The following publication Xue, Q., Zhang, Z., Ng, B. K.. Y., Zhao, P., & Lo, B. T. W. (2021). Recent advances in the engineering of single-atom catalysts through metal–organic frameworks. Topics in Current Chemistry, 379(2), 11 is available at https://doi.org/10.1007/s41061-021-00324-y.

Recent Advances in the Engineering of Single-Atom Catalysts Through Metal–Organic Frameworks

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Abstract

Thanks to the recent advancement in characterisation techniques, the preparation methodologies of single-atom catalysts (SACs) are increasingly unravelled and optimised. This mini-review highlights some key recent progress in the engineering of SACs within metal-organic frameworks (MOFs) and their catalytic applications. Briefly, the preparation methods can be categorised into (1) anchoring onto the functional ligand sites, (2) anchoring onto the nodal centres, and (3) by pyrolysis. The development of comprehensive characterisation techniques enables scientists to elucidate the structure-activity relationship of these catalysts, which aids the subsequent engineering of more superior catalytic systems at an atomistic perspective.

1. Introduction

The efficient and reliable provision of energy and fine chemicals has been a critical consideration in the formulation of many global and regional policies. It relies on the use of heterogeneous catalysts, thanks to the ease of catalyst-product separation and their high thermal and chemical stabilities. A common type of heterogeneous catalyst is porous materials. Porous materials possess high surface area and high ratio of catalytic active sites. To the greatest extent, the ratio can be maximised by establishing 'single-atom' catalyst (SAC) active centres. Akin to the homogenous and biological enzyme analogues, isolated metal species in heterogeneous catalysis can offer great catalytic possibilities due to the tuneable geometric and electronic properties. Many catalytic reactions show high activity or selectivity dependent on the solid or surface structures, indicative of more than one catalytic active sites involved.

Crystalline and porous zeolites and metal-organic frameworks (MOFs) can be used as the scaffold to host SACs with well-defined structures (*cf*. zeozymes).[1,2] The framework structures of zeolites and MOFs can readily stabilise the isolated extra-framework single atomic species.[3–7] Thanks to the intrinsic framework Brønsted acidity of zeolites, both positively and negatively charged metal species can be 'anchored' onto the framework. The single atoms in zeolites have been extensively studied and possess high commercial values and applications, such as for fuel upgrade and biomass conversions.

MOFs are a relatively new type of micro/mesoporous solid-state materials, which are constructed by an assembly of metal/metal-cluster nodal centres and organic linker molecules. Various organic linker molecules were explicitly designed for the engineering of different MOF structures. MOFs are accepted as an array of self-assembled molecular catalysts rather than conventional semiconductors. The HOMO-LUMO band gap terminology is believed to be more appropriate to describe these assembled molecular entities. MOFs have captured broad interest in various applications, such as gas separation,[8] proton conductivity,[9] biomedicine,[10] and catalysis.[11-12] The MOF framework can be chemically modified or functionalised that has offered great potential in the decoration of extra-framework single-atom species using different approaches. This mini-review will provide a focussed view on highlighting some recent advances in using MOFs as the host to achieve site-isolation for active extra-framework single-atom species.

2. MOF as Supporting Material

Based on fundamental coordination chemistry, MOFs are constructed by an infinite array of metal nodal/cluster centres that are coordinated with multifunctional organic linker molecules. Hence, MOFs are often considered as an array of self-assembled molecular catalysts rather than conventional semiconductors. Some earlier reports have utilised this concept and further stabilise extra-framework single-atom species onto either the metal nodal centres or onto the specific moieties of the organic linker molecules. However, limited by various thermodynamic constraints, the concentrations of the single-atom species with respect to the framework functionality are usually quite low. A new method that employs high-temperature pyrolysis (in the absence of oxygen) to turn MOFs into an ideal porous N-doped carbon-based supporting matrix to stabilise single-atom metal species has been later developed.

In brief, we can categorise the preparation methods of SACs supported on MOFs into three main types: (1) anchoring onto functional ligand sites, (2) anchoring onto the coordinatively unsaturated nodal centres, and (3) by pyrolysis. Each method has its advantages and disadvantages.

2.1 Ligands Anchoring

The self-assembly of metal nodal centres and organic molecular linkers makes MOFs different from conventional solid-state materials.[13,14] Thanks to the adjustable functional groups on the organic building blocks, MOFs could have the same topology but demonstrate notably different chemical properties. The organic linkers can be further modified to introduce more extensive functionalities. In the past decades, the post-synthetic metalation method has been commonly employed to synthesise mixed-metal metal-organic frameworks (MM-MOFs) by utilising the chemical moieties of the organic linkers.[15] Recently, more N-containing organic linkers (such as, porphyrin, amine and bipyridyl) have been specifically applied to anchor SACs metal species for catalytic purposes.[16,17] The periodic and crystalline array of MOF motifs are stabilised by the intrinsic acid-base interactions between Lewis acidic metal (or metal cluster) nodal centres and Lewis basic organic linkers.[18,19] Meanwhile, additional functional groups on the organic linker molecules can coordinate with extra-framework metal species to avoid further metal aggregation. Highly homogeneous distribution of the single sites can be therefore achieved within crystalline MOF frameworks.[20,21] The extra-framework sites are typically catalytically active due to unsaturated coordination.

