:

The lack of earth-abundant OER catalysts is arguably the biggest challenge facing the implementation of an artificial fuel economy because the OER is the ideal counter reaction for fuel-generating reduction reactions such as the HER and CO₂ reduction.^{312,325,327} To improve the stability of earth-abundant transition-metal-based OER catalysts, as well as to optimize the kinetics, the OER is often studied under extreme alkaline conditions (pH = 13, 14). However, while metal oxides are most stable under these conditions, few analogous MOFs are.^{328,329}

Nonetheless, a number of MOF OER catalysts have recently been reported and are mostly composed of Ni, Fe, Mn, Co, and Cu, as listed in Table 3. The vast majority of these materials involve transition metal ions mixed with a π -conjugated carboxylic acid-containing molecule. For comparison, we also provide five model OER catalysts as benchmarks (Table 4). All of the catalysts are listed with their OER overpotentials at 10 mA cm⁻² and Tafel slopes, both common benchmarks for electrocatalytic reactions.³³⁰ To briefly describe these concepts, the overpotential (η) is a measure of the additional potential required above the thermodynamic potential (E_0) required to carry out an electrocatalytic reaction at a given current density; the Tafel slope is a kinetic measurement that describes the potential required to increase the rate of an electrochemical reaction by one order of magnitude. The former is an absolute measure of the additional energy needed to drive a reaction at a given rate; whereas the latter describes the kinetics of the reaction between rates. More information can be found in dedicated sources.³³¹ In general, while other values including turnover frequency at a given overpotential or catalyst loading provide more site-specific information, not all studies have reported these values or possessed the means to determine them easily. Subsequently, we operate on the assumption that all catalysts reported here have been optimized for the highest activity within the constraints of the experimental system, and from which, a comparison is at least reasonable.

Table 3. Recent and notable MOF OER catalysts.

MOF	Substrate	Electrolyte	η (–10 mA cm ⁻²)	Tafel slope (mV dec ⁻¹)	Ref.
Ni-Co-TPA	Cu foam	1 M KOH	189	42	332
Fe-TPA	Ni foam	1 M KOH	190	72	333
Fe-Co-2-amino-TPA/TPA	Ni foam	1 M KOH	192	39	334
Ni-TPA	Ni foam	1 M KOH	197	123	335
Ni-Cu-TPA	Ni foam	1 M KOH	202	107.2	182
Co-Fe-TPA	Nafion binder	0.1 M KOH	211	46	336
Ni-Fe-TPA	Ni foam	1 M KOH	213	31.3	337
Fe-Ni.Co-TPA	Ni foam	1 M KOH	219	53.5	338

Fe-Ni-Mn-TPA	Ni foam	1 M KOH	220	71.3	338
Ni-Fe-2,5-dihydroxy-TPA	Ni foam	1 M KOH	223	71.6	339
Ni-Fe-2,6-NDC	Ni foam	0.1 M KOH	240	34	340
Ni-Fe-2-amino-TPA	Ni foam	1 M KOH	240	58.8	341
Fe-Ni-TPA	Ni foam	1 M KOH	244	48.7	338
Ni-Co-TPA	Glassy carbon	1 M KOH	250	-	332
Mn(TCNQ) ₂	Cu foam	1 M KOH	256 _a	166	342
Co-TPA	Nafion binder	1 M KOH	263	74	343
Ni-TPA + Fe-TPA	Nafion binder	1 M KOH	265	82	344
Co-Ni-NDC	Cu foil	1 M KOH	265	56	345
Co-Fe-2,5-dihydroxy-TPA	Ni foam	1 M KOH	280	56	346
ZIF-67 on Co(OH) ₂ nanosheets	Graphite foil	1 M KOH	280	63	347
Ni-diiminobenzosemiquinonate	FTO	1 M KOH	300	74	287
Prussian Blue Analogues (Co-Fe)	Nafion binder	1 M KOH	330	70	348
ZIF-67	Carbon cloth	1 M KOH	330	104.9	349
Fe(TCNQ) ₂	Fe foil	1 M KOH	340	110	350
Ni-BTC	Nafion binder	1 M KOH	346	64	351
Fe-Ni Biphenyl-3,4',5-tricarboxylic acid	Nafion binder	0.1 M KOH	365	81.8	338
Ni-Fe-2,6-NDC	Glassy carbon	0.1 M KOH	406	-	340
[CoW ₁₂ O ₄₀] ⁶⁻ POM on ZIF-8 (Zn)	Nafion binder	0.1 M Na ₂ SO ₄	1568	783.6	352

^a Deposited directly on high surface area substrate or support.

Table 4. Benchmark OER catalysts.

Catalyst	Substrate	Electrolyte	η (–10 mA cm ^{–2})	Tafel slope (mV dec ^{–1})	Ref.
Fe-Co-W oxyhydroxides	Nafion binder	1 M KOH	223	~30	353
Ni-Fe Hydroxide Nanosheets	Nafion binder	1 M KOH	230	42	354
Co-Ni-P Nanosheets	Nafion binder	1 M KOH	273	45	355
Amorphous Ni-Fe Oxide Nanoparticles	Nafion binder	1 M KOH	280	30	356
Co-Mn Layered Double Hydroxide	Glassy carbon	1 M KOH	293	43	357

While an initial overview of MOF OER catalysts demonstrates competitive, if not superior activity to non-MOF OER catalysts, it should be immediately noted that the most active MOF catalysts are united not by any fundamental property of the MOF but by the metal foam substrate that they are deposited on.^{182,332-335,338-342,346} The use of metal foams and other high-surface-area supports is problematic for performance benchmarking because the current density is a descriptor that assumes a flat catalyst. Realistically, 3D supports increase the actual catalytic surface area of an electrocatalyst deposited on them while maintaining the apparent surface area (defined by the geometric area of a “flat” catalyst).^{358,359} Furthermore, foams (especially Ni) can also be catalytic with respect to the OER; oxidized Ni foam (which forms *in situ* during the OER) has a reported overpotential close to 400 mV at 10 mA cm⁻²,³⁶⁰ so it is not clear that the observed catalytic activities are entirely due to the deposited material. For example, while Zhao et al.³³² reported the best performing MOF electrocatalyst for the OER, they also demonstrated that the same catalyst grown on a flat glassy carbon electrode expressed an increased OER overpotential of 61 mV at 10 mA cm⁻². The bifunctional NiFe-based catalyst reported by Duan et al.³⁴⁰ presented a 166 mV increase in overpotential at 10 mA cm⁻² when grown on flat glassy carbon as opposed to nickel foam. The difference in the improvements between these two systems should serve as a warning on the limits of foam-deposited catalysts. Using 61 mV as an imperfect (and optimistic) estimate of the difference between catalysts grown on foam and on flat substrates, most of the Ni/Fe/Co/Cu/Mn-containing MOFs would have overpotentials between 250 mV to 400 mV. In comparison, Ni-Fe oxide, the model non-noble alkaline OER catalyst, exhibits a “base” overpotential of 350 mV when classically prepared using cathodic electrodeposition³⁶¹; however, more recently reported preparations can have overpotentials as low as 280 mV (amorphous Ni-Fe nanoparticles)³⁵⁶ and 230 mV (Ni-Fe nanosheets).³⁵⁴ Other notable earth-abundant transition metal oxides that can achieve overpotentials <300 mV at 10 mA cm⁻² include Mn-Co layered double hydroxides conditioned

for 20 hours (293 mV),³⁵⁷ Fe-Co-W oxyhydroxides (223 mV),³⁵³ and Co-Ni-P nanosheets (273 mV).³⁵⁵ Similarly, MOF OER catalysts provide good Tafel slope values, but for the most part, provide no improvement over non-MOF catalysts. In short, MOF OER catalysts mostly perform as might be expected being related to first-row transition metal oxides but do not exhibit an exceptional activity for the OER.

The analysis of the activity of these materials becomes further complicated by the poor aqueous stability of MOFs, particularly those based on carboxylate linkers. In the case of OER-catalysing MOFs, the combination of alkalinity and oxidizing potentials can lead to the hydrolysis and condensation of metal centres into metal oxides and hydroxides, particularly with weak binding ligands such as carboxylates.^{328,329} In the worst case scenario, the MOF disintegrates after a relatively short operational period (20 h), as was demonstrated for Co-TPA.³⁴³ In most cases, the indications of degradation are more subtle and only visible under spectroscopic characterization. For example, the diffraction patterns and Raman spectra of post-catalytic materials have shown the formation of new phases, mostly oxides and hydroxides, in a significant number of reports where a post-catalytic characterization was performed.^{334-336,339,344-346,351} Raman spectroscopy is particularly helpful as bridging metal oxides, indicative of MOF conversion to metal oxides, can often be observed. In contrast, changes in the bulk structure assessed by techniques such as diffraction are problematic for stability assessments; these approaches require significant levels of decomposition to observe changes and are therefore dependent on the length of the testing period. Functional testing alone is the most problematic due to the strong catalytic activity of metal oxides for the OER.^{362,363} The risk of metal oxide formation to proper catalyst characterization is that the functional activity attributed to a designer MOF catalyst may instead arise from the metal oxide decomposition product. Since carboxylate-based MOFs often demonstrate an instability, the high activity of these MOFs may be due to metal oxide formation.

Alternatively, while stability may preclude any role for designer reaction sites in MOF OER catalysts, the formation of amorphous metal oxides from metal centres also demonstrates that MOFs are effectively converted into catalysts by an *in situ* activation without need for further preparation. For example, Huang et al.³³⁶ demonstrated that stacked layers of 2D MOFs specifically designed with an easily oxidized and removed MOF linker (2,3-dihydroxyterephthalic acid) yielded high-surface-area OER-active nanosheets. The resulting catalyst carried out water oxidation at 10 mA cm⁻² and at an overpotential of 211 mV, the lowest reported overpotential amongst all non-foam-grown OER catalysts discussed here. The conversion of an ordered MOF to an amorphous oxide was demonstrated by XRD, confirming that *in situ* electrochemical conversion is a simple route to prepare high-surface-area oxide catalysts.

In contrast, MOFs based on nitrogen-containing (mainly azole and cyanide) linkers show excellent alkaline stability due to their strong metal-interactions,^{287,347-350} which are key to limiting the hydrolysis and condensation of metal centers.³⁶⁴ TCNQ-based MOFs, which coordinate to metal centres *via* the nitrogen of the cyano groups of TCNQ, have shown no evidence of degradation for Mn³⁴² and Fe³⁵⁰ and have realized overpotentials of 256 mV and 340 mV at -10 mA cm⁻², respectively. For cyanide-based MOFs, Prussian blue analogues have also been directly used and provide the added benefit that it is easy to prepare mixed metal MOFs from them.³⁴⁸ A few groups have also explored the potential for Co-based imidazoles (particularly ZIF-67) for the OER, with little sign of broader structural degradation under alkaline OER conditions.^{347,349} ZIF-67 itself is not a particularly good OER catalyst³⁴⁹; however, by growing ZIF-67 on Co(OH)₂, the catalyst activity improved to 280 mV at -10 mA cm⁻². Finally, Ni-based porphyrins with NiN₄ sites in both the centre of the porphyrin as well as the linker nodes were reported to have an overpotential of 300 mV for the OER at -10 mA

cm⁻².²⁸⁷ No post-catalysis stability study performed on any of these nitrogen linker-based catalysts demonstrated significant degradation.

A final interesting application of MOFs toward the OER, without converting them to alternative catalysts, is to use MOFs as scaffolds to protect catalysts from degradation and aggregation. The only recent report of this approach applied to OER catalysts was when Zn-based ZIF-8 was used as a host for a Co Keggin polyoxometallate.³⁵² Despite the sluggish performance of the catalyst ($\eta = 1568$ mV @ -10 mA cm⁻²), the MOF was noted for working under neutral conditions. Furthermore, since the goal of a scaffold system is to extract charge while preventing catalyst aggregation, future POMOFs could be improved by selecting more conductive MOF scaffolds. Overall, while these catalysts do not have competitive OER activities (partly as a result of the catalysis taking place in kinetically unfavourable electrolytes), the stabilization provided by MOF scaffolds could be an important design for future electrocatalysts.

5.1.2 *H₂ evolution*

In the HER, protons are reduced to form H₂:

In contrast to the OER, the HER is generally more kinetically favoured under acidic conditions, and most MOF HER catalysts have been designed to operate and test at low pH. The few alkaline MOF HER catalysts that have been reported are bifunctional electrodes that are also active for the OER (Table 5).^{340,341,348,365} These alkaline catalysts, are mostly composed of Ni, Fe, and Co materials and have HER overpotentials of $\sim 100 - 200$ mV, making them similar in performance to cathodically electrodeposited alloys³³⁰ (despite being oxidized).

However, most of these catalysts also utilize Ni foam substrates, which itself has a sufficiently high native activity for the HER (<250 mV vs. RHE at -10 mA cm^{-2}).³³⁰ Finally, since the HER is associated with an increase in pH (*via* the consumption of protons), alkaline HER MOF electrocatalysts must withstand even more extreme conditions (i.e., pH >14) requiring even greater stability considerations. In short, while carboxylate-based MOFs show potential as bifunctional water splitting electrodes, it remains unclear if, as in the case of OER catalysts, this activity arises from the MOF or from a decomposition product.

