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Recent Advances in Metal-Organic Frameworks for Heterogeneous Catalyzed Organic Transformations

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Abstract

In this review, we summarize recent advances on Metal-Organic Framework (MOF) based heterogeneous catalytic chemistry. Catalytic performance of varied configurations of MOFs including active sites, post synthetic modification, and MOF derived catalysts, is summarized in the context of various organic transformation reactions. Post synthetic modification of MOFs via functionalization of organic linkers with active catalytic moieties is deliberated. Also, efficacy of carbonaceous catalysts derived from MOFs is discussed. Overall, an outlook on MOF's application in heterogeneous catalysis is presented.

Keywords: Metal-Organic Framework (MOF); Heterogeneous catalysis; Post synthesis modification; Organic transformations; Catalyst

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Introduction

Nanoporous Metal-organic frameworks (MOFs) are an important class of new materials that have attracted researchers owing to their special properties [1-7]. The main advantage of MOFs is their versatility in chemical composition, organic and inorganic building units, and the bifunctional metal/acid sites for insertion using isoreticular chemistry [8,9]. Owing to their crystalline characteristics, tunable porous structure with high surface areas (up to 10000 m^2/g) and large pore volumes, made them superior materials for various applications in gas/vapor sorption, separation, drug delivery and heterogeneous catalysis [10-15]. Specifically, the potential inner porosity similar to that of zeolites and the ease of access to the metal ions in the pore, made them superior in heterogeneous catalysis [16,17]. Moreover, both metal centers and organic linkers contribute to the catalytic activities while pores serve as a host for small molecules and/or supports for metal/metal oxide nanoclusters [18,19]. Though the low thermal and chemical stability of MOFs definitely limit the use of MOFs in high temperature vapor phase catalysis reactions, MOFs can compete with or even outperform the existing zeolites in low temperature liquid phase reactions [20]. Here, we report a brief overview on the recent progress of MOFs used in heterogeneous catalysis of different organic reactions. We evaluated the heterogeneous catalysis of MOFs by considering: (i) Active sites in MOFs for organic transformations; (ii) Post-synthesis modification; and (iii) MOF derived catalysis.

Active sites in MOFs for organic transformations

MOFs with exotic topologies and chemical activities have shown outstanding catalytic performance in various organic transformation reactions and to name a few are oxidation, acetylation, epoxidation, hydrogenation, coupling, condensation, alkylation, hydroxylation and cyclization. The catalytic activity in MOFs is generated at both metal nodes (largely acting as Lewis acids) and also any exposed terminal ligands (usually Lewis basic sites). Specifically, the Lewis acid sites from the metal nodes can be generated by removing the coordinated water molecules from the MOF framework by exposing the metal sites. Kaskel et al. demonstrated the dehydration of HKUST-1 ($Cu_3(btc)_2$) to produce open Cu(II) sites for cyanosilylation of aldehydes, but later when they attempted with large pore Cr-MIL-101 ($Cr_3F(H_2O)_2O(BDC)_3$), where Cr(III) sites showed higher Lewis acidity than Cu(II) sites for the same cyanosilylation reactions [21,22]. A specific list of the organic transformation reactions catalyzed by MOFs are discussed in detail and also summarized in **Table 1**.

Acetylation: Acetylation of alcohols is an important and fundamental reaction in organic synthesis, mainly because of many hydroxyl groups' presence in biological/synthetic systems. Copper salts proved to be better catalytic materials for such O-acetylation reactions in the literature. By considering this, Singh et al., demonstrated O-acytalizaiton of alcohols by using copper based Cu-BDC MOF and achieved up to 93% yield at ambient conditions **(Figure 1)** [23]. The MOF showed excellent catalytic activity for both primary and secondary aliphatic alcohols due to free and accessible metallic sites (Cu(II) with 39.96% of active site content) within the pore interacting with the -CO- group of acetic anhydride for the activation of acetyl group for product formation. Various acetyl derivatives were synthesized with more than 70% yield.

Epoxide activation: The regioselective and enantioretentive epoxide activation in the context of quantitative chemical fixation of CO_2 into five membered cyclic carbonates under ambient conditions was demonstrated by Beyzavi et al. [24] using a polyoxohafnium cluster (Hf_6) based NU-1000. By considering the fact of stronger dissociation enthalpies of the Hf-O bond (802 kJ/mol) over the Zr-O bond (776 kJ/mol), authors synthesized Hf-cluster based NU-1000 and successfully demonstrated its stronger Bronsted acid character compared to the parent Zr-based NU-1000. For a test reaction of cycloaddition of styrene oxide using CO_2 at 1 atm pressure, Hf-NU-1000 showed 100% yield at room temperature while Zr-NU-1000 showed just less than half (~46% yield), respectively **(Figure 2)**. This MOF bearing stronger M-O bonds with more oxophilic nature showed as a multifunctional catalyst for the regioselective and enantioretentive formation of 1,2-bifunctionalized systems via solvolytic nucleophilic ring opening of the epoxides.