While the Lewis acidic metal nodes interact with the multi-Lewis basic organic linkers, the ligands can stabilise extra-framework single-atom metal species. Note that the extra-framework metal species cannot form a repeating array of MOF lattice as the reaction substrates required to form original host MOF frameworks. Canivet et al. have reported a one-pot post-functionalisation method to incorporate single-atom Ni onto the unsaturated nodal clusters in (Fe)MIL-101-NH_2.[22] It was prepared by the in-situ formation of $Ni(PyCHO)Cl_2$ (from $NiCl_2$ and 2-pyridine carboxaldehyde (PyCHO)) within the MOF cavity and followed by imine condensation with the framework -NH_2 moiety. A diimino Ni complex is hence encapsulated by the MIL-101. Extra measures have been taken to avoid the competitive *N*-coordination of the pyridyl moieties to the coordinatively unsaturated metal sites on the metal nodes of the (Fe)MIL-101-NH_2. This material has been shown effective for the catalytic triphasic ethylene dimerisation to produce 1-butenal; the reported catalytic performance was higher than the molecular Ni diimino analogue which has been ascribed to the site-isolation of Ni complex.

Hou et al. reported a one-pot synthesis of UiO-67 with single atomic Ru and Pt species by making use of a mix-and-match approach for photocatalytic hydrogen evolution from water (Figure 1).[23] The mix-and-match approach typically refers to using highly related metal precursors to construct bimetallic MOF frameworks; in such case, Ru^{II}-2,2′-bipyridyl and Pt^{II}-2,2′-bipyridyl were used as the precursors. While the Pt^{II} site acts as a proton-reduction catalyst, the Ru^{II} site acts as a photosensitiser. The increased catalytic performance can be attributed to the synergetic effect between the Ru and Pt single sites, which can enhance the electron transfer from the photosensitiser to the proton-reduction catalyst. The photocatalytic property has been ascribed to the singlet character metal-to-ligand charge transfer (MLCT) process from $Ru(d_{\pi}^{6})$ to $Ru(d_{\pi}^{5})$ 2,2′-bipyridyl(π^*).

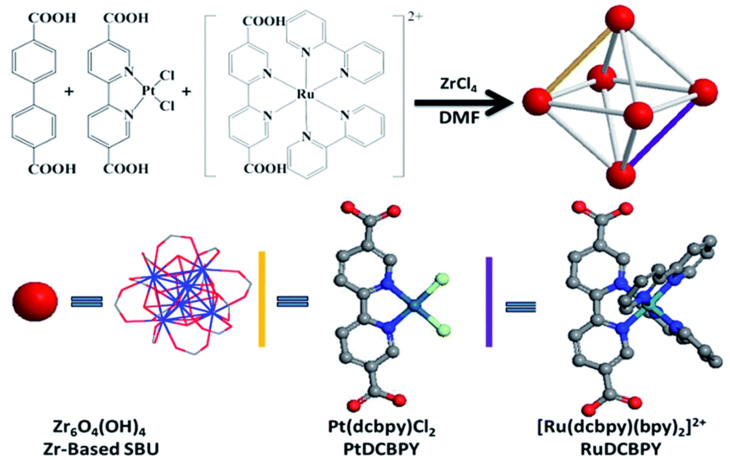

Figure 1. Schematic representation of the solvothermal synthesis reaction leading to the incorporation of bpdc, PtDCBPY and RuDCBPY into U¡O-67. The octahedral cavity represents the backbone of the MOFs. The red balls represent the SBUs. The grey, yellow, and purple building ligand rods denote bpdc, PtDCBPY and RuDCBPY, respectively.[23]

Single-atom metal species can also incorporated into the MOF cavity onto the porphyrin groups by a post-metalation approach.[24–26] For instance, Ye et al. reported the coordination of unsaturated single-atom Co species on the porphyrin units into a MOF-525 substrate. The organic linker, 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl) tetrabenzoate, provides nitrogen sites to graft incoming metal cations.[27] The post-metalation method was facile, which involves the direct mixing of cobalt(II) nitrate and MOF-525 in N,N-dimethylformamide (DMF) solvent. The porphyrin MOF has led to atomically dispersed catalytic centres that significantly enhances the performance of photocatalytic conversion of CO_2. From the structural findings based on the extended X-ray absorption fine structure (EXAFS) spectroscopy, the square-planar configuration of the unsaturated Co site has been confirmed (Figure 2). The improved catalytic ability was ascribed to the increased electron-hole pairs separation ability. The photo-generated electrons can be transferred to the Co single atom, which results in the facilitated charge separation in the MOF.