Table 5. MOF catalysts for the alkaline HER.

MOF	Substrate	Electrolyte	η (-10 mA cm^{-2})	Tafel slope (mV dec^{-1})	Ref.
Ni-Fe-2-amino-TPA	Ni Foam	1 M KOH	87	35.2	341
Ni-Fe-NDC	Ni Foam	0.1 M KOH	134	-	340
Prussian Blue Analogues (Co-Fe)	Nafion binder	1 M KOH	170	173	348
Ni-Co-NDC	Ni-mesh	0.1 M KOH	210	73	365

For acid-based HER-catalytic MOFs, catalysts with Co,^{366,367} Ni,^{366,368} Fe,³⁶⁶ and Cu^{369,370} single-atom nodes and MoS_x clusters^{371,372} have been reported (Table 6). Overall, while some of these catalysts have shown promise, most are not particularly competitive considering the overpotentials of optimized Co- and Ni-based catalysts (<100 mV)³⁷³⁻³⁷⁶ and flat Pt (40 mV)³³⁰ at -10 mA cm^{-2} . In contrast, only one MOF HER catalyst has generated an overpotential below 100 mV. Nonetheless, these approaches provide important insights into catalyst design.

Table 6. MOF catalysts for the acidic HER.

MOF	Electrolyte	η (-10 mA cm^{-2})	Tafel slope (mV dec^{-1})	Ref.
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Mo ₃ S ₇ -1,4-benzenethiol	0.5 M H ₂ SO ₄	89	57	371
Co ₅ (μ ₃ -OH) ₂ (bcpt) ₄ (bib) ₂ /4 wt% graphene	0.5 M H ₂ SO ₄	125	91	377
Co-CTGU/43 wt% AB	0.5 M H ₂ SO ₄	128	87	367
Co-BHT	0.05 M H ₂ SO ₄	185	88	366
Cu-BTC/1.7 wt% AB	0.5 M H ₂ SO ₄	208	80	378
Ni-BHT	0.05 M H ₂ SO ₄	331	67	366
Ni-BHT	0.05 M H ₂ SO ₄	370	128	368
Co-NDC	0.5 M H ₂ SO ₄	388	125	379
Cu-BHT	0.5 M H ₂ SO ₄	450	95	369
Fe-BHT	0.05 M H ₂ SO ₄	473	119	366
MoS _x -SIM	0.5 M H ₂ SO ₄	Redox mediator assisted		372

The first notable observation is the diverse range of linkers used in HER-active MOFs. While metal oxide hydrolysis and condensation are the primary stability concerns under alkaline conditions, the instability of MOFs under acidic conditions mainly arises from linker protonation and decoordination; subsequently, linkers exploit either strong metal-ligand bonds (thiols and azoles) or low pK_a values (carboxylates) to prevent hydrolysis.^{328,329,364} However, these precautions may be insufficient to protect the catalyst stability. In 2016, Kaeffer et al.³⁸⁰ demonstrated that hydrogen-evolving molecular Co catalysts based on imine-amine metal bonds formed Co-containing deposits *in situ* during the acidic HER, which were responsible for the observed HER activity. The Co-containing nanoparticles were found to form and desorb transiently, making them difficult to isolate. Evidence on the long-term stability of the MOFs reviewed here is limited; however, the complete post-catalysis oxidation of Ni was found in the case of Ni-aminobenzenethiolate nanosheets, even when both amines and thiols were involved in the node formation, suggesting that neither amines nor thiols are stable under acidic conditions.³⁶⁸ Indeed, linker selection remains a challenge.

A variety of metal centres can also be used for HER-active MOFs. Co is the most-active first-row transition metal for the HER, based on not only a general survey of reported catalysts but also the work of Downes et al.,³⁶⁶ which demonstrated that, of the benzenhexathiolate-based MOFs, Co had the best activity compared to Ni- and Fe-based catalysts by over 100 mV. Other Co-based MOFs with azole linkers have displayed notable activities for the HER, particularly when mixed with conductive binders ³⁶⁷; however, given the aforementioned instability of Co-N molecular catalysts,³⁸⁰ the performances of these catalysts as MOFs should be carefully considered, especially in the absence of thorough stability testing. Mo-based MOFs have recently seen more success as HER-active MOFs due to the stability of Mo in acid as well as the good HER activity of Mo-based materials. Ji et al.³⁷¹ reported Mo₃S₇-containing MOFs capable of carrying out the HER at record low overpotentials and turnover frequencies for molybdenum sulfides at pH 0. By changing the linkers, it was possible to modulate and study the catalytic activity (Figure 25). The MOF was deposited in thin layers to reduce the likelihood of conduction and diffusion effects reducing the activity. No structural changes were reported after catalysis; based on the structure presented, the thiolate linker was likely coordinated to Mo sites, preventing protonation and hydrolysis due to the high strength of the Mo-S bond. ³⁸¹

Figure 25. Controllable configurations of Mo_3S_7 cluster-based MOFs using dithiolate linkers. Reproduced with permission from reference 371. Copyright 2018 American Chemical Society

Strong non-MOF HER catalysts such as MoS_x are useful benchmarks for activity, making them good systems to study the fundamental properties of MOFs. Noh et al.³⁷² prepared MoS_x -based catalysts by impregnating NU-1000 with Mo, followed by an H_2S treatment. The structure itself was not noticeably active for the HER, and only MoS_x sites within the 20 nm closest to the FTO electrode were suspected to be redox active. However, carrying out voltammetry in the presence of various soluble redox mediators allowed for greater use of the whole volume of the catalyst. The implication that only the 20 nm closest to the electrode were HER-active independently underscores the need to consider conductivity carefully since native, non-modified NU-1000 is an insulating MOF.^{382,383}

5.1.3 O_2 reduction

The ORR is the reverse reaction of the OER where O_2 is reduced to water or hydroxide species.

As the ORR is the limiting reaction in fuel cell catalysis, research in the field is moving away from traditional acidic PEM systems (where the ORR kinetics are less favourable) towards alkaline fuel cells.³⁸⁴ Consequently, MOF catalysts are moving in the same direction (Table 7). Since the ORR is limited by the diffusion of O₂ to the catalyst, different metrics – namely onset and E_{1/2} potentials in O₂-saturated solutions – are used to assay activity. The E_{1/2} potential of an ORR catalyst is the potential at which the catalyst reaches one-half of its maximum ORR activity, while the onset potential is broadly defined to the potential at which electrocatalytic activity becomes significant. Since ORR catalysts are seldom described based on their overpotential for the ORR, the onset is instead provided here. A more positive onset represents a more active catalyst.

Table 7. MOF ORR catalysts. All values measured in 0.1 M KOH.

MOF	Onset (mV vs. RHE)	E _{1/2} (mV vs. RHE)	Ref.
(Co ₃ (μ ₃ -OH)(BTB) ₂ (BPE) ₂)(Co _{0.5} N(C ₅ H ₅))	810	~650	385
Fe-triazolate	838	683	386
Ni-hexaiminotriphenylene	840	-	387
Cu-hexaiminotriphenylene	890	~740	387
ZIF-67/pomelo-derived carbon	900	820	388

As with the OER and HER, the primary goal of studying new materials for the ORR is to develop noble-metal (particularly Pt)-free catalysts. The model catalyst for this reaction, 20 wt. % Pt supported on carbon black (Pt/C), has an onset potential of 1.07 V vs. RHE and an

$E_{1/2}$ of 0.91 V vs. RHE under alkaline conditions; under acidic conditions, the onset potential is 0.95 V vs. RHE, while the $E_{1/2}$ remains as 0.91 V vs. RHE.³⁸⁹ In contrast, the premier noble-metal-free catalysts (typically nitride-, particularly porphyrin-based) exhibit more negative ORR onsets under alkaline (1.00 – 0.96 V vs. RHE) and acidic (~0.90 V vs. RHE) conditions, while Pt-competitive $E_{1/2}$ values exist for the alkaline but not acidic ORR.³⁹⁰ Recently reported MOF ORR catalysts all have nitride-based active sites, but none have produced comparable onset and $E_{1/2}$ potentials.

In the recently reported ORR-active MOFs, nitrogen-coordinated metal centres are the most attractive ORR catalysts. A direct comparison of equivalent amine- and hydroxyl-containing coordination polymers demonstrates that amine linkers have the higher activity than oxygen linkers for ORR.³⁸⁷ However, all recently reported amine- and oxygen-based systems experience some degree of functional decomposition over the course of 1 – 10 hours of catalytic testing.^{385,387} Alternately, azole-based catalysts have been found to have comparable activities as well as good stabilities.^{386,388} While such catalysts can confirm the stability and activity of conjugated nitrogen linkers, their poor activities compared to those of other MN₄ ORR catalysts suggests that these catalysts can be further optimized.

5.1.4 CO₂ reduction

Electrocatalytic CO₂ reduction is generally more complicated than the other reactions considered here as it refers to not one but multiple reactions with different products and overlapping intermediates.^{391,392} Since all of these individual reactions possess similar electrochemical potentials, the catalysts are seldom selective for a single product. The purity is further reduced as the HER often takes place simultaneously. Finally, CO₂ has poor solubility in water, limiting the reaction rates. Nonetheless, MOF electrocatalysts are better-suited for CO₂ reduction than the other reactions discussed here for several reasons.^{392,393} Firstly, CO₂

reduction is typically carried out either under near-neutral carbonate-buffered conditions or in organic electrolytes to improve CO₂ solubility, resulting in improved MOF stability. Second, MOFs can be functionalized to allow for better CO₂ capture, and even, for secondary catalytic sites to enable tandem catalysis. Subsequently, CO₂ can be reduced into more complex molecules. In reality, these possibilities are limited by several realities regarding CO₂ reduction. First, CO₂ reduction product distributions are generally governed by the identity of the metal centre, with Cu MOFs tending to produce more complex acids and hydrocarbons, while MOFs containing other metals mostly catalysing the simpler but less valuable reduction of CO₂ to CO. Second, as Cu molecular catalysts rapidly degrade under operating conditions into metallic clusters,^{394,395} pristine MOF electrocatalysts capable of producing economically significant products have been difficult to actualize.

Figure 26. POMOF based on a porphyrin and Keggin POM for CO₂ reduction. Reproduced with permission from reference 396. Copyright 2018 Nature Publishing Group.

A good example of the functionalization possibilities that can be achieved by electrocatalytic MOFs was reported by Wang et al.,³⁹⁶ who developed a POMOF with a high ($\geq 94\%$) faradaic efficiency and activity (-20 to -30 mA cm⁻²) for CO production between $-$

0.8 and -1.0 V *vs.* RHE (Figure 26). The MOF consisted of carboxy-terminated porphyrins linked to Keggin-type POMs. Keggin-type POMs exhibit a characteristically delocalized and concentrated electron density, making them excellent for improving conductivity when utilized in combination with conjugated organics. The authors were also able to vary the identity of the first-row transition metal, confirming the strong activity of N-coordinated Co for reducing CO₂ to CO,³⁹⁷ as Zn, Ni, and Fe porphyrins presented Faradaic efficiencies of less than 20% in the same potential ranges (and current densities less than -20 mA cm⁻²). The use of POMs for electronic purposes contrasts with most POMOFs, where POMs are directly used as catalysts^{352,398-400}; given the strong performance of POMOFs designed for conductivity enhancement compared to that of others, using POMs as electron reservoirs appears to be another good strategy to pursue.

MOFs can also be designed with CO₂-capturing properties, particularly given the poor solubility of CO₂ in aqueous electrolytes. MOFs such as Cu₃(BTC)₂ (HKUST-1) provide excellent adsorption properties for CO₂ (>5 mmol g⁻¹).⁴⁰¹ Although HKUST-1 was amongst the first reported MOF CO₂ electroreduction catalysts,⁴⁰² at the time, it was demonstrated as being functional (albeit unstable) in organic electrolytes. More recently, HKUST-1 was also found to exploit its gas capture properties to function effectively in water.⁴⁰¹ The improved CO₂ capture was used to rationalize the improved faradaic efficiency for CH₄ production at high potentials (-2.5 V *vs.* SCE), which increased from less than 3% to 18%. Concurrently, the H₂ faradaic efficiency fell from 90% by 70% under the same conditions. However, the MOF degraded after 24 h of operation, as observed *via* FTIR. MOFs can also be used to change the surface of a catalyst to control product distribution, for example, resulting in a change in the hydrocarbon products obtained from CO over an Au catalyst, as reported by De Luna et al.⁴⁰³ However, the authors' strategy led to the formation of small amounts of other hydrocarbons, with H₂ becoming the greatest beneficiary. Therefore, despite the potential for

MOFs as CO₂ reduction catalysts, the potential of CO₂ reduction-active MOFs remains unfulfilled.