Hydrogenation: Kozachuk et al. [25], demonstrated the defect-engineered framework structure with controlled instruction of defect-generating linkers sites into a Ruthenium analogue of HKUST-1. Here, by using a mixed-linker solid-solution approach, introduced structural defects by incorporating similar/same sized ligand pyridine-3-5-dicarboxylate (pydc) in Ru-HKUST-1 synthesis.

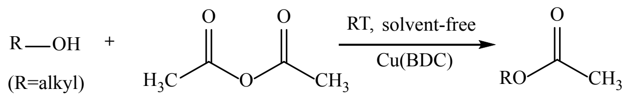

Figure 1 Acetylation of alcohols using acetic anhydride in Cu(BDC) at RT and solvent free conditions [23].

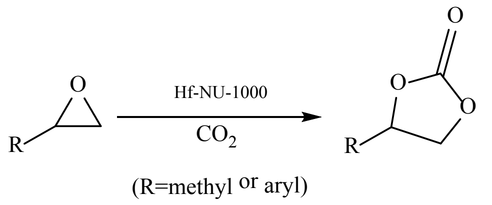

Figure 2 Cycloaddition reactions of CO_2 with epoxides in presence of Hf-NU-1000 [24].

Table 1 Summary of known catalytic MOFs for organic transformations. (BDC=1,4-benzenedicarboxylic acid; H_4TBAPy=1,3,6,8-tetrakis(*p*-benzoic acid) purene; H_3btc=benzene-1,3,5-tricarboxylate; H_2pydc=pyridine-3,5-dicarboxylate; H_2tdc=2,5-thiophenedicarboxylic acid; bpe=1,2-bis(4-pyridyl) ethane; H_2bpdc-NH_2=2,2′-diamino[1,1′-Biphenyl]-4,4′-dicarboxylic acid; H_2dcppy=6-(4-carboxyphenyl)nicotinic acid; BDC=1,4-benzene dicarboxylate; H_3btb=1,3,5-tris(4-carboxyphenyl)benzene tribenzoic acid).

MOF	Linker	Active sites	Reaction(s)	Reactant	Conversion	Ref
Cu–BDC	BDC	Cu(II)	O-acetylation	Alcohols	80%	[23]
Hf-NU-1000	H_4TBAPy with benzoic acid	Hf(II)	Regioselective Enantioretentive Epoxide activation	Epoxides/styrene oxide	90 %	[24]
$Ru_3(btc)_2$-x$(pydc)_xX_y$	H_3btc and H_2pydc	Ru(III)	Hydrogenation	1-octene	100%	[25]
MOF-199	H_3btc	Cu(II)	Oxidative C-C coupling	N,N-dimethyl aniline and phenylacetylene	96%	[27]
[Cu(tdc)(bpe)] n·2n(H_2O)·n(MeOH)	H_2tdc; bpe	Cu(II)	Glaser homo-coupling	Phenylacetylene and K_2CO_3	82 %	[28]
Zn(II)-IRMOF-9-Irdcppy- NH_2	H_2bpdc-$(NH_2)_2$; H_2dcppy	Ir(I) -NH_2	Knoevenagel condensation Allylic N-alkylation	Indoline-7-carboxyaldehyde and malonitrile	95%	[29]
Cz-POF-1	Cz-1, 3,3,5,5-tetra(9H-carbazol-9yl)-1,1-biphenyl	π-conj.	Hydroxylation α-alkylation Dehalogenation	Arylboronic acids Aldehydes Phynacyl bromide	94% 90% 99%	[59]
Cu(BDC)	1,4-benzene dicarboxylate	Cu(II)	Oxidative cyclization	α-hydroxyketones and 1,2-aryldiamines	82%	[30]
NUGRH-1	N,N'-di[3,5-di (4-carboxy phenyl) phenyl]urea	Urea	Friedel–Crafts	Indole, β-nitrostyrene	98%	[31]
InPF-110	H_3btb	In(III)	Strecker reaction	Acetophenone	99%	[32]

The Pydc incorporation in the framework showed lower charge and induced the partial reduction of ruthenium sites at the paddle-wheel moieties, which triggered high reactivity in the Olefin hydrogenation catalysis. 1-Octene, as a model compound was clearly observed, and the defect–engineered sample showed enhanced hydrogenation performance with less than 1 h for full conversion when compared to 3-4 h taken by the parent Ru-MOF **(Figure 3)**. The enhanced activity is attributed to the rate-determining step of Ru-H species formation during pretreatment and the Pydc assisting the heterolytic activation by acting as the base ligand pyridyl-N site.