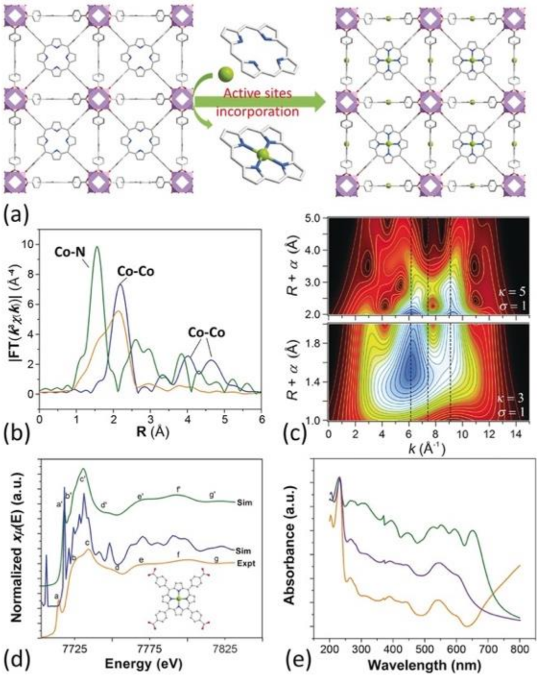

Figure 2. (a) View of the 3D network of MOF-525-Co featuring a highly porous framework and incorporated active sites. (b) Fourier transform magnitudes of the experimental Co *K*-edge EXAFS spectra of samples (not corrected for phase shift). Key: Co foil (blue), Co@C (orange), MOF-525-Co (green). (c) Wavelet transform for the k^3-weighted EXAFS signal of MOF-525-Co, based on Morlet wavelets with optimum resolution at the first (lower panel) and higher (upper panel) coordination shells. Vertical dashed lines denoting the *k*-space positions of the Co-N and Co-Co contributions are provided to guide the eye. (d) Comparison between the Co K-edge XANES experimental spectrum (orange) of MOF-525-Co and the theoretical spectrum calculated with the depicted structure. For clarity, the non-convoluted theoretical spectrum is also shown. (e) UV/Vis spectra of MOF-525 (green), MOF-525-Co (purple), and MOF-525-Zn (orange).[27]

Besides the use of Lewis basic amino moieties of the linker of the MOF, other types of functional groups have also been designed to stabilise single-atom metal species. Gao et al. have first employed sulphoterephthalic acid as the precursor prepared MIL-101(Cr)-SO_3H MOF.[28] The -SO_3H moiety can further anchor various Lewis acidic Cu^{II} species to offer site-isolation effect for enhanced catalytic properties. The sulphonate-functionalised MOF, MIL-101(Cr)-SO_3H, provides a platform for the post-synthetic modification via metal coordination.[29] A similar approach can also aid to the fabrication of Lewis acid sites (LASs) in proximity with Brønsted acidic MOF frameworks. It is commonly known that the synergy effect between different catalytic active sites can promote catalytic performance.[30,31] Ma et al. have incorporated Al^{III} (LASs) onto the -SO_3H moiety of MIL-101(Cr)-SO_3H (Figure 3)[32]. Because of the synergy between the Al^{III} sites and the Brønsted acidic MOF framework, the material exhibits more superior catalytic performance in the benzylation of aromatic hydrocarbons with benzyl alcohol than typical zeolite catalysts (H-Beta and H-MOR).

Several metal ions have been loaded on MIL-101(Cr)-SO_3H to enhance the activity of MOFs in other applications. For instance, the Ag(I)-functionalised MOF (MIL-101(Cr)-SO_3Ag) has been used for olefin–paraffin separation, desulphurisation, and iodide removal.[33] Thiol-functionalised MOFs have been reported for various applications, such as for fast removal of Hg to safe drinking water level (<2 ppb) [34] and to anchor Co for photocatalytic reduction of CO_2[35].

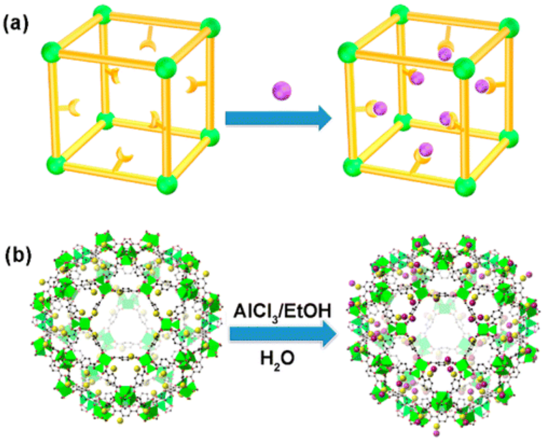

Figure 3. (a) Schematic presentation of the synthesis strategy for Lewis acid@Brønsted acidic MOF, in which the framework stands for the Brønsted acid functionalised MOF and the violet balls stand for Lewis acid centres; (b) Schematic presentation of the synthesis process for MIL-101-Cr-SO_3H·Al(III).[32] Reprinted (adapted) with permission from Ref. [32]. Copyright (2015) American Chemical Society.

Incorporating single-atom metal species on the ligand of the MOF frameworks by using the molecular specificities can typically maintain the crystallinity of the structures and the original physicochemical properties. As the extra-framework metal species are generally connected to the MOF framework via acid-base interactions, enhanced catalytic performance has often been ascribed to various electronic properties, such as redox hopping.[36,37] This approach has also been used as a pre-step to graft Ru single-atom in UiO-66-NH_2 for subsequent thermal treatment.[38]

2.2 Supported on Nodal Centres

Although the metal/cluster nodal centres are highly coordinated with organic linker molecules, some can still possess vacant coordination sites that are only temporarily occupied by solvent molecules like water or DMF. The solvent molecules can be removed through simple heating or vacuum treatment, which consequently leaving ‘unsaturated’ sites at the nodal centres; two notable examples are NU-1000 and MIL-101. These unsaturated sites are typically Lewis acidic that can offer room for modification with extra-framework species.