5.2 Derived electrocatalysts

In addition to the advantages discussed above, MOF-derived solids offer the additional benefit of improved conductivity. When MOFs are pyrolysed in controlled atmospheres, the decomposition of carbon-containing linkers results in the formation of conductive carbons that improve charge extraction. Recent papers in the field of MOF-derived electrocatalysts have focused on three major themes: the preparation of complex, multimetallic or novel inorganic anion compounds; the formation of catalytic heterostructures, whereby two unique and independent materials are fused to make a common catalyst with unique synergies; and the carefully controlled decomposition of MOF precursors that enables some control over the final catalyst.

5.2.1 Strategies for materials – OER

Phosphide catalysts have recently been explored for use in the OER, and this research was driven by the discovery that metal phosphides, first discovered as HER catalysts,³⁷³ have OER activities comparable to that of oxides.⁴⁰⁴ While the mechanism for improvement is still under debate, MOFs provide a valuable route as a starting material for phosphides as well as other potentially active inorganic anions. It should be noted that, due to the cost of phosphide- and selenide-containing organic precursors, all of the phosphide and selenide materials reported here were prepared *via* post-pyrolytic modifications, such as *via* annealing in a furnace. Furthermore, benchmarking of the innate activity of these materials is difficult since many of the phosphides are deposited on high-surface-area scaffolds. Regardless, assuming that the

trends in activity would also hold on flat electrodes, phosphides (particularly of Co and Ni) exhibit good OER activities compared to that of other MOF-derived catalysts (Table 8).

Table 8. Recent MOF-derived OER catalysts.

Catalyst	Electrolyte	η (-10 mA cm^{-2})	Tafel slope (mV dec^{-1})	Ref.
CoP/Fe-PO ₄ ^a	1 M KOH	190	62	405
Co ₃ O ₄	1 M KOH	208	50.1	406
NiCo ₂ O ₄ /CoMoO ₄ ^a	1 M KOH	234	102	407
Co ₃ O ₄ ^a	1 M KOH	245	78	408
CoP ^a	1 M KOH	251	82.1	409
CoP ^a	1 M KOH	258	91.7	410
Ni ₂ P ^a	1 M KOH	260	62	411
Co ₃ O ₄	1 M KOH	261	70	412
FeNi	1 M KOH	261	40	413
Ni ^a	1 M KOH	265	54	414
CoS/CeO _x	1 M KOH	269	50	415
CoFeNiS _x	0.1 M KOH	270	114	416
Ni ₂ P/CoN _x	1 M KOH	270	65	417
Co ₉ S ₈ /Fe ₃ O ₄	0.1 M KOH	280	87	418
CoWP	1 M KOH	281	68	419
CoN _x ^a	1 M KOH	286	62	420
CoP	1 M KOH	292	64	421
NiFe ₂ O ₄ ^a	1 M KOH	293	98	422
Co ₃ O ₄ /CoFeO _x	1 M KOH	297	61	423
CoNiP	1 M KOH	297	57.35	424
CoNiSe	1 M KOH	300	87	425
CoN _x	6 M KOH	301	66	426
Co ₉ S ₈	1 M KOH	302	54	377
CoO _x ^a	1 M KOH	302	70	427
Co/Mo ₂ N	1 M KOH	302	90	428
CoSe ₂	1 M KOH	306	46	429
Co ₃ O ₄ /Fe ₂ O ₃	1 M KOH	310	67	430
CoP/CeO _x	1 M KOH	313	69	431
CoN _x	1 M KOH	315	75.7	432
Co ₃ O ₄ /CoMoO ₄	1 M KOH	318	63	433
MoO ₂ /Co ₂ Mo ₃ O ₈	1 M KOH	320	88	434

CoNiS _x	1 M KOH	320	59	435
CoO/CoFe ₂ O ₄	1 M KOH	330	64	436
Co/Co ₃ O ₄	0.1 M KOH	331	37	437
Co/Co ₃ O ₄	1 M KOH	333	69	438
CoSe ₂	1 M KOH	335	54.2	439
Co/NiCo ₂ O ₄	0.1 M KOH	339	60	440
Co(OH) ₂	0.1 M KOH	340	44.6	441
NiO/NiCo ₂ O ₄	1 M KOH	340	66	442
CuO	1 M KOH	340	156	443
CoNi/CoNiO ₂	1 M KOH	341	84	444
CoS _x /MoS ₂	1 M KOH	347	147	445
CoN _x /CoO _x	0.1 M KOH	350	79	446
CoNiN _x	0.1 M KOH	361	72	447
Co ₂ P/Mo ₂ C/Mo ₃ Co ₃ C	1 M KOH	362	82	448
FeNi LDH	1 M KOH	364	-	449
CoNiS _x	1 M KOH	365	58.2	450
Co ₃ O ₄ ^a	1 M KOH	371	74	451
Co ₉ S ₈	0.1 M KOH	390	72	452
CoN _x	1 M KOH	400	61	453
CoN _x	0.1 M KOH	401	89	454
CoN _x	0.1 M KOH	410	85	455
CoNi	1 M KOH	420	107	456
CoN _x	0.1 M KOH	431	89	457
Zn _x Co _{3-x} O ₄	1 M KOH	435	66.3	458
CoN _x	0.1 M KOH	450	118.3	459
CoN _x	0.1 M KOH	451	94	460
CoZnO _x	0.1 M KOH	471	-	461
CoB _x N _y	0.1 M KOH	509	48.6	462
CoN _x /MnO	0.1 M KOH	531	78	463

^a Deposited directly on a high-surface-area substrate or support.

Sulfides and nitrides are generally easier to prepare without post-pyrolytic modifications as the ligands are not prohibitively expensive, such as nitrogen-containing catalysts derived from imidizolate-based MOFs.^{426-428,432,438,447,455,460,462,464,465} Sulfides are also simple to prepare, as the MOF can be infiltrated with sulfide precursors, such as thiourea,⁴⁴⁰ thioacetamide,^{445,453} or even sulfides *via* ligand exchange in the case of Prussian Blue

analogues.⁴¹⁶ Sulfides can also be introduced into MOF-derived materials *via* decomposition of metal compounds such as Zn or Cd. Zn for example is a relatively low-boiling metal, and so a MOF precursor can be pyrolysed at 900°C to remove Zn.⁴⁶¹ Similarly, Co-based MOFs grown on CdS nanowires undergo sulfidation when calcined at 850°C due to the sublimation of Cd, resulting in Co₉S₈.³⁷⁷ While there are potential hazards to consider from volatile Cd, the knowledge of CdS nanomaterial shape control is extensive due to the long-running interest in CdS materials for optoelectronics, unlocking a wide potential range for shape control in MOF-derived sulfides.

5.2.2 Strategies for materials – HER

MOF-derived HER catalysts share several important design insights with OER catalysts. First, the volatilization of a low-boiling metal can be integrated into the pyrolysis process, to not only form new compounds but also create a porous structure. For example, to prepare a Ni-based HER catalyst, a bimetallic Ni-Zn MOF was calcined under N₂, resulting in a porous carbon-supported Ni structure with a good HER activity under alkaline conditions (40 mV overpotential at –10 mA cm^{–2}).⁴⁶⁶ Second, HER-active Group VI metals (primarily Mo and W) can be directly integrated into MOFs for a high HER activity.^{419,428} Since alloys of these and first-row transition metals exhibit uniquely high activities for the HER, MOF-derived catalysts are therefore an easy route to incorporate these elements. Both strategies show promise, as evidenced by the competitive activities of materials prepared by such methods. Finally, since phosphides were used for the HER before the OER,³⁷³ it is unsurprising that phosphide ligands take up a significant share of MOF-derived HER catalysts (Tables 9, 10).

Table 9. MOF-derived HER catalysts under alkaline conditions.

MOF	Electrolyte	η (–10 mA cm ^{–2})	Tafel slope (mV dec ^{–1})	Ref.
Ni _a	1 M KOH	37	57	414
Ni	1 M KOH	40	77	467
CoWP	1 M KOH	67	66	419
CoP _a	1 M KOH	70	83.2	410
Co/Mo ₂ N	1 M KOH	76	47	428
CoP/Fe-PO ₄ _a	1 M KOH	78	92	405
Ni ₂ P	1 M KOH	94	41	417
CoFeNiS _x	0.1 M KOH	~110	49	416
CoO _x _a	1 M KOH	117	146	427
NiCo ₂ O ₄ /CoMoO ₄ _a	1 M KOH	121	77	407
CoP/CeO _x	1 M KOH	127	56.7	431
CoN _x	1 M KOH	133	96	420
CoP	1 M KOH	140	59	421
Ni ₂ P _a	1 M KOH	142	58	411
CoPS	1 M KOH	148	78	468
Co ₂ P/Mo ₂ C/Mo ₃ Co ₃ C	1 M KOH	182	68	448
CoSe ₂	1 M KOH	250	72	425
Co/Co ₃ O ₄	0.1 M KOH	350	57	437
Co/CoFe ₂ O ₄	1 M KOH	365	52	436

_a Deposited directly on high surface area substrate or support.

Table 10. MOF-derived HER catalysts under acidic conditions. All reactions carried out in 0.5 M H₂SO₄.

MOF	η (–10 mA cm ^{–2})	Tafel slope (mV dec ^{–1})	Ref.
CoWP	35	35	419
CoPS	80	68	468
Ni/NiO _x	108	44	469
Co ₂ P/Mo ₂ C/Mo ₃ Co ₃ C	154	65	448
Ni ₂ P	198	113.2	470
FeNiP _x	222	69	345

CoS _x /MoS ₂	239	103	445
CoN _x	260	80	346
CoN _x	305	107	453

5.2.3 Strategies for materials – ORR

Given the potential for nitrogen-coordinated first-row transition metals to replace Pt for the ORR, MOF-derived catalysts possess great potential. First-row transition metals, especially Co and Fe, have been extensively incorporated into nitrides derived from MOFs but so too have Mn and Cu. Unusual additions of heavier elements such as Pt⁴⁷¹ and Ce⁴⁷² have also been reported recently. Pt was added in a post-synthetic modification after MOF decomposition, but then reannealed to form Pt₃Co/C for use in the acidic ORR. In the case of Ce, Ce³⁺ was prepared as part of the MOF precursor and subsequently decomposed. CeO₂ has long been known to have a high propensity for O₂ storage,⁴⁷³ allowing it to bring O₂ molecules closer to the catalytic sites.

Table 11. MOF-derived ORR catalysts.

MOF	E _{onset}	E _{1/2}	Ref.
Fe/Fe ₃ C-NC	0.85	0.7	464
15%PANI-ZIF67	0.85	0.75	437
Co-N/PC@CNT	0.92	0.78	454
Co-N-CNR	-	0.78	457
Co-CNT _a	0.9	0.78	420
Co-N-C	0.93	0.8	474
Fe-N/C-800	0.92	0.81	475
Fe single atoms on nanoplate	-	0.81	449
Co-N _x -900	-	0.82	446
Co-N/C-800	0.8936	0.8236	459
Co@NPC-900	1.05	0.824	476
FeCo@NC	0.9	0.827	465
MnO@Co-N/C	-	0.83	463
CoNC-CNF-800	-	0.83	460

Ce-HPCN	0.923	0.831	472
Co-B/N codoped-CG	0.914	0.831	462
CoNi-NC	0.93	0.84	447
Co-SAC	0.99	0.84	346
Co/HCNP	-	0.845	438
P-Co-NC-4	0.9	0.85	432
Co ₉ S ₈	0.92	0.86	452
Co single sites on CNTs	0.99	0.86	455
NiCo ₂ O ₄ /Co,N-CNTs	-	0.862	440
Fe ₃ Mn ₁ /N-CNTs-100	-	0.865	477
Ni ₂ P/CoN-PCP	0.972	0.871	417
ZIF-67/PEI/GO	0.89	0.8736	478
Co-N _x	-	0.877	426
Fe _{0.3} Co _{0.7} /NC	0.98	0.88	479
HC-5Co ₉₅ Zn	-	0.88	461
Fe/N/S-CNTs	0.987	0.887	370
Cu@Fe-N-C	1.01	0.892	480
Pt/40Co-NC-900	1.05	0.92	481

^a Deposited directly on high surface area substrate or support.

While the results of these catalysts are promising (Table 11) , it should be remembered that nitrogen-doped carbons themselves are ORR active.⁴⁶⁶ This catalytic activity may represent a problem for separating the innate activity of the support with that of the metal nitride; however, since catalytic activity is an innate property of the support, MOF-derived catalysts are proving to be an effective route to prepare ORR catalysts.