Coupling reactions: Copper containing MOFs are reported to be ideal active and stable solid catalysts for coupling reactions with excellent selectivity and scope. Luz et al. [26], demonstrated the synthesis of imidazopyridine derivatives by three-component coupling of 2-aminopyridine, benzaldehyde, and phenylacetylene in the presence of two copper based MOFs, Cu(2-pymo)$_2$ (2-pymo=2-hydroxypyrimidinolate) and Cu(BDC) as catalysts. Though both showed decent catalytic performance, the lamellar Cu(BDC) outperformed the domino three-component coupling reaction with >97% yield. Likewise, Dang et al. [27], reported the synthesis of propargylamine via direct oxidative C-C coupling of *N,N*-dimethylaniline and phenyl acetylene using copper based HKUST-1. This copper-catalyzed C-C coupling results with 96% conversion within 3 h at 120°C in the presence of 5 mol% HKUST-1. The catalyst was recovered and reused significantly without degradation of the catalytic activity. Different derivatives of *N,N*-dimethylaniline with electron donating groups (ex: methyl) and electron withdrawing groups (ex: bromo) were successfully coupled to obtain more than 55% yield **(Figure 4)**. Similarly, a copper based 2D pillared-bilayer flexible MOF Cu(tdc)(bpe)$_n$.2n(H_2O).n(MeOH) (tdc=2,5 thiophene dicarboxylic acid; bpe=1,2-bis(4-pyridyl)ethane) has been used in Glaser type homo-coupling reaction by Parshamoni et al. [28] The home coupling of Phenylacetylene with 5 mol% of the catalyst showed almost ~82% yield of the Glacer product at 110°C for 6 h where the same reaction with Cu(BDC) as a catalyst did not lead to the homo-coupled product even after days of the reaction. The leaching study shows that the catalysis is heterogeneous and catalyst can be reused after several cycles without any structural changes. A good conversion and selectivity to the homo-coupling product of variety of other aromatic alkynes were also observed.

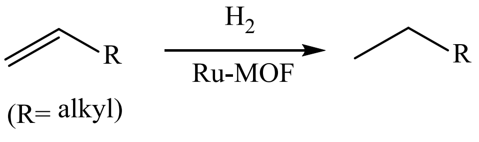

Figure 3 Olefin hydrogenation reaction in presence of Ru-MOF [25].

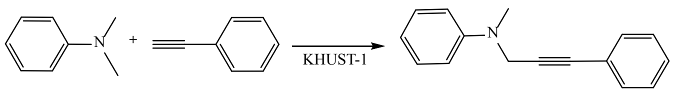

Figure 4 Oxidative C-C coupling reaction in presence of HKUST-1 as catalyst [27].

Condensation: The Knoevenagel condensation of Indoline-7-carboxyaldehyde and malonitrile was successfully achieved by Dau et al. [29] using site isolated tandem catalyst, a Zn(II) based Zn(II)-IRMOF-9-Irdcppy-NH_2 with >95% conversion. In this catalysis, the isolated amine and Ir(I) sites of the MOF show independent catalytic activity performing Knoevenagel condensation and allylic N-alkylation, respectively, owing to the bifunctionality of the catalyst. The authors utilized the mixed linker approach to integrate H_2bpdc-$(NH_2)_2$ and H_2dcppy (bpdc=1,1'-Biphenyl-4,4'-dicarboxylic acid; dcppy=6-(4-carboxyphenyl)nicotinic acid) to produce a new MOF, IRMOF-9-dcppy-NH_2, and ~95% conversion was shown at 55C **(Figure 5)**. The authors demonstrated the potential use of MOF to engender complex catalytic systems that were not limited to any single class of catalytic species.