Various metal complexes can be used as the precursors to prepare SACs supported on MOFs, such as in NU-1000.[39,40] A Zr_6 node of NU-1000 contains 4 internal bridging oxo groups, 4 bridging μ_2-OH groups and 4 external H_2O groups; thus, a dehydration treatment can remove the H_2O groups to provide sites for SACs anchoring. For instance, Martinson et al. reported the incorporation of $In(CH_3)_3$ and $Al(CH_3)_3$ complexes onto the Zr_6 metal nodal centres of NU-1000 through atomic layer deposition.[41] The nodal hydroxyls and ligated water of NU-1000 were used as the Lewis basic sites (LBSs) to anchor Lewis acidic $In(CH_3)_3$ and $Al(CH_3)_3$ complexes under a highly saturated environment. The crystallinity and internal surface area of NU-1000 have only been altered marginally. Interestingly, the metal loading can be tuned through the number density of reactive handles (nodal hydroxyls and ligated water of NU-1000) that are dehydration temperature-dependent. This method is commonly known as atomic layer deposition in MOFs (AIM). Farha et al. later applied a similar AIM approach to host single-atom Zn species by saturating the NU-1000 with $Zn(C_2H_5)_2$.[42] The Zn-modified MOF can be further transmetalated to yield with uniformly distributed isolated Cu, Co, or Ni extra-framework species within the crystalline NU-1000 framework. In another work, Farha et al. also reported the use of NU-1000 to stabilise single-atom-based vanadium oxide species.[43] Lercher et al. have reported a supported Cu-oxo clusters on NU-1000 that exhibits activity for selective oxidation of methane to methanol.[44] By combined elemental analysis, X-ray absorption spectroscopy (XAS) and density functional (DFT) calculations, the Cu-loaded MOF contained Cu-oxo clusters of a few Cu atoms.

Besides the use of reactive handles for AIM as reported widely in NU-1000, the nodal centres can also offer LASs to coordinate incoming Lewis basic substrates. Román-Leshkov et al. have incorporated single-site $[Co(CO)_4]^-$ onto the framework Cr^{III} site of MIL-101(Cr), see Figure 4.[45] Based on the experimental evidence, this Lewis acid-base adduct within the MOF framework has shown more superior catalytic properties for β-lactone carbonylation when compared with pristine MIL-101(Cr) and $Na^+[Co(CO)_4]^-$, likely due to the presence of $Co(CO)_4^-$ required for CO insertion and strong LASs required for substrate activation. A carbonylation mechanism has been proposed accordingly, where the β-lactone substrate is first activated by the framework Cr^{III} site, followed by ring-opening by the $Co(CO)_4^-$, and lastly by CO insertion to extrude the anhydride product. The unique structural properties would benefit the development of an improved class of heterogeneous *β*-lactone carbonylation catalysts. The promoted catalytic performance has been ascribed to the advantages of the MOF framework that provides high surface area, and large pore diameters for a low diffusional barrier to active sites.

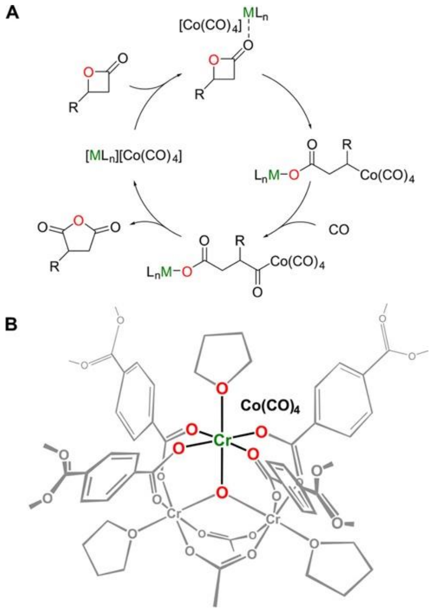

Figure 4. (A) Proposed catalytic cycle for the ring-expansion carbonylation of β-lactones by [Lewis acid]$^+$[$Co(CO)_4$]$^-$. (B) Illustration of the metal cluster structure of $Co(CO)_4 \subset$Cr-MIL-101 with coordinated tetrahydrofuran molecules.[41] Reprinted (adapted) with permission from Ref. 41. Copyright (2015) American Chemical Society.

As an ideal crystal with an infinite periodic array of lattice does not exist, most MOFs can contain defects and structural irregularities to a considerable extent. The defects are resulted from compositional inhomogeneities, which can alter the physicochemical properties of the materials.[47,48] Although both the UiO family and NU-1000 contain a Zr_6 cluster as the nodal centre, in perfect UiO MOFs, the Zr_6 nodes are fully (12) coordinated with bridging oxo groups and linkers. Structural defective sites (by missing linkers) can readily coordinate with incoming metal species and offer single-site environments. Hence, another recently employed approach to anchor single-atom metal species is to utilise the defective sites caused by the missing of organic linker molecules.[49,50]

The defects at the nodal centres of UiO-66, UiO-67, UiO-68, and UiO-69 (a family of Zr-based MOFs with a $Zr_6O_4(OH)_4$ nodal clusters) can be controlled upon the synthesis conditions, such as by modulating the synthesis temperature, varying the concentration of the acetic acid modulator, and the time for synthesis.[51,52] They are receiving increasing attention as effective supports to host single-atom metal species. Briefly, the concentrations of the defect sites can be determined by the extrapolation of thermogravimetric analysis data. Highly defective UiO-66 crystals were prepared by Yaghi et al., which have been used to stabilise single-atom Cu (Figure 5).[53] The preparation method was relatively straightforward. The sample has been extensively characterised, where the coordination of Cu to -OH/-OH_2 species was studied by DFT calculations and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The geometric and electronic properties of the single-atom Cu species was studied by time-resolved operando

XAS measurements. Upon the hydrogen reduction condition, the valence state of the Cu sites was changed from +2 to +1.

By utilising the defects on the Zr_6 nodes, other types of single atoms can also be stabilised. Lin et al. have prepared single-atom Co and Fe species on the defect sites of the $Zr_3(\mu_3\text{-}OH)$ sites of UiO-68.[54] It is achieved by deprotonating the $Zr_3(\mu_3\text{-}OH)$ using nBuLi followed by reaction with $CoCl_2$ or $FeBr_2{\cdot}2THF$. Complete metalation at the $Zr_3(\mu_3\text{-}OH)$ sites, corresponding to four Co/Fe centres per Zr_6 node, has been observed. Based on the structural analysis using EXAFS, the Co and Fe sites are coordinated with three O atoms. High crystallinity of the MOF framework has also been maintained as revealed from the PXRD patterns. The authors also have functionalised UiO-66 and UiO-67 with $CoCl_2$ in a similar fashion as UiO-68.