5.2.4 General strategies – heterostructures

Sometimes, second elements are added at specific steps during a synthesis such that the new combined precursor decomposes into a heterostructure when calcined. Many heterostructures have been reported, including core-shell, yolk-shell, and hollow configurations. In some cases, such as the previously discussed Ce-incorporated Co-N_x structure,⁴⁷² heterostructures are the result of decomposing a single material into two structurally incompatible materials. Zhang et

al.⁴⁸² reported an analogous case of a Ag/Co₃O₄ hybrid material derived from a single MOF by annealing at 350°C. The resulting heterostructure presented a superior activity for CO₂-to-CO electrocatalysis compared to that of pure Co₃O₄; however, since Ag also possesses an activity for the same reaction and no controls were performed for pure Ag, it is unknown whether there were synergistic effects. Despite the close atomic parameters of Co and Fe, mixtures of the two elements have also been used for heterogeneous MOF-derived electrocatalysts, including oxides,^{430,436} sulfides,⁴⁸³ and phosphides.⁴⁰⁵ In the case of phosphides and sulfides, Fe remains oxidized while Co is phosphidized. Core-shell type heterostructures can also be prepared by controlling the synthetic order of a material. Co-ZIFs have recently been popular for this purpose as a route to Co-containing mixed metal heterostructures, which can be impregnated with Mo POMs,⁴³³ Fe,^{423,446} and Ni⁴⁴⁰; and grown on Mo-based materials (MOFs⁴²⁸ and oxides⁴³⁴) and ZnO.⁴⁴⁹

Overall, MOF-derived heterostructures represent an excellent approach to obtain interesting nanomaterials. However, special synergies are often proposed to be responsible for the good catalytic activities without rationale. Furthermore, the catalytic activities of most synergistic heterostructures are not strong enough to be competitive with the best conventional catalysts. Until our understanding of these materials increases, it is unlikely that heterostructures will find relevance in electrocatalysis.

5.2.5 General strategies – controlled decomposition of MOFs to preserve ideal structural features

High-temperature pyrolysis can often lead to a larger particle size and represents a process that can be prevented by the presence of a graphitic carbon network. By controlling the decomposition of a MOF, such as by using lower temperatures or indirect heating, nanostructures can be preserved more easily. Nam et al.³⁹⁴ demonstrated that by changing the

coordination of Cu sites in HKUST-1 through low-temperature (250°C) heating without destruction or graphitization, the selectivity of the reaction for CO₂ reduction to ethylene improved across the entire tested potential range. However, when heating was carried out beyond 3 hours, the faradaic efficiency dropped again. This change in behaviour was associated with a minimum in the Cu coordination number, suggesting that the short heating periods resulted in more uncoordinated Cu catalytic sites. Microwave heating is another effective method for controlled decomposition, as conductive carbons can act as antennae for microwaves leading to local heating.⁴⁸⁴ To exploit this behaviour, Bu et al.⁴¹³ grew Ni and Fe hexacyanides MOFs onto graphene oxide and carbon cloth composites (Figure 27). With its microwave-induced composition, the derived catalyst maintained an overpotential of 261 mV at 10 mA cm⁻² in 0.1 M KOH. This relatively strong OER performance was attributed to the graphitization process depositing only thin layers of carbon on the surface of the nanoparticles, resulting in improved reactant and product diffusion. Finally, MOFs can decompose during electrochemical operation to yield a catalytically active material; Wang et al. utilized this approach to convert Ag-MOFs into Ag nanostructures that were catalytically active for the electrochemical reduction of CO₂ to CO with high (>96%) Faradaic efficiency.⁴⁸⁵

Figure 27. Synthetic scheme for a MOF derived from Prussian blue analogues for OER using microwave heating. Reproduced with permission from reference ⁴¹³. Copyright 2018 Royal Society of Chemistry.

5.2.6 General strategies – 2D MOF decomposition

Controlled decomposition can be further extended to 2D MOF-derived electrocatalysts. When 2D MOFs are decomposed at low temperatures ($\leq 400^\circ\text{C}$), the macrostructure of the MOF is sufficiently preserved so that the resulting structures retain a 2D appearance. In particular, Zhou et al.⁴⁰⁶ were able to achieve an overpotential of 208 mV on a flat glassy carbon substrate through their reported method for preparing Co_3O_4 via 2D MOF decomposition (Figure 28); this value represents a record low for catalysts not deposited on foams. The key to the success of the system was the conversion of the MOF into an array-like structure. Various reports of phosphide^{409,428,435} and sulphide⁴⁵⁰ catalysts have detailed the annealing of MOFs in the presence of subliming precursors. In contrast, Cong et al.⁴⁵³ prepared nitrides by decomposing 2D MOFs with N-containing hypoxanthine linkers; however, this system was prepared at elevated temperatures (800°C), contained substantially larger features than that of the others reported here and delivered high overpotentials for the HER in 0.5 M H_2SO_4 . Nonetheless, the overall activities of catalysts derived by the low-temperature decomposition of 2D MOFs indicate greater promise in the future.

Figure 28. Derivation of 1D, 2D, and 3D MOFs into electrode structures. Reprinted with permission from reference 406. Copyright 2018 American Chemical Society

6 Photocatalysis

Figure 29. Strategies for using MOFs as photocatalysts

6.1 MOFs in photocatalysis

Since the discovery of photo-assisted electrochemical water oxidation on an n-type TiO₂ by Fujishima and Honda,⁴⁸⁶ the interest in photocatalytic materials has been rising. In a classical photocatalytic process, light with energy exceeding the band gap energy is absorbed by a semiconductor, and charge separation takes place. Electrons from the valence band of the material are excited to the conduction band leaving behind positively charged holes, and the photogenerated charge carriers migrate to the surface of the semiconductor. Once the charge carriers reach the surface, the holes and electrons can drive reduction and oxidation reactions, when thermodynamically favourable.⁴⁸⁷

Since the discovery of MOFs, it was only a matter of time until the first reports on photocatalytic applications appeared. Since then, different approaches based on the immobilization/incorporation of photoactive catalytic sites of different MOF structures^{488,489} and the utilization of MOFs as catalyst precursors^{234,392,490} have been proposed. In this section we give an overview of the recent progress on these topics and the different photo-driven processes explored. We intentionally did not cover photocatalytic transformations in organic synthesis, topic for which we refer the interested reader to these very recent reviews on the topic.^{18,491}

6.1.1 MOF-based photocatalysts

The first experimental evidence of photocatalytic activity on a MOF (MOF-5) was published in 2007.⁴⁹² It was postulated that UV light absorbed by the terephthalate linker resulted in the transfer of photoinduced electrons to the Zn₄O clusters of MOF-5.⁴⁹³ This type of transition is referred as ligand-to-metal charge transfer (LMCT). Later, with the discovery of more stable structures of MOFs, other systems such as UiO-66(Zr)⁴⁹⁴ and MIL-125(Ti)⁴⁹⁵ were proposed

to undergo similar charge transfer mechanisms. Although later, it was clearly demonstrated that charge separation in UiO-66(Zr) does not occur.⁴⁷

At the same time, the effect of linker functionalization on light absorption and its consequences for visible-light photocatalysis was explored. With the first reports dating from 2010,⁶ the use of visible-light-absorbing linkers has since been customary.^{496,497} More recently, Han et al.⁴⁷¹ explored a new visible-light-promoted photocatalyst derived from MIL-125 by using a double methylthio group on the terephthalic acid linker, H₂BDC-(SCH₃)₂. The authors synthesized 20%-MIL-125-(SCH₃)₂ and 50%-MIL-125-(SCH₃)₂ MOFs by replacing the BDC linker of the parent MIL-125 through a solvent-assisted ligand exchange process since the direct synthesis of H₂BDC-(SCH₃)₂ MIL-125 was not successful. The resulting band gap of the final material was 2.6 eV, significantly lower than the 3.8 eV of the parent MIL-125.

Post-synthetic modification is an interesting approach to enhance the photocatalytic properties of otherwise non-photocatalytically active MOFs. An outstanding example involves the case of UiO-66. Although several articles have claimed the exchange of Zr cations by Ti atoms in the metal clusters,⁴⁹⁸ later reports have pointed to the grafting of Ti units, rather than an actual exchange and the formation of bimetallic clusters.⁴⁹⁹

As can be seen from the above, the direct use of “pristine MOFs” in photocatalytic applications, besides organic transformations, remains limited by the few MOF structures in which LMCT has been shown and by the relatively low photocatalytic activity shown by these structures, which in most cases is due to the very fast charge recombination.

6.1.2 Single-site MOF photocatalyst

Another approach is the direct incorporation of molecular photocatalysts or photosensitizers in the secondary building units for an efficient system. For example, Yang et al.⁵⁰⁰ reported the charge separation dynamics between [Ru(dcbpy)(bpy)₂]²⁺ and Pt(dcbpy)Cl₂ on the

functionalized UIO-67 MOF (Ru-Pt-UIO-67) (Figure 30), which demonstrated efficient H₂ generation from water as evidenced *via* a combination of optical transient absorption (OTA) and X-ray transient absorption (XTA) spectroscopy. Using optical transient absorption (OTA) spectroscopy, the researchers showed that charge separation in this hybrid MOF occurred *via* electron transfer (ET) from the Ru-photosensitizer to Pt-catalyst. Using Pt L3-edge X-ray transient absorption (XTA) spectroscopy, the authors observed an intermediate reduced Pt site, directly confirming the formation of a charge separated state due to ET from the Ru-photosensitizer and unravelling their key roles in photocatalysis. It is worth highlighting that, in this case, the Zr nodes acted as molecular catalyst “separators” but did not directly participate in the photocatalytic process.

Figure 30. Synthetic scheme for the [Ru(dcbpy)(bpy)₂]²⁺ and Pt(dcbpy)Cl₂-functionalized UIO-67 MOF (Ru-Pt-UIO-67). Reproduced with permission from reference 500. Copyright 2018 American Chemical Society.

Later, the same group⁵⁰¹ developed another single-site MOF system that consisted of a molecular Co catalyst and a Ru-based photosensitizer in the structure of Zr-based-UiO-67(bpy)-MOF. After the optimization of the photocatalytic process parameters, the authors obtained the following ratio: Co:Ru = 5.26:1 for Co-Ru-UIO-67(bpy). Control experiments in the absence of TEOA or H₂O demonstrated no H₂, suggesting their key roles as sacrificial donor and proton source. It is worth mentioning that Co-Ru-UIO-67(bpy) showed an

unchanged activity for at least three recycling runs, and just 3.2% leaching of Co was observed. Moreover, the XANES and EXAFS measurements demonstrated that the local structure of Co remained unchanged after the photocatalytic process. In a similar line, He et al.⁵⁰² immobilized single atoms of noble metals (Ir, Pt, Ru, Au, and Pd) on square-planar zirconium-porphyrinic MOF hollow nanotubes (HNTM). HNTM-Pt, HNTM-Ir, and mixed HNTM-Ir/Pt catalysts were tested in H₂ photocatalytic production. Among these systems, HNTM-Ir/Pt demonstrated the best activity because of the better charge carrier combination and less charge-transfer resistance.

Ni²⁺ ions are known as an efficient cocatalyst for hydrogen production. An et al.⁵⁰³ investigated an Al-based MOF consisting of aminoterephthalic acid and AlO₄(OH)₂ clusters with incorporated Ni²⁺ cations, Al-ATA-Ni, for overall water splitting. Based on the results of the X-ray absorption near-edge structure (XANES), extended X-ray absorption fine-structure (EXAFS) and FTIR and XRD analyses, the local environment of Ni²⁺ was established. Ni²⁺ ions were coordinated to the amino nitrogen of deprotonated ATA²⁻, the O of an AlO₆ octahedron and four OH groups. Experiments in pure water gave a stoichiometric ratio of 2:1 for H₂ and O₂, respectively. Control experiments with bare Al-ATA MOF and sacrificial agents (AgNO₃ and MeOH) confirmed that Ni²⁺ ions acted as the H₂ evolution sites and that they could improve activity for the O₂ evolution reaction. The results of photoluminescence and transient photocurrent measurements suggested that Ni²⁺ incorporation led to an increase in electron-hole separation, and eventually, resulted in a higher number of photogenerated charge carriers.

6.1.3 MOFs as supports

Thanks to their high porosity, MOFs can act as hosts for the encapsulation of photocatalytically active species. In some cases, the resulting solids display an enhanced photocatalytic

performance compared to that of homogeneous photocatalysts. The MOF usually plays the role of the matrix for the active components, preventing degradation and clustering while maintaining a high accessibility.