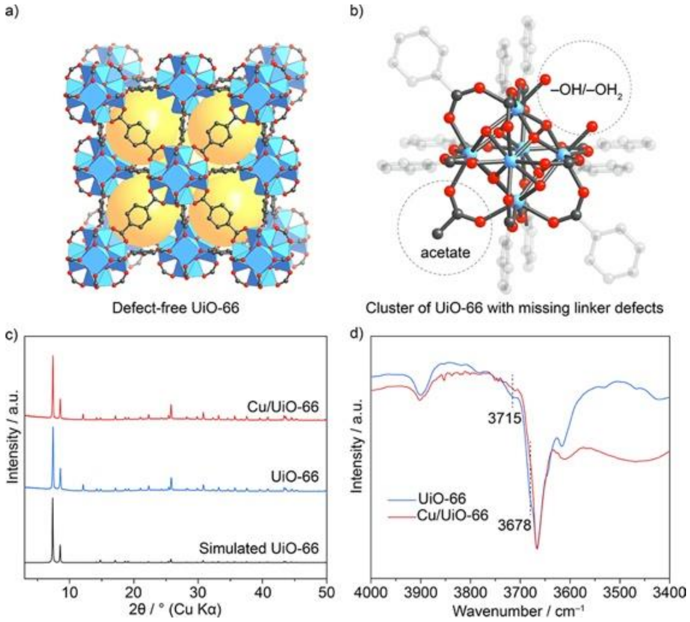

Figure 5. (a) Crystal structure of defect-free UiO-66 (yellow spheres represent the space in the framework). (b) Zr oxide cluster of UiO-66 with $–OH/–OH_2$ and acetate molecules replacing terephthalate linkers. Atom labelling scheme: C: black; O: red; Zr: blue (H atoms are omitted for clarity). (c) Measured PXRD diffractograms of UiO-66 and Cu/UiO-66 in comparison with a simulated diffractogram of UiO-66. (d) DRIFTS spectrum of UiO-66 overlaid with that of Cu/UiO-66.[53] Reprinted (adapted) with permission from Ref. [53]. Copyright (2019) American Chemical Society.

Lin et al. have reported single-atom Mg species stabilised by the $Zr_3(\mu_3\text{-}OH)$ metal nodes of TPHN-MOF (with the UiO-69 framework topology; TPHN = 4,4'-bis-carboxyphenyl-2-nitro-1,1'-biphenyl).[55] Through the reaction of $Mg(CH_3)_2$ with pristine TPHN-MOF in the tetrahydrofuran solvent, complete metalation at the $Zr_3(\mu_3\text{-}OH)$ sites have been achieved as characterised by elemental analysis (inductively coupled plasma-mass spectrometry). This is also verified by an equivalent amount of methane generated during the metalation process. High crystallinity of the MOF framework can be maintained upon metalation. However, as the four $MgCH_3$ moieties are randomly distributed among the eight μ_3-oxo positions (creating high crystallographic disorder), the structural determination of the MOF-$MgCH_3$ by X-ray crystallography could not be achieved. The MOF-$MgCH_3$ displayed excellent activity in the hydroboration of a wide range of carbonyl compounds with pinacolborane, via either (a) σ-bond metathesis involving the insertion of a C═O into a Mg–H bond, or (b) Zwitterionic mechanism without the involvement of Mg–H bond species. The versatile metalations of these MOF materials have demonstrated that the site-isolation approach can be a practical alternative to obtain active catalysts, without relying on bulky ligands for stabilisation as in the homogeneous analogues.

By placing different single-atom metal species in proximity, more superior catalytic properties can be achieved due to synergistic effect. Lin et al. have prepared a single-atom Cu on the Ru-functionalised UiO-67 framework (Cu-Ru-UiO).[56] The Ru-UiO framework was prepared by reacting $ZrCl_4$ with two highly related types of linker substrates, namely, biphenyl-4,4′-dicarboxylic acid (the original linker of UiO-67 MOF) and $[Ru^{II}(2,2'$-bipyridine$)_2$(2,2′-bipyridine-5,5′-dicarboxylic acid$)]Cl_2$ (the Ru^{II}-modified linker) (Figure 6). Cu was incorporated via a double-solvent impregnation approach, followed by adding a phosphate buffer solution. The single-atom nature of the Cu species was characterised by electron microscopic techniques and elemental analysis. The Cu site was supported on the Zr_6 nodal centre, locating near the Ru site from a crystallographic perspective. The Cu-Ru-UiO was found active for the photocatalytic hydrogenation of CO_2 to ethanol. Under light illumination, the Ru^{II}-complex undergoes single-electron transfer to both Cu^{II} and Cu^0 to generate Cu^I for catalytic ethanol production.

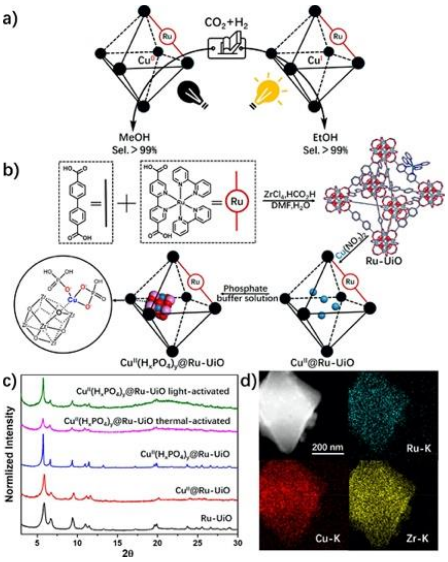

Figure 6. (a) Controlling catalytic selectivity of CO_2 hydrogenation using low-intensity light. (b) Synthesis and structure of $Cu^{II}(H_xPO_4)_y$@Ru-UiO. (c) Powder X-ray diffraction (PXRD) patterns of the precatalysts, catalysts, and catalysts after reactions. (d) TEM image and energy dispersive X-ray spectroscopy mapping of Ru(cyan), Cu (red), and Zr (yellow) in $Cu^{II}(H_xPO_4)_y$@Ru-UiO.[56] Reprinted (adapted) with permission from Ref. [56]. Copyright (2020) American Chemical Society.

These supported single-atom metal species have not altered the framework structure of the host MOFs; the physicochemical properties have hence been maintained to a large extent. The examples have either employed the defective sites of the MOF nodal centres or created additional functionality to fabricate single-atom metal species in MOFs. MOFs can truly offer a versatile platform for site-isolation that aid the discovering of new catalytic transformations for the sustainable synthesis of fine and commodity chemicals.

2.3 By pyrolysis

Thanks to the low thermal stability from the coordination framework between the metal sites and the organic linker molecules, MOFs have been demonstrated to be ideal precursors to produce porous carbon-based supporting material via pyrolysis. Pyrolysis is straightforward to achieve site-site isolation of metal species in MOFs, which typically relies on anaerobic heating of the materials. Most reported SACs, prepared by the pyrolysis of MOFs, require the co-existence of C- and N-containing organic linkers. The materials after pyrolysis treatment are hence based on N-doped carbon microporous framework.[57,58] Using hydrogen as the reaction gas for pyrolysis can further reduce the metal to a lower valence state. However, a significant drawback is the destruction of the crystalline MOF framework. This process can more likely lead to ill-defined SACs, which poses extra challenges during structural elucidation.

In recent years, the carbon matrices derived from the pyrolysis of MOFs have been widely employed as supporting materials.[59,60] The carbon matrices are prepared by anaerobic pyrolysis. The metal sites can be removed by evaporation at elevated temperatures, leaving porous carbon matrices with high surface area. Uniformly distributed atoms (such as N, O and S) can be found in the carbon matrices that are directly derived from the organic linker molecules. These sites have been utilised to anchor incoming single metal species via typical acid-base interactions. The formation of the acid-base pairs can inhibit the metal species from clustering. These single-atom metal species are often found with relatively high thermal and chemical stabilities. The single-atom metal species can also be loaded before the pyrolysis treatment, where the MOF precursors are predesigned with significant metal loading. As certain metal species can resist evaporation at a controlled environment, this can create a carbon matrix with high concentrations of metal sites.

Zeolitic imidazolate frameworks (ZIFs) are a major sub-group of MOFs. ZIFs are constructed by metal nodes such as Co^{II} (in ZIF-67) and Zn^{II} (in ZIF-8) with 2-methylimidazolate ($C_4H_5N^-$) as the organic linkers. In ZIF-8, the Zn^{II} species can be evaporated relatively easily during pyrolysis. This high-temperature treatment will leave behind a nitrogen-rich carbon matrix, which is ideal for supporting incoming ionic metal species. The metal-support interaction can also avoid metal species from aggregation. Chen et al. prepared supported Pd nanoparticles on N-doped carbon materials from the pyrolysis of ZIF-8.[61] Li et al. have reported the use of homogenous bimetallic Zn^{II}/Co^{II} ZIF to prepare supported single-atom Co species (Co-SACs/N-C) with high concentration (4 wt%).[62] Due to the preferential evaporation of framework Zn^{II} species at high environmental temperature in the absence of oxygen, isolated Co species within the as-generated microporous N-doped carbon frameworks was yielded. At the pyrolysis of 800 °C and 900 °C, the EXAFS and high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) characterisation results suggested the absence of Co aggregation. It should be noted that the lack of metal-metal path from EXAFS analysis has been commonly used as indirect evidence to show the presence of single-atom isolated species in recent years. The active sites were accordingly postulated as planar Co-N_4 and Co-N_2, respectively (Figure 7). Nano-sized Co species were observed when the pyrolysis temperature was elevated up to 1000 °C, as the thermal energy was sufficient to break the Co-N bonds. The SACs also exhibit outstanding chemical stability during electrocatalytic oxygen reduction reaction (ORR) from the durability tests. This pyrolysis specific method is, however, limited to the bimetallic Co^{II} and Zn^{II} in ZIF. A homogeneous distribution of Co^{II} and Zn^{II} sites connected via 2-methylimidazolate linkers has been prepared thanks to the compatible structural parameters of their parent ZIF-67 and ZIF-8 frameworks. The report by Li et al. has inspired many subsequent scientific findings thanks to the atomic dispersion, high metal loading, and excellent molecular accessibility from the pyrolysis of MOF/ZIF materials.