Many polyoxometalates (POMs) have been reported to possess a photocatalytic activity under visible-light irradiation. Unfortunately, their high solubility in solution make recovery and recycling a complicated task. Several studies have reported the successful incorporation of POMs into MOF cavities.⁵⁰⁴⁻⁵⁰⁶ Li et al.⁵⁰⁷ studied several Wells–Dawson-type polyoxometalate anions $P_2W_{15}V_3$, $P_2W_{17}Ni$ and $P_2W_{17}Co$ immobilized in MIL-101(Cr) with charge compensation by the cationic photosensitizer (PS) ruthenium(II) tris(bipyridyl) ($Ru(bpy)_{32+}$). $P_2W_{15}V_3@MIL-101$ resulted in the highest activity toward the HER among all the studied POM@MIL-101 composites. It is worth noting that their photocatalytic activities were greater than that of the homogeneous catalytic systems. Paille et al.⁵⁰⁸ used the porphyrin MOF MOF-545/PCN-222/MMPF-6 as a visible-light sensitizer to immobilize $[(PW_9O_{34})_2Co_4(H_2O)_2]_{10-}$ (named $P_2W_{18}Co_4$) polyoxometalate (POM) known for homogeneous photocatalytic activity towards the OER. DFT calculations revealed the anchoring of the POM in the vicinity of the Zr_6 -cluster with a strong host-guest interaction (~ 176 kcal mol⁻¹). The OER activity of the $P_2W_{18}Co_4@MOF-545$ was studied under visible-light irradiation with $Na_2S_2O_8$ as the electron acceptor. $P_2W_{18}Co_4@MOF-545$ showed a good activity with a turnover number per POM of 70 after 1 h of reaction. A Ti-substituted Keggin-type polyoxometalate $[PTi_2W_{10}O_{40}]_{7-}$ (PTiW) encaged in an HKUST-1 MOF decorated with Au nanoparticles was developed by Liu et al.⁵⁰⁹ for photocatalytic CO₂-to-CO reduction. In that case, PTiW was claimed to act as an electron and proton reservoir and a reactive active centre, with HKUST-1 as a microreactor to concentrate CO₂ and Au NPs for visible-light harvesting.

Tilgner and Kempe⁵¹⁰ synthesized a core-shell material by using MIL-101 (Cr) as a core material and anatase and gold nanoparticles as the shell. The obtained composite was tested in the visible-light degradation of dyes (Rhodamine B, methyl orange and methylene blue) and the antibiotic ciprofloxacin from wastewater.

Another example of using MOFs as an inert host was given by Wang et al.⁵¹¹ Here, the authors reported the incorporation of cocatalyst Ni(dmgh)₂ into MIL-101(Cr). Together with Erythrosin B dye, which was used as a photosensitizer, Ni(dmgh)₂/MIL-101(Cr) were tested in the HER with TEOA as a sacrificial agent. Another strategy involves encapsulating or immobilizing catalytically active species into the pores of an MOF through a one-pot-synthesis or a post-synthetic impregnation. Wang et al.⁵¹² reported about the co-immobilization of the molecular catalyst [Cp*Rh(4,4'-bpydc)]₂₊ and the molecular photosensitizer [Ru(bpy)₂(4,4'-bpydc)]₂₊ (bpydc=bipyridinedicarboxylic acid) in MIL-101-NH₂(Al). The MOF represented an “inert” host for both the molecular catalyst and the photosensitizer and played the role of a nanoreactor. The resultant material was tested in the visible-light photoreduction of CO₂ to formate.

An important point to mention in the case of encapsulated active species is that probing and demonstrating the actual configuration of the active species within the MOF porosity is always difficult.^{513,514}

6.1.4 MOF-derived photocatalysts

Yan et al.⁵¹⁵ applied the solid-state pyrolysis of MIL-125-NH₂ followed by the photodeposition of Pd nanoparticles to yield Pd-loaded hierarchical TiO₂. Valero-Romero et al.⁵¹⁶ followed a similar approach to synthesize Fe-doped titania. Shi et al.⁵¹⁷ synthesized a family of NiS/Zn_xCd_{1-x}S heterojunctions with an average size of 12 nm and a uniform distribution (Figure 31) *via* doping of Cd-MOF ([Cd(bdc)-(DMF)]_n, H₂bdc=1,4-benzenedicarboxylate,

DMF=N,N-dimethylformamide) by Zn and Ni, which was followed by solvothermal sulfidation and thermal annealing. NiS/Zn_{0.5}Cd_{0.5}S was an optimal composition for the HER (839 $\mu\text{mol/h}$) with a high stability and recyclability under visible-light irradiation (420 nm) in the presence of Na₂S and Na₂SO₃, as sacrificial electron donors. A ZnO/ZnS heterojunction was prepared by the same research group using MOF-5 as a precursor.⁵¹⁸ In all these cases, the calcination temperature and time allowed were used to tune the visible-light absorption properties of the resulting solids.

Figure 31. a) Synthetic scheme for NiS/Zn_xCd_{1-x}S. b) PXRD of different NiS/Zn_xCd_{1-x}S compositions. c) TEM and the particle size distribution of NiS/Zn_{0.5}Cd_{0.5}S. d) Elemental distribution obtained by EELS. e) High-resolution TEM of NiS/Zn_{0.5}Cd_{0.5}S. Reproduced with permission from reference 517. Copyright 2018 John Wiley & Sons.

Chen et al.⁵¹⁹ synthesized CdS/Zn_xCo_{3-x}O₄ (CDS/ZCO) by the pyrolysis of ZnCo-ZIF followed by the hydrothermal deposition of CdS. Lan et al.⁵²⁰ used a bimetallic ZnCo-zeolitic-imidazolate-framework as a template for Pt-ZnO-Co₃O₄, Pt-ZnS-CoS, and Pt-Zn₃P₂-CoP heterojunction photocatalysts. MIL-53(Al) was utilized as a template to obtain a CdO replica, which was further converted into hierarchically porous CdS by sulfidation.⁵²¹ Kumar et al.⁵²² prepared slice-type Co₄S₃ by pyrolysing a Co-MOF, which was further utilized as a cocatalyst with CdS nanoparticles for the HER. A C-doped ZnO composite, C@ZnO, was synthesized by the pyrolysis of MOF-5. The resulting hybrid retained the porous morphology of the original MOF with evenly distributed ZnO nanoparticles.⁵²³

Xu et al.⁵²⁴ synthesized a C-doped ZrO₂/g-C₃N₄/Ni₂P heterostructure by the thermal decomposition of a UiO-66-NH₂ MOF coated with g-C₃N₄ nanosheets, followed by a Ni₂P cocatalyst deposition. The ternary C-ZrO₂/g-C₃N₄/20%Ni₂P composite exhibited a 35.5% AQE at 420 nm irradiation in a water/YEOA/Eosin Y (photosensitizer) system for H₂ production. Another example involves a CN/FeNiP polyhedron derived from the phosphidation of NH₂-MIL-101(Fe)/Ni(OH)₂, which was further used as a cocatalyst in an EY-sensitized g-C₃N₄ system for photocatalytic H₂ evolution.⁵²⁵

Hu et al.⁵²⁶ fabricated a three-component heterojunction photocatalyst consisting of carbon-coated copper(I) sulfide loaded on g-C₃N₄ (C-Cu_{2-x}S@g-C₃N₄) by sulfidation and the calcination of Cu-based MOF HKUST-1 for the production of C-coated Cu_{2-x}S (C-Cu_{2-x}S) tubes with a hollow architecture (Figure 32).

Figure 32. Scheme of C-Cu_{2-x}S@g-C₃N₄ composite fabrication. Reproduced with permission from reference 526. Copyright 2019 John Wiley & Sons.

6.1.5 Composites

MOFs can play the roles of photoabsorbers, supports and even a part of the heterojunction in photocatalytically active composites. Indeed, a plethora of examples can be found in the literature on the formation of composites containing a MOF and different semiconductors: MIL-125-NH₂/g-C₃N₄/Ni_{15.8}Pd_{2.1},⁵²⁷ ZIF-8/g-C₃N₄,⁵²⁸ Na_x-C₃N₄/Pt@UiO-66,⁵²⁹ electrostatically assembled Cu-BTC and ZnO/GO,⁵³⁰ Cd_{0.2}Zn_{0.8}S@UiO-66-NH₂,⁵³¹ etc.

Maina et al.⁵³² fabricated a Cu–TiO₂ doped ZIF-8 membrane for the photocatalytic CO₂ reduction under UV light. The authors used a rapid thermal deposition for the controllable encapsulation of Cu-TiO₂ nanoparticles within a ZIF-8 membrane deposited onto a graphene oxide (GO)-coated stainless-steel mesh. Zhang et al.⁵³³ used the so called “post-solvothermal” approach - soaking with a thioacetamide ethanolic solution and heating to 200 °C for 2 h- to transform pristine MIL-125-NH₂ into MIL-125-NH₂@TiO₂ core–shell particles with an HER activity 70 times higher than that of the original MIL-125-NH₂. Karthik et al.⁵³⁴ used the wet impregnation method to synthesize a MIL-125-NH₂/rGO composite. Based on the UV-Vis, FTIR and PL spectroscopy analyses, the authors proposed that strong π – π interactions facilitated a fast electron transport and reduced the electron–hole pair recombination, which allowed for a significantly enhanced photocatalytic H₂ production. Another example of semiconductor@MOF heterostructures is ZnIn₂S₄@MIL-125-NH₂, as reported by Liu et al.⁵³⁵ The optimized MIL-125-NH₂ content in the composite for H₂ photocatalytic production was 40 wt%, and an apparent quantum efficiency of 4.3% at 420 nm was achieved, a value substantially higher than that obtained with the pure ZnIn₂S₄.

Zhang et al.⁵³⁶ constructed a MOF/COF hybrid material by anchoring NH₂-UiO-66 onto the surface of TpPa-1-COF (Figure 33a). The resulting NH₂-UiO-66/TpPa-1-COF exhibited a 20-times higher activity for photocatalytic hydrogen evolution than did the parent TpPa-1-COF. A similar approach was used by Peng et al.⁵³⁷ First, the authors functionalized the In-based MOF NH₂-MIL-68 with a building unit of TPA-COF (tris(4-formylphenyl)amine (TFPA)) to form the aldehyde-functionalized NH₂-MIL-68 (NH₂-MIL-68(CHO)). Then, TPA-COF was constructed on the surface of NH₂-MIL-68(CHO) through a condensation reaction with tris(4-aminophenyl)amine (TAPA), forming the NH₂-MIL-68@TPA-COF hybrid material (Figure 33b).

Figure 33. a) Synthetic scheme for $\text{NH}_2\text{-UiO-66/TpPa-1-COF}$. Reproduced with permission from reference 535. Copyright 2018 John Wiley & Sons. b) Synthetic scheme for $\text{NH}_2\text{-MIL-68@TPA-COF}$. Reproduced with permission from reference 537. Copyright 2018 John Wiley & Sons.

It is well known that the solar spectrum is constituted by 5% UV, 42-45% visible, and more than 50 % near-infrared (NIR) light. Most of the currently investigated systems absorb UV light only or some visible light, therefore, not utilizing the full potential of sunlight. In the case of the NIR, lanthanide-doped upconversion nanoparticles (UCNPs) can convert longer wavelength irradiation into shorter wavelength emission (e.g., UV and visible) to then pass this energy to adjacent UV/vis-responsive components.⁵³⁸ In 2017, this approach was used by Li et al.⁵³⁹ A MIL-53(Fe) shell was controllably grown on the upconversion nanoparticles ($\text{NaYF}_4\text{:Yb,Tm}$) to obtain a NIR-responsive composite photocatalyst.

Li et al.⁵⁴⁰ proposed to use UCNPs (UCNPs denote $\text{NaYF}_4\text{:Yb, Tm, Er}$) to prepare broadband spectrum-responsive MOF composites (Figure 34). In the core-shell composite UCNPs-Pt@MOF/Au, the MOF (UiO-66-NH_2) was mostly responsive to UV-light absorption, the plasmonic Au nanoparticles responded to visible-light absorption, and the UCNPs upconverted NIR light to UV and visible light (Figure 34a). The tests of the resultant composite and its separated components in photocatalytic H_2 production for the first time revealed considerable activities under UV, visible and even NIR irradiation.

Figure 34. a) Mechanism for photocatalytic hydrogen production on broad-light-absorbing UCNPs-Pt@MOF/Au composites. b) A scheme of the synthetic process for the UCNPs-Pt@MOF/Au composites. Reproduced with permission from reference 540. Copyright 2018 John Wiley & Sons.

Re-containing UiO-67 (Re_n-MOF) composed of ReI(CO)₃(BPYDC)(Cl) (ReTC, BPYDC = 2,2'-bipyridine-5,5'-dicarboxylate) and zirconium MOF UiO-67 was applied to the photocatalytic reduction of CO₂ to CO.⁵⁴¹ Zhou et al.⁵⁴² used a similar approach to obtain a CFB/MIL-125-NH₂ composite through the functionalization of g-C₃N₄ by benzoic acid, acting as an electron mediator between g-C₃N₄ and MIL-125-NH₂. The obtained Z-scheme allowed one to not only increase the stability of the catalyst but also improve the electron transfer rate

between g-C₃N₄ and MIL-125-NH₂, resulting in a photocatalytic activity that was higher than that of its components.

The integration of plasmonic nanoparticles, including Au or Ag, is a well-known strategy to enhance visible-light absorption.⁵⁴³⁻⁵⁴⁵ Xiao et al.⁵⁴⁶ synthesized two metal-MOF interfaces integrating the plasmonic effect of Au nanorods (NRs) and the Schottky junction of Pt nanoparticles into a wide band gap MIL-125 (Figure 35). In that approach, plasmonic hot electrons were injected from Au into the LUMO of the MOF, allowing for long-wavelength light absorption. Pt formed a Schottky barrier, allowing the trapping of electrons across the interface, thus, greatly promoting the e–h separation and photocatalytic efficiency.