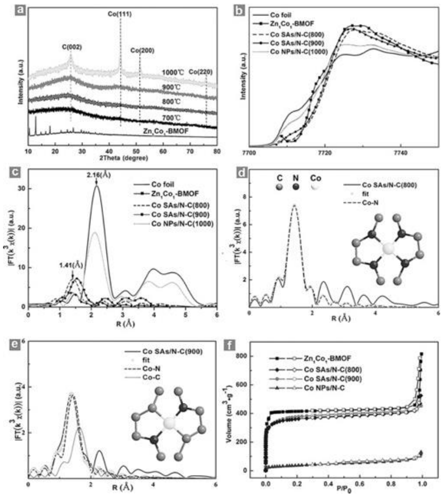

Figure 7. (a) The PXRD of the as-prepared samples by annealing of Zn,Co-BMOF at different temperatures. (b) Co K-edge XANES spectra and (c) the k^3-weighted c(k)-function of the EXAFS spectra. The corresponding EXAFS fitting curves for the samples (d) Co-SACs/ N-C(800) and (e) Co-SACs/N-C(900). Insets are the proposed Co-N_x architectures. (f) N_2 adsorption and desorption isotherms for Zn_1Co_1- BMOF, Co-SACs/N-C, and Co NPs/N-C.[62]

Li and co-workers have further applied this ZIF-assisted strategy to generate single-atom Ni species distributed in N-doped carbon matrix (Ni-SACs/N-C, Ni loading of 1.53%) for electrocatalytic CO_2 reduction.[63] Ni-SACs/N-C presented a high turnover frequency of CO2 (5273 h^{-1}), with a Faradaic efficiency for CO production of over 71.9% and a current density of 10.48 mA cm^{-2} at an overpotential of 0.89 V. Unlike the Co-SACs/N-C example, the Ni species were incorporated into small pores of ZIF-8 framework using a double-solvent approach (Figure 8). The material was heated, under the protection of Ar, at 1000 °C, where the organic linkers were transformed into an N-doped carbon matrix. Similarly, through characterisation by EXAFS and HAADF-STEM, isolated Ni species interacting with three N moieties of the N-doped carbon matrix was observed.

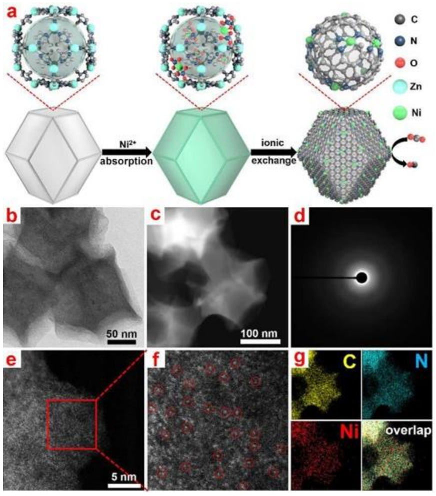

Figure 8. (a) Scheme of the formation of Ni SAs/N-C. (b) TEM and (c) HAADF-STEM images of Ni SAs/N-C. (d) Corresponding SAED pattern of an individual rhombododecahedron. (e, f) Magnified HAADF-STEM images of Ni SAs/N-C. The Ni single atoms are marked with red circles. (h) Corresponding EDX maps revealing the homogeneous distribution of Ni and N on the carbon support.[63] Reprinted (adapted) with permission from Ref. [63]. Copyright (2017) American Chemical Society.

The ZIF-assisted strategy can be further applied to design bimetallic analogues. Gong et al. have reported a material consisted of two different single-atom species, Fe and Mn, supported on the N-doped carbon matrix (Fe,Mn-SACs/N-C) (Figure 9).[64] This dual single-site catalyst shows high electrocatalytic activity for ORR than those with only Fe-N$_x$ or Mn-N$_x$ active sites, with a half-potential of 0.904 V and kinetic current density of 33.33 mA cm^{-2} at 0.85 V. More importantly, through XANES and DFT calculations, it is found that the Mn ions could alter the electronic structure of Fe ions at the Fe-N$_x$ active sites. The synergy between the Fe and Mn sites can effectively lower the energy barrier of the electrocatalytic ORR process.

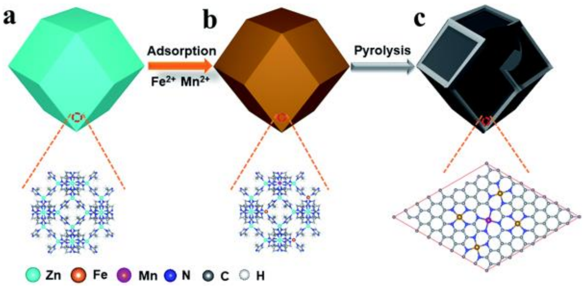

Figure 9. (a) ZIF-8 MOF. (b) Fe- and Mn-doped ZIF-8 precursor. (c) Hollow Fe,Mn-SACs/N-C after pyrolysis.[64]

Besides preparing single-atom species on the N-doped matrix as prepared by the ZIF-assisted pyrolysis approach, Li et al. have also employed this concept to prepare supported single-site trinuclear metal clusters. $Ru_3(CO)_{12}$ was used as the precursor of the trinuclear Ru_3 clusters. It was first encapsulated into the pore of ZIF-8 in one-pot along with the assembly of Zn^{2+} and 2-methylimidazole during ZIF-8 crystallisation.[65] By heating the sample under 5% H_2/Ar atmosphere at 800 °C, $Ru_3(CO)_{12}$@ZIF-8 was decomposed to yield Ru_3/N-C, where the uniformly dispersed Ru_3 clusters were stabilised by the N moieties on the N-doped carbon matrix (Figure 10). From the HAADF images, groups of three-bright-dots have been correlated with the triangular Ru_3 structure. The EXAFS analysis has suggested the co-existence of Ru-N and Ru-Ru paths that can be originated from the triangular Ru_3 structure. Interestingly, the authors compared the catalytic properties of Ru-SACs/N-C with that of Ru_3/N-C using the oxidation of 2-amino-benzyl alcohol as a model reaction. Based on the first-principles calculations, the more superior catalytic performance in Ru_3/N-C can be caused by the difference in adsorption energies and adsorption geometries of 2-amino-benzyl alcohol over the two Ru active sites.