Figure 35. Scheme of the synthetic process for the P@MIL-125/Au, Pt/MIL-1225/Au and MIL-125/Au composites. Reproduced with permission from reference ⁵⁴⁶. Copyright 2018 John Wiley & Sons.

In a similar way, Wang et al.⁵⁴⁷ encapsulated Pt nanoparticles in UiO-66-NH₂ and then used graphene oxide to wrap the external surface of the composite. The resultant material displayed a significantly enhanced electron-hole separation, as confirmed by PL spectroscopy.

6.2 Most studied photocatalytic processes on MOF-related materials

Hydrogen production,⁵⁴⁸ CO₂ reduction,^{392,549,550} pollutant degradation^{551,552} and organic transformations^{18,491,553} are by far the most studied photo-driven processes in the field of MOF catalysis. Unfortunately, comparing catalytic performance among different publications remains a complex task. In spite of recent efforts by the semiconductor community to develop standards for reporting data,^{554,555} the MOF community seems to ignore these practices. Since photocatalytic reactors differ strongly among different labs, apparent quantum efficiencies (AQE) should always be reported. A general misconception persists that the photocatalytic rate is proportional to the amount (weight) of photocatalyst, but this is not true. The rate constant depends on the AQE, incident light intensity, light path, and extinction/absorption coefficients. Thus, reporting rates per unit weight (common practice in MOF photocatalysis) and using these values as a descriptor of photocatalytic efficiency is simply wrong. Therefore, it is recommended to report photocatalytic rates in HER, OER and overall water splitting in $\mu\text{mol}\cdot\text{h}^{-1}$ under optimal reaction conditions (Figure 36) (which will be different for every catalyst).

Figure 36. Rate of gas evolution dependence on the photocatalyst amount in a particular photoreactor. The plateau regions represent the optimal loading conditions. Reproduced with permission from reference 554. Copyright 2017 American Chemical Society.

6.2.1 Hydrogen and oxygen evolution, overall water splitting

Most of the known MOFs, by themselves, cannot be used for overall water splitting. This is the reason why the large majority of research has concentrated on the half HER reaction. Hence, most authors have made use of cocatalysts and/or sacrificial electron donors. The recent progress in photocatalytic water splitting on MOF-related materials is summarized in Table 12.

Leng et al.⁵⁴³ reported an indium-based MOF, USTC-8(In), that exhibits an excellent photocatalytic activity for H₂ production in comparison with its isostructural, in-plane porphyrinic MOF counterparts (USTC-8(M) (M = Cu, Co, Ni)). Authors showed that thanks to the out-of-plane porphyrin structure, the In(III) ions could be reduced and detached from the

porphyrin rings, leading to the inhibition of e-h recombination. Lan et al.⁵⁵⁶ synthesized two novel MOFs, Ru-TBP and Ru-TBP-Zn, based on a Ru₂ paddlewheel SBUs and porphyrin-derived tetracarboxylate ligands 5,10,15,20-tetra(p-benzoic acid)porphyrin (H₄TBP). The HER catalytic activity of Ru-TBP-Zn was higher than that of Ru-TBP because of the better photosensitizing ability of the TBP-Zn ligand. Photoluminescence spectroscopy and cyclic voltammetry helped to establish that the HER in Ru-TBP-Zn occurred *via* electron transfer from the excited TBP-Zn to the Ru₂ SBU.

There are only a few MOFs able to perform the HER without a cocatalyst (Pt) or photosensitizer ((Ru, Ir)- based complexes). Shi et al.⁵⁵⁷ developed a self-sensitized and cocatalyst-free Cu-based MOF series. Cu-X-bpy (X= Cl, Br, I; bpy=4,4'-bipyridine) with band gap energies (E_g) of 1.85, 1.90, 2.00 eV for Cu-Cl-bpy Cu-Br-bpy Cu-I-bpy, these materials showed good stabilities in aqueous solutions over a wide pH range (3-13). Photocatalytic tests for hydrogen generation under UV-light irradiation with TEA as sacrificial agent demonstrated that Cu-I-bpy was the most active MOF in the series. The proposed mechanism presented in Figure 37 implied the formation of Cu₀ centres from Cu_I, which further form Cu_I hydrides by protonation and highlights the importance of Cu₂X₂ clusters.

Figure 37. Plausible mechanism for H_2 evolution on the Cu-X-bpy MOF. Reproduced with permission from reference 557. Copyright 2017 John Wiley & Sons.

Castells-Gil et al. 558 reported a new family of titanium-organic frameworks with a heterometallic structure. MUV-10 (MUV = material of Universidad de Valencia) is based on heterometallic SBUs and was tested for photocatalytic H_2 production. Especially, MUV-10(Ca) $[\text{Ti}_4\text{V}_3\text{Ca}_{11}(\mu_3\text{-O})_2(\text{btc})_4(\text{H}_2\text{O})_6] \cdot \text{solvent}$ and its Mn counterpart, with a band gap of 3.1 eV, showed interesting performances with 3.1 and $6.8 \mu\text{mol} \cdot \text{h}^{-1}$ evolved, respectively. The same group recently reported the direct synthesis of a new Ti-based MOF with MIL-100 topology.⁵⁵⁹

It is well known that the cocatalyst plays an important role in the HER. While most literature on MOFs has focused on Pt nanoparticles, a few works have been devoted to the use of earth-abundant cocatalysts. Kampouri et al.⁵⁶⁰ used nickel phosphide (Ni_2P) nanoparticles deposited onto MIL-125- NH_2 for the photocatalytic HER. Under optimized conditions and Ni_2P loading (9.2 wt %), $\text{Ni}_2\text{P}/\text{MIL-125-NH}_2$ exhibited a high activity 300 times that of the

pristine MOF and an activity almost three times that of a benchmark Pt/MIL-125-NH₂ system. The calculated AQEs were 6.6 % and 27 % at 450 nm and 400 nm light irradiation, respectively. According to photocurrent and PL spectroscopy measurements, using a Ni₂P cocatalyst resulted in a significant drop in the electron-hole recombination and a more efficient electron transfer from MIL-125-NH₂ to Ni₂P, rather than to Pt nanoparticles. Nguyen et al.⁵⁶¹ combined two molybdenum-sulphide-based cocatalysts, Mo₃S₁₃₂- and 1T-MoS₂ (T-trigonal symmetry), with MIL-125-NH₂. Both Mo₃S₁₃₂-/MIL-125-NH₂ and 1T-MoS₂/MIL-125-NH₂ displayed exceptionally high catalytic activities for H₂ production with apparent quantum yields of 11.0 and 5.8% at 450 nm, respectively.

It is interesting that most studies focus on the half-reaction of water splitting over MOFs, even when some MOFs span the redox potential of water. However, An et al.⁵⁶² demonstrated overall water splitting on MIL-125 under UV/Vis-light irradiation in the presence of the co-catalysts CoPi and Pt for oxygen and hydrogen evolutions, respectively. Impedance analysis and photoluminescence spectroscopy proved that Pt and CoPi do not only act as reactive sites but also lead to the suppression of the electron-hole recombination. Xiao et al.⁵⁶³ reported a π -conjugated 2D layered cadmium-based MOF (Cd-TBAPy) that exhibited the dual functions of water reduction and oxidation. Both reduction and oxidation reactions were performed separately with Pt and CoPi as cocatalysts and appropriate scavengers (TEOA and AgNO₃). It is worth mentioning that the apparent quantum efficiency (AQE) of water oxidation reaches 5.6% at 420 nm, which is the highest AQE value among the reported MOF-related photocatalysts. Additionally, Remiro-Buenamañana et al.⁵⁶⁴ recently demonstrated overall water splitting into H₂ and O₂ by using MIL-125-NH₂ modified with appropriate co-catalysts: Pt and RuO_x nanoparticles for the HER and OER, respectively. The AQE was 0.32% for 400 nm light irradiation.

Table 12. Summarized information about the MOFs mentioned in hydrogen and oxygen evolutions and the overall water splitting section.

Photocatalyst	Irradiation	Solution	Cocatalyst	H ₂ or O ₂ evolution rate	Apparent Quantum efficiency	Stability test	References
Pt/20%-MIL-125-(SCH ₃) ₂	300 W Xe lamp $\lambda > 400$ nm	50 mg 80 mL 0.01 M TEOA aqueous solution	1.5 wt.% Pt	191 $\mu\text{mol}\cdot\text{h}^{-1}$	5.99 % 420 nm	1 run 120 min	⁴⁷¹
Ru-Pt-UIO-67	150 W Xe lamp $\lambda > 420$ nm	0.5 mg 4 mL, 3 mL CH ₃ CN, 0.3 mL H ₂ O, 0.3 mL DMA		0.57 $\mu\text{mol}\cdot\text{h}^{-1}$		3 runs per 10 h	⁵⁰⁰
Co-Ru-UIO-67(bpy) Co:Ru = 5.26:1	9 mW LED 447 nm	1 mg TEOA (0.3 mL) H ₂ O (0.4 mL) CH ₃ CN (3 mL)		0.7 $\mu\text{mol}\cdot\text{h}^{-1}$		3 runs per 5 h	⁵⁰¹
HNTM-Ir/Pt	300 W Xe lamp $\lambda > 400$ nm	50 mg 45 mL CH ₃ CN, 1 mL H ₂ O, 4 mL TEOA	1.05 wt.% Ir and 2.54 wt.% Pt	10.1 $\mu\text{mol}\cdot\text{h}^{-1}$		3 run per 5 h	⁵⁰²
Al-ATA-Ni	Xe lamp 300 W	30 mg 30 mL H ₂ O		0.8 $\mu\text{mol}\cdot\text{h}^{-1}$ (H ₂) 0.4 $\mu\text{mol}\cdot\text{h}^{-1}$ (O ₂)			⁵⁰³
		HER (+6 mL CH ₃ OH)		36 $\mu\text{mol}\cdot\text{h}^{-1}$			
		OER (+30 mg AgNO ₃)		155 $\mu\text{mol}\cdot\text{h}^{-1}$			

Pt@MIL-125/Au	300 W Xe lamp $\lambda > 380$ nm	5 mg 18 mL CH ₃ CN, 0.3 mL H ₂ O, 2 mL TEOA	0.49 wt.% Pt	8.72 $\mu\text{mol}\cdot\text{h}^{-1}$		3 runs per 2 h 1 long run for 100 h	546
USTC-8(In)	300 W Xe lamp $\lambda > 380$ nm	10 mg 23 mL CH ₃ CN, 0.5 mL H ₂ O, 2 mL TEA	1.5 wt % Pt	3.4 $\mu\text{mol}\cdot\text{h}^{-1}$			543
Ru-TBP-Zn	230 W solid state light source $\lambda > 400$ nm	0.1 mg 2 mL CH ₃ CN, 0.1 mL H ₂ O, and 0.5 mL TEOA.		0.024 $\mu\text{mol}\cdot\text{h}^{-1}$			556
Cu-I-bpy	500 W Hg lamp	1 mg, 3.0 mL 5% TEA aqueous solution, pH 11.5	-	7.09 $\mu\text{mol}\cdot\text{h}^{-1}$		5 runs per 20 h	557
MUV-10(Mn)	300 W Xe 140 mW/cm ²	1 mg/mL of MOF (25 mg) H ₂ O:MeOH (4:1, v:v)	-	6.8 $\mu\text{mol}\cdot\text{h}^{-1}$		1 run 24 h	558
MIL-100(Ti)	300 W Xe lamp 100 mW/cm ²	1 mg/mL of MOF (20) H ₂ O:MeOH (4:1, v:v)		0.83 $\mu\text{mol}\cdot\text{h}^{-1}$		5 runs per 24 h	559
Ni ₂ P/MIL-125-NH ₂	300 W Xe lamp $\lambda > 420$ nm	17 mg CH ₃ CN:TEA:H ₂ O v:v 5 : 1 : 0.1	9.2 wt.% Ni ₂ P	15.2 $\mu\text{mol}\cdot\text{h}^{-1}$	27 % 400 nm 6.6 % 450 nm	7 runs per 12 h	560
Mo ₃ S ₁₃ ²⁻ /MIL-125-NH ₂	Xe Lamp $\lambda > 420$ nm	17 mg 17.0 mL CH ₃ CN:TEA:H ₂ O (79.0:16.1:4.9 v:v:v)	0.82 wt. % both cases	35.6 $\mu\text{mol}\cdot\text{h}^{-1}$	11% (450 nm)	Loses in activity after 72 h	561

1T-MoS ₂ /MIL-125-NH ₂				24.7 $\mu\text{mol}\cdot\text{h}^{-1}$	5.8% (450 nm)	6 runs per 12 h	
MIL-125(Ti)CoPi-Pt	300 W Xe lamp	30 mg 30 mL H ₂ O	Pt and CoPi	1.84 $\mu\text{mol}\cdot\text{h}^{-1}$ (H ₂)		1 run 9 h	562
				0.93 $\mu\text{mol}\cdot\text{h}^{-1}$ (O ₂)			
Cd-TBAPy	300 W Xe lamp $\lambda > 420$ nm	50 mg 90 mL CH ₃ CN, 2 mL H ₂ O, 10 mL TEOA	3.5 % Pt	4.3 $\mu\text{mol}\cdot\text{h}^{-1}$		1 run 3 h	563
		50 mg MOF 90 mL CH ₃ CN, 2 mL H ₂ O, 10 mM AgNO ₃	0.4 % CoPi	81.7 $\mu\text{mol}\cdot\text{h}^{-1}$	5.6% 420 nm		
Pt-RuOx-MIL-125(Ti)-NH ₂	300 W Xe lamp 150 mW cm ²	20 mg 20 mL H ₂ O 35 °C	0.12 (Pt)- 0.24 (Ru)	4.36 $\mu\text{mol}\cdot\text{h}^{-1}$ (H ₂) 1.7 $\mu\text{mol}\cdot\text{h}^{-1}$ (O ₂)		1 run 22 h	564

6.2.2 CO₂ reduction

MOFs hold great promise for applications in the field of CO₂ reduction thanks to the possibility of designing them to have open metal sites, specific heteroatoms, and functionalized organic ligands, which are crucial for the development of better CO₂ reduction performance photocatalysts. More information regarding chemical pathways and thermodynamic

requirements can be found in the next review.⁵⁶⁵ The recent progress in CO₂ photoreduction on MOF-related materials is summarized in Table 13.