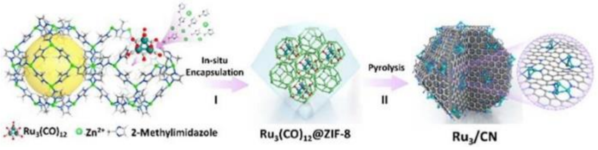

Figure 10. Illustration of the Ru_3/CN Preparation Process.[65] Reprinted (adapted) with permission from Ref. [65]. Copyright (2017) American Chemical Society.

Indeed, pyrolysis is a facile way in stabilising single-atom metal species while maintaining high microporosity as templated by the ZIF/MOF framework.[66,67] The N-doped carbon matrix can readily coordinate metal species and offer stable site-isolation effect to promote catalysis.[68,69] In particular, the N-doped carbon matrix is conductive, leading to the vast applications of this class of supported SACs in photo- and electrocatalysis. Interested readers may refer to the recent review articles by Jiao and Jiang (2018)[26], and Han et al. (2019)[37] for more examples in these areas. Using dilute hydrogen as the pyrolysis atmosphere can often selectively reduce the metal ions encapsulated in the ZIF framework. It can be beneficial if the catalysis reactions require lower metal valence states. The reductive reaction atmosphere might however also induce reactions on the MOF frameworks. The reaction conditions, as well as the potential applications, should therefore be carefully considered at the stage of reaction design. The destruction of the ZIF crystalline framework, however, can hinder the characterisation by typical crystallographic techniques. The lack of sharp Bragg's peaks in the PXRD patterns after pyrolysis can only provide limited information when compared with those from the original structures. Also, the pyrolysis approach will sacrifice the physiochemical properties of the MOF structures.

3. Perspectives and Conclusion

Single-atom catalysts (SACs) are receiving increasing attention in recent years. Due to the highly tuneable electronic structures, they exhibit extremely high potential in different catalytic applications. The progressive advancement in characterisation techniques also offers more accurate and reliable elucidation of the structural and atomic information. MOF materials, thanks to their physicochemical properties, are ideal for the stabilisation of SACs with high surface energy and mobility. With the structural properties akin to the inorganic counterpart, zeolites have limited applications in photo- and electrocatalysis due to the large bandgap and insulating structures. In contrast, MOFs exhibit high potential in photo- and electrocatalysis thanks to their extensively tuneable frameworks and electronic structures. The SACs can be stabilised via acid-base interactions. We have summarised recent preparation approaches into three main categories: (1) via traditional ligand functionality, (2) via nodal defect sites, and (3) by pyrolysis. Each has its advantages and disadvantages. (1) and (2) approaches can provide charge transfer systems, such as LMCT and MLCT, to promote the catalytic properties. The synergetic effect between various catalytically active sites has been shown promising to promote catalytic performance.[70,71] In the preparation approaches described, the incorporation metal sites can be located specifically according to the chemical properties of the MOF structures. When two active sites are in proximity to each other, the catalytic properties can be promoted noticeably due to the synergetic effect between the two catalytic centres. MOFs are accepted as an array of self-assembled molecular catalysts rather than conventional semiconductors. The HOMO-LUMO band gap terminology is believed to be more appropriate to describe these assembled molecular entities. Discrete optical transitions, such as ligand-to-cluster charge transfer (LCCT: from the linker to the metal nodal clusters), ligand-to-metal charge transfer (LMCT), metal-to-metal charge transfer (MMCT), and metal-to-ligand charge transfer (MLCT), are observed.[72–74] The more recent pyrolysis method employs the thermal property of ZIF-based MOFs to yield SACs supported on N-doped carbon matrices at high concentration. However, the original physicochemical properties of MOF are however sacrificed. Therefore, we aspire to the development of more superior and highly optimised different catalytic systems in the near future for the sustainable provision of various commodity chemicals.

In the recent years, a majority of MOF-related SACs uses the ZIF-assisted pyrolysis method. A vast recognised advantage is the simplicity in the preparation procedure. The thermal treatment however destroys the crystallinity of the support, making characterisation using scattering techniques broadly inaccessible. In many recent works, EXAFS is one of the primary techniques to reveal the single-atom nature of the metal sites. An absence of M-M contribution from the EXAFS spectrum is believed to be indicative of metal clustering. In contrast with the more crystalline counterparts, namely the SACs prepared by utilising the functional organic linkers and vacant nodal centres, the lack of long-range ordering hinders the use of whole-pattern refinement techniques over X-ray diffraction data (such as Rietveld refinement) for structural elucidation. Besides using single-crystal X-ray diffraction, high-resolution powder X-ray diffraction can also provide essential structural information in terms of atomic resolution. The capability of using high-resolution synchrotron powder X-ray diffraction and Rietveld refinement has been well-demonstrated in zeolitic materials, where not only the active sites and the adsorbate structures, but the key information associated with catalytic and chemical properties can also be revealed.[75] We aspire, in the near future, in-situ/operando high-resolution synchrotron powder X-ray diffraction will be broadly applied to elucidate the structure-activity relationships and hence offer rational guides to design more superior functional materials.

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