Han et al.⁵⁶⁶ used Ni MOF monolayers (Ni MOLs) for the selective photoreduction of CO₂. The authors demonstrated that Ni MOLs, with abundant coordinatively unsaturated Ni sites, exhibited a 2.2 % apparent quantum yield at 420 nm with a CO selectivity of 97.8 % when using [Ru(bpy)₃]Cl₂·6H₂O (abbreviated as Ru, bpy=2'2'-bipyridine) as a photosensitizer and triethanolamine (TEOA) as an electron donor (Figure 38).

Figure 38. a) CO₂ photoreduction performance depends on the reaction conditions. b) Ni and Co MOL photocatalytic performances in pure and diluted CO₂ (10%). c) DFT-calculated CO₂ and H₂O adsorption energies for Ni and Co MOLs. d) A potential energy diagram for the CO₂-to-CO reductions on Ni and Co MOLs. Reproduced with permission from reference ⁵⁶⁶.

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When dealing with diluted CO₂ (10% CO₂, typical concentration of exhaust gas), Ni MOFs still exhibited an AQE of 1.96% with a CO selectivity of 96.8%.

Ye et al.⁵⁶⁷ studied a 2D Zn porphyrin (5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin)-based MOF (Zn-MOF nanosheets) as a photosensitizer coupled with a dinuclear cobalt complex (or ZIF-67) as a co-catalyst for CO₂ photoreduction. A comparison of the Zn-MOF nanosheets with the Zr-MOF bulk demonstrated an enhanced photocatalytic efficiency and selectivity for CO evolution when using Zn-MOF nanosheets, which was supported by the results of PL and photoelectrochemical impedance measurements. Wang et al.⁵⁶⁸ investigated how cooperation between neighbouring hydroxide ligands with catalytically active metal centres could boost the photocatalytic CO₂ reduction. Six cobalt-based MOFs with different coordination environments were studied under the same reaction conditions. The authors chose three existing MOFs [Co₂(μ-Cl)₂(bbta)] (MAF-X27-Cl, H₂bbta = 1H,5H-benzo(1,2-d:4,5-d')bistriazole), [Co₂(μ-H)₂(bbta)] (MAF-X27-OH) and [Co₂(dobdc)] (MOF-74-Co, H₄dobdc = 2,5-dihydroxyl-1,4-benzenedicarboxylic acid), which are isostructural/isorecticular honeycomb-like MOFs bearing open metal sites with the same coordination geometry. A new MOF [Co₂(μ-OH)₂(btdd)] (MAF-X27l-OH, H₂btdd = bis(1H-1,2,3-triazolo-[4,5-b],[4',5'-i])dibenzo[1,4]dioxin), obtained by the ion exchange treatment of [Co₂(μ-Cl)₂(btdd)] (MAF-X27l-Cl). MAF-X27l-Cl and MAF-X27l-OH represent the expanded analogues of MAF-X27-Cl and MAF-X27-OH, respectively. The results of the photocatalytic experiment exhibited that MOFs bearing μ-OH- ligands and neighbouring the open Co centres posed the highest CO selectivities of up to 98.2% (Figure 39). Moreover, in diluted CO₂ their activities were reduced by only ca. 20%, while MOFs without the μ-OH- moiety retained only approximately 10% of their initial activity. Based on periodic density functional theory calculations, the CO₂ binding strength of MAF-X27-OH (208 kJ mol⁻¹) was considerably stronger than that for MAF-X27-Cl (41 kJ mol⁻¹).

Figure 39. CO production rate for Co-based MOFs with different coordination environments in pure and diluted (10%) CO₂. Reproduced with permission from reference 568. Copyright 2018 American Chemical Society.

Yan et al.⁵⁶⁹ investigated an Eu-Ru(phen)₃-MOF (phen = phenanthroline) obtained by assembling the triangular Ru(phen)₃-derived tricarboxylate ligand as a photosensitizer with Eu₂(μ_2 -H₂O) secondary building units for the visible-light-driven selective photoreduction of CO₂ to formate. The results of the time-resolved photoluminescence spectroscopy, femtosecond transient optical absorption spectroscopy and EPR measurements (Figure 40) suggested that charge transfer occurred from Ru(phen)₃-derived tricarboxylate ligand to Eu-O cluster forming the (Eu(III))₂ catalytic centres for the photoreduction of CO₂. Recycling experiments with ¹³CO₂ showed no noticeable degradation after three consecutive reactions.

Figure 40. a) Schematic illustration of the electron transfer from Ru to the Eu₂ oxo-cluster. b) In situ EPR spectra of Eu-Ru(phen)₃-MOF. Reproduced with permission from reference 569. Copyright 2018 Nature Publishing Group.

As mentioned earlier, the synthesis of MOF/semiconductor composites can provide several advantages, such as a better charge separation and the generation of additional active sites and adsorption centres. For instance, Xu et al.⁵⁷⁰ combined BIF-20 (BIF = boron imidazolate framework), a Zn-based MOF that contained a high density of B–H sites, with graphitic carbon nitride (g-C₃N₄) nanosheets. The formation of the BIF20@g-C₃N₄ nanosheet composite was possible through electrostatic interactions between the two components. BIF-20@g-C₃N₄ with 20 wt % g-C₃N₄ loading exhibited the highest photocatalytic performances for CO₂ reduction to CH₄ of 15.524 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (yield of 1.763 μmol) and for CO of 53.869 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (yield of 6.117 μmol) among the g-C₃N₄ nanosheet, bulk-g-C₃N₄ and ZIF-8@g-C₃N₄ nanosheets, and a composite with a similar architecture but without B–H bonding.

Luo et al.⁵⁷¹ proposed a new CO₂/water MOF-interfacial route for photocatalytic CO₂ reduction where MIL-125-NH₂ played the role of an emulsifier for the two immiscible solvents (liquid CO₂ and water) and a photocatalyst for CO₂ reduction to HCOO⁻. At pressures up to

6.89 MPa, without the formation of the emulsion, the reaction rate was approximately $11.5 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$. However, when the pressure was higher than 6.89 MPa, the HCOO^- production rate was significantly improved by the emulsion. Eventually, the activity reached $58.1 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ at 11.02 MPa. The authors fairly claimed that such an improvement in activity required a high mass transfer across the interface due to the existence of several interfaces in the emulsion system.

Table 13. Summarized information about the MOFs mentioned in the CO_2 reduction section.

MOF	Light source	Proton donor	Conditions	Carbon product	Reaction rate/Selectivity	AQE, %	Ref
Ni MOLs	5 W white LED light (400 nm $\leq \lambda \leq$ 800 nm)	TEOA	1 mg MOF catalyst 7.5 mg $\text{Ru}(\text{bpy})_3[\text{Cl}_2 \cdot 6\text{H}_2\text{O}]$ 2 mL H_2O 3 mL CH_3CN 1 mL TEOA pure CO_2 ,	CO	$12.5 \mu\text{mol} \cdot \text{h}^{-1}$ /97.8 %	2.2 420 nm	⁵⁶⁶
Zn-MOF nanosheets /ZIF-67	Xe lamp (120 mWcm^{-2}) $\lambda > 420$ nm	TEOA	ZIF-67 (0.18 μmol), Zn-MOF nanosheets (10 mg), 6 mL CH_3CN /MeOH/TEOA=4:1:1 CO_2 (99.999%)	CO	CO (TON _{CO} =117.8, TON _{H₂} =11.6, Selectivity 91.0%)	0.97 435 nm	⁵⁶⁷
MAF-X27-OH	LED light $\lambda = 420$ nm	TEOA	0.03 mmol MOF 5 mL H_2O 1 atm (pure CO_2) 25 °C $n\text{Co}^{2+} = 30$ nmol $[\text{Ru}(\text{bpy})_3[\text{Cl}_2 \cdot 6\text{H}_2\text{O}]]$ 2 μmol TEOA (0.3 M) $\text{CH}_3\text{CN} / \text{H}_2\text{O}$ (v/v = 4:1, 5 mL)	CO	98.2%	2.0	⁵⁶⁸

Eu-Ru(phe n) ₃ -MOF	420 nm < λ < 800 nm	TEOA	CH ₃ CN/TEOA (20:1 v/v)	HCOO-	4.7 $\mu\text{mol}\cdot\text{h}^{-1}$		569
BIF-20@g-C ₃ N ₄	300 W Xe lamp 400 nm < λ < 800 nm	TEOA	20 mg 2 mL of solution (CH ₃ CN /TEOA = 4:1)	CH ₄ and CO	CH ₄ 0.31 $\mu\text{mol}\cdot\text{h}^{-1}$ and CO 1.077 $\mu\text{mol}\cdot\text{h}^{-1}$		570

6.2.3 Pollutant treatment

Pollutants include dyes, antibiotics and heavy metals in water and VOCs and other toxic gases in the gas phase. In principle, photocatalytic degradation should proceed *via* the formation of highly reactive species, such as superoxide radicals (O_2^-).⁵⁷² Unfortunately, based dyes cannot be considered as appropriate model systems for evaluating the photocatalytic activity of novel photocatalysts, especially under visible light.^{573,574} This is because these dyes can act as photosensitizers and because adsorption, rather than degradation, occurs more often than not. The recent progress in pollutant degradation on MOF-related materials is summarized in Table 14.

In the MOF literature, a large range of MOF composites have been reported.⁵⁷⁵⁻⁵⁸⁰ Kampouri et al.⁵⁸¹ proposed a very interesting approach, the simultaneous degradation of dyes and H₂ generation using Ni₂P/MIL-125-NH₂, where Ni₂P nanoparticles were used as the HER cocatalyst and RhB as a sacrificial agent/organic pollutant.

The photocatalytic degradation of chemical warfare agents has also been studied by several authors. For instance, Goswami et al.⁵⁸² reported two PCN-57-modified MOFs with benzoselenadiazole (PCN-57-Se) or benzothiadiazole (PCN-57-S) linkers known for their ability to isolate diazoles and to sensitize the photochemical formation of singlet oxygen. Both photocatalysts were evaluated under violet LED irradiation and 1 atm O₂ in the selective photocatalytic partial oxidation of 2-chloroethyl ethyl sulfide (CEES) to 2-chloroethyl ethyl

sulfoxide (CEESO). PCN-57-Se catalyses photooxidation with 100% conversion within 12 min ($t_{1/2}$ = 3.5 min), and PCN-57-S completes the reaction in 25 min ($t_{1/2}$ = 7.5 min) under UV irradiation. Additional experiments with steady-state and time-resolved emission spectroscopy, together with computations, have proposed efficient excited-state singlet-to-triplet intersystem crossing for PCN-57-Se as the main reason for the higher catalytic activity.

Hydrogen sulfide (H_2S) is a well-known hazardous and toxic gas with a strong odour, even at very low concentrations. Sheng et al.⁵⁸³ synthesized urchin-like double-shell hollow TiO_2 @MIL-101 particles, which provided both adsorption and the catalytic degradation of H_2S . TiO_2 @MIL-101 exhibited a 90.1 % H_2S conversion, which was 31% and 114% higher than that of hollow and bulk TiO_2 . The authors coated preliminary prepared hollow TiO_2 particles with MIL-101 through its repeated formation onto the surface. A high surface area and the H_2S -adsorption ability of MIL-101 was crucial for the photocatalytic performance. Gao et al.⁵⁸⁴ modified MIL-125- NH_2 by coating a thin TiO_2 layer onto its surface. Coupled with CdS quantum dots resulted in the composite $\text{CdS}/\text{MIL-125-NH}_2/\text{TiO}_2$ exhibiting an improved performance and stability for NO removal. Graphene oxide (GO)-modified MIL-125- NH_2 crystals (GO/MIL-125- NH_2) through a microwave solvothermal process and was used for the photocatalytic oxidation of gaseous pollutants (Figure 41), such as nitric oxide (NO_x) and acetaldehyde, under visible light ($\lambda > 420$ nm) irradiation.⁵⁸⁵ The strong interaction between GO and MIL-125- NH_2 in a heterojunction allowed for an increase in the electron-transfer rate from MIL-125- NH_2 to GO, which inhibited electron-hole recombination. Apart from hazardous toxic gases, a few examples of photocatalytic volatile organic compounds being degraded on MOF-base composites exist. Ag_3PO_4 @UMOFNs⁵⁸⁶ consists of Ag_3PO_4 -coated by Ni- and Co-bimetallic ultrathin two-dimensional MOF nanosheets for the degradation of phenol and TiO_2 @ $\text{NH}_2\text{UiO-66}$ ⁵⁸⁷ composite for styrene degradation.

Figure 41. Proposed mechanism for pollutant elimination on GO/NH₂-MIL-125. Reproduced with permission from reference 585. Copyright 2018 Elsevier.

Another application field is the removal of pollution caused by the pharmaceuticals industry.⁵⁸⁸ Yang et al.⁵⁸⁹ studied a MIL-68(In)-NH₂/GO composite for the photocatalytic degradation of amoxicillin, a broad-spectrum and semisynthetic β -lactam antibiotic. Ibuprofen (IBP), one of the most consumed non-steroidal anti-inflammatory drugs was successfully eliminated by using an Ag/AgCl@MIL-88A(Fe) nanocomposite.⁵⁴⁴ Tilgner et al.⁵⁹⁰ synthesized an Fe₂O₃/TiO₂@MIL-101 composite for the visible-light-driven degradation of antibiotics such as ciprofloxacin, levofloxacin and diclofenac.

As the wastewater generated in many industrial processes often contains inorganic heavy metal ions and organic compounds,⁵⁵¹ a significant part of the literature on photocatalytic pollutant degradation deals with Cr(VI) photoreduction studies. Zhao et al.⁵⁹¹ reported a new Zn-based pillared-layer MOF NNU-36 (Figure 42), with 9,10-bis(4'-pyridylethynyl)-anthracene (BPEA) as a pillaring ligand with visible-light harvesting properties. The MIL-53(Fe)/SnS nanocomposite was prepared by a simple deposition method and was also applied for Cr(VI) photoreduction, exhibiting a significant reduction rate compared that of its

counterparts.⁵⁹² A few more examples of merging MOF with semiconductors have been studied.⁵⁹³⁻⁵⁹⁵

Figure 42. a) Pillared layer structure of NNU-36. b) The layer structure constituted by the BPDC ligand and a zinc dimer. c) Pillaring ligand coordinated to the layer in the structure. Reproduced with permission from reference ⁵⁹¹. Copyright 2017 American Chemical Society.

Table 14. Summarized information about the MOFs mentioned in the pollutant treatment section.

Photocatalyst	Light source	Pollutant	Ref
PCN-57-Se	violet LED	2-chloroethyl ethylsulfide	582
TiO ₂ @MIL-101	UV light	H ₂ S	583
CdS/NH ₂ -MIL-125@TiO ₂	50 W tungsten halogen lamp, $\lambda > 420$ nm	NO	584

GO/NH ₂ -MIL-125(Ti)	2*150 W tungsten halogen lamps $\lambda > 420$ nm 300 W Xe lamp, $\lambda > 420$ nm	NO CH ₃ CHO	585
Ag ₃ PO ₄ @UMOFNs	400 W halide lamp $\lambda > 420$ nm	Phenol and biphenyl A	586
TiO ₂ @NH ₂ -UiO-66	300 W Xe lamp	Styrene	587
MIL-68(In)-NH ₂ /rGO	300 W Xe lamp $\lambda > 420$ nm	Amoxicillin	589
Fe ₂ O ₃ /TiO ₂ @MIL-101	50 W blue LED 470 nm	Ciprofloxacin	590
NNU-36	300 W Xe lamp $\lambda > 420$ nm	Cr(VI)	591
MIL-53(Fe)/SnS	300 W Xe lamp $\lambda > 420$ nm	Cr(VI)	592

7 Outlook, challenges and future perspectives

Metal Organic Framework related catalytic applications are advancing at an unprecedented pace. We have to admit that at more than one point during the preparation of this review we felt overwhelmed about the amount and breath of the recent publications. After more than one decade, MOFs are finding their place in catalysis and sooner rather than later we may witness the first large scale catalytic applications of MOFs or MOF derived materials.

When it comes to MOF materials with intrinsic catalytic activity and MOF supported metal nanoparticles, although great progress has been achieved over the last few years, we believe the limitations of these systems in terms of chemical and thermal susceptibility are still a great question mark in terms of utilization. Although very interesting developments have been published in the application of such MOFs in different organic transformations, one always wonders if MOFs will be able to beat classical homogeneous catalysts in this field. The same

holds for low temperature CO₂ chemistry, especially considering that electrocatalysis and thermal catalysis seem like more attractive approaches. In this field, we would like to highlight the recent developments in characterization of defective MOFs as one of the most important outcomes of the last few years. The possibility of visually observing defects, the great deal of understanding that is being gained through molecular modeling and the characterization protocols that are being developed will not only be of great importance for the catalysis community and for MOF experts but may find application in many other fields. For instance, understanding defects in perovskites seems to be key for the design of the next generation solar cells and a lot of similarities could be drawn between defective MOFs and this family of materials.

Something similar can be said about the use of MOFs as supports for metal nanoparticles. A lot of effort has been dedicated over the last few years to this field, yet, fair comparisons with state of the art catalysts and long term stability tests are still lacking.

The use of MOFs as precursors for the synthesis of advanced catalytic materials is a clear response to the issues highlighted above and, so far, is proving very successful. The unique structures obtained from the transformation of MOFs *via* thermal decomposition has opened a new field for the synthesis of highly advanced heterogeneous catalysts. Tunable porosity, unprecedented dispersion and high metal loading with exceptional control of the particle size can be easily achieved. Moreover, the final structure can be extensively tuned with simple treatments (*i.e.* modification of the carbonization atmospheres, introduction of external templates, addition of promoters) in order to obtain porous metal oxides, porous bimetallic oxides, porous carbons, or combinations all these structures that would be impossible to synthesize with conventional methods. The exceptional features displayed by MOFMSs have driven researchers to apply these structures in multiple catalytic reactions^{14,18,235,419} and, commonly, these MOF mediated catalysts yield superior performances than their conventional

counterparts. This is certainly the key, if the manufacture of a catalyst through a MOF offers properties that cannot be achieved otherwise, then the method may become attractive from a commercial standpoint. Specially if base metals and cheap ligands are used for the synthesis of the MOF and if no solvents are used for MOF activation.

However, despite these exceptional features of MOFMSs there is still plenty of room for improvement and a great number of chemistries to be explored. First, as it can be interfered from Table 2, most of the reactions studied are CO oxidation, Fischer-Tropsch or the hydrogenation of nitro-compounds. Therefore, the expansion to other catalytic process should be addressed by the scientific community. Second, although more than 20,000 MOFs have been reported, most of the MOF used derive from ZIF structures ^{244,248,259,277-284,286-288,306,307,317,369,596}, CuBTC ^{243,250,266,267,294-300} or Fe based MOFs ^{231,232,239,240,254,290-293,597} such as MIL-100 or Basolite-F300. Exploring other types of MOFs as precursor should be addressed as well. Third, few works report deep investigations on the morphological transformations occurring during pyrolysis^{253,254}. These investigations are crucial as the morphology, particle size, porosity and composition greatly depend on the pyrolysis conditions. Therefore, *in situ* operando techniques such as *in situ* TEM should be performed during pyrolysis in order to shed light on the transformation of MOFs into their derived materials. Finally, scale up of the MOFMSs synthesis methods are also a must in order to pave the way for the mass production of these promising structures. Given the exceptional features of MOFMSs, we strongly believe that MOFMSs will continue to receive extensive attention in the near future and all these issues will be addressed by the catalysis community.

MOF electrocatalysts have the potential to provide crucial insights into electrocatalysis, but to do so several questions regarding catalyst conductivity and stability must be overcome. The problems facing electrocatalytic MOFs can be summarized into three major categories – conductivity, stability, and activity. Conductivity remains an issue, but a number of practical

approaches, such as mixing the catalyst with a conductive binder and nanostructuring anisotropic 2D MOFs, have resulted in significant improvements. However, improving the innate conductivity of MOFs has been more problematic; while it is clear that any electrocatalytic MOF requires π -conjugated linkers for good conductivity, the integration of other electron-rich materials, such as POMs,³⁹⁶ may also serve as a viable route to improve the conductivity. Infiltrating the MOF with a conducting molecule, as is often the case for MOFs used in other electronic applications,⁵⁹⁸ is not sensible for electrocatalysis as the voids within MOFs are necessary for reactant and product diffusion.

Stability remains the primary challenge for MOF electrocatalysts since most of the current electrocatalytic reactions of interest take place under extreme acidic or alkaline conditions. Considering that most MOFs possess stability limits even in neutral aqueous electrolytes,³²⁴ the stability challenge continues to be significant. In addition, the decomposition products must be carefully analysed, as the potential for MOF decomposition into a catalytic material, such as an amorphous metal oxide ³⁶² or Cu metal cluster,³⁹⁵ could give the impression of MOF stability. The broad analysis of the reported OER catalysts covered here shows that MOFs containing first-row transition metals that are coordinated to a variety of moieties usually contain hydroxide-like species at the end of catalytic testing. While the formation of new catalytic phases of MOFs under *operando* conditions is not necessarily problematic, it does prevent the preparation and use of precision-designed reaction sites. Beyond bulk structural characterization techniques such as PXRD, post-catalytic spectroscopy can be used to examine catalysts for signs of decomposition. In particular, Raman spectroscopy can be used to examine used catalysts for newly formed metal-oxo-metal motifs, indicating the de-coordination of organic linkers.

For extreme acidic and alkaline conditions, a constant theme has been instability. Careful selection of linker and metal are critical to successful, unambiguous activity. From a functional

perspective, while stability challenges remain substantial, some catalysts formed by *in situ* MOF decomposition have competitive catalytic activities. While it may be difficult to ultimately construct electrocatalytic MOFs that are stable and efficient, recent reports demonstrate how MOFs might eventually become their own class of electrocatalytic materials. MOF electrocatalysts remain relatively lower in activity compared to their peers in other material classes, as evidenced by some of the benchmarking papers discussed here. Some individual approaches have succeeded in excelling over non-MOF catalysts; exfoliated 2D MOFs formed by partially decomposing a 2D MOF are amongst the most-active OER catalysts that have yet been reported.³³⁶ While not true “native” MOFs, the high activity of the final catalyst warrants a serious look. For HER catalysts, MoS_x clusters serving as both MOF nodes and catalysts have registered the highest activities for MoS_x materials despite the need to deposit them in thin layers due to their poor conductivities.³⁷¹ Both reports clearly demonstrate that MOFs have much to offer electrocatalysis, and that performance will likely come in time as approaches improve.

MOF-derived catalysts are effective electrocatalysts due to their incorporation of conductive carbons during the derivation process, but the utility of the MOF preparation process also means that metals and light elements can also be included. However, in the case of heterostructures, strong cases for synergy need to be better demonstrated in the future. In addition to compositional control, two recent and successful trends stand out amongst recent literature in the field. First, there is increased interest in controlling aspects of the derivation process such as *via* the use of unconventional heating, resulting in catalysts with specific morphologies, activities and optimal active site utilization.⁵⁹⁹ Applying these techniques to all derived MOFs has the potential to fine-tune catalytic activities. Second, 2D MOF catalysts have been increasingly used for derivation due to their high surface areas and anisotropic

structures. Ultimately, the ability of MOF-derived electrocatalysts to incorporate a vast number of useful features necessitates continuing study on these materials. Very recent developments in this field⁴⁸⁵ certainly point at MOF derived materials as excellent playgrounds in electrocatalytic devices.

In the same line, when it comes to photocatalytic applications, activity reported for most MOF catalysts is still very low, and only in a few cases MOFs have been shown to i.e. perform overall water splitting. The way of reporting data and the need for standardization, as already done in the semi-conductor field, has been highlighted in this review and we see it as a critical point in the success of MOF photocatalysis. Looking forward, an enormous variety of new MOF-based or MOF-supported, solar-fuels-relevant photocatalytic systems can be envisioned, with perhaps most of them no better or no worse than the few dozen proof-of-concept systems already in the literature. The challenge then is not to expand the number of examples but to deploy MOF-centric chemistry for evaluation of ideas and development of attractive new catalysts or light-absorbers that may be difficult or impossible to evaluate or develop by other means. We for instance see a great opportunity in the development of (i) catalysts based on well-defined, few atom clusters and (ii) panchromatic light-absorbers comprising MOF-organized ensembles of chemically simple, narrow-band chromophores where a MOF-centric approach will prove especially informative.

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Conflict of interest

The authors declare no competing financial interest.

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