Oxidative cyclization: The copper based Cu(BDC) MOF is used as an efficient heterogeneous catalyst for the synthesis of quinoxaline via oxidative cyclization catalysis by Truong and Dang et al. [30] The lamellar Cu(BDC) showed higher catalytic activity over other copper based HKUST-1, MOF-118, and $Cu_2(BDC)_2$(DABCO) and even higher than that of Mn(BDC) and $Ni_2(BDC)_2$(DABCO). The catalyst showed very high recyclability and reusability for several times without a significant degradation in catalytic activity. The catalytic oxidative cyclization of α-hydroxyacetophenone gives 100% conversion with *O*-phenylenediamine within 3 hours **(Figure 6)**. This study also explored the cyclization with different derivatives of phenylenediamine with time variations.

Friedel-crafts activator: A urea containing Zn based hydrogen bond donor MOF with novel architecture (NU-GRH-1) was constructed by Hall et al. [31] using urea functionalized tetracarboxylate struts for Lewis acid activation in the Friedel-Craft reactions **(Figure 7)**. The ideal combination of Lewis acidity and H-bond donor

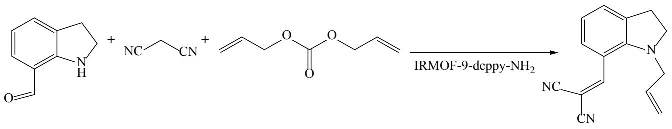

Figure 5 Tandem catalytic Knoevenagel condensation using Zinc based IRMOF-9-dcppy-NH_2 as catalyst [29].

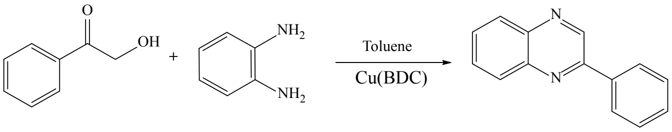

Figure 6 The oxidative cyclization reaction using Cu(BDC) catalyst [30].

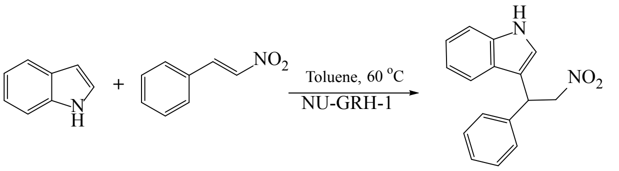

Figure 7 Indole Friedel-Crafts reactions catalyzed by NU-GRH-1 [31].

capability of this new MOF showed enhanced catalytic activity for new bond-forming reactions such as Friedel-Craft reactions. The enhanced catalytic performance of the MOF is enhanced through pre-activation with silyl Lewis acid. The reaction rates in these Friedel-Crafts reactions using the new MOF were greater than those of common homogeneous hydrogen bond donors.

Strecker reaction: A mesoporous indium based MOF, InPF-110 has been synthesized by Fisac et al. [32] with a large density of active Indium metal centers**.** The MOF showed outstanding catalytic performance for the formation of substituted α-aminonitriles through Strecker reaction of ketones. The MOF, InPF-110 catalyzed one-pot three component Strecker reaction of acetophenone, phenylamine and trimethyl silyl cyanide in activation solvents such as water, methanol and ethanol solvents with excellent (~99 %) yields **(Figure 8)**. Other conversions with the derivatives of the acetophenone have been also carried out with more than 80% yield in methanol and ethanol solvents.

Post synthetic modified MOF as a catalyst

Introducing the catalytic active site in the MOF pore is of substantial interest; as such sites may add properties that facilitate applications with enhanced properties, specifically towards sorption and catalysis. The direct synthesis of such desired active MOF structures not only can be hard to predict the formation, but also challenging to design and synthesize. Post synthetic modification (PSM) is a great approach that can use covalent modification of the pre-formed MOF structure to introduce such active sites for effective catalysis [33-34]. A schematic representation of PSM presented in **Figure 9**, where Wenbin Lin et al. developed regioselective and enantioselective catalyst for accelerating the rates of specific reactions and enhancing the selectivity to the desired product [35].

Another example of PSM is the metalation or encapsulation of active species such as metal complexes or metal nanoparticles (MNP) in the framework of porous MOFs. Here the MOF framework is used as a support or host for the catalytic species, which was positioned in the cavity by noncovalent interactions using a 'ship-in-a-bottle or bottle-around-the-ship' approach. Metalation with MNPs inside MOFs can be achieved by a stepwise process of particle infiltration followed by decomposition in which, the size and shape of the nanoparticle governs the pore size, shape, and channel structure of MOF [34,36] Recently developed and known PSM MOFs are summarized in **Table 2** with corresponding organic transformations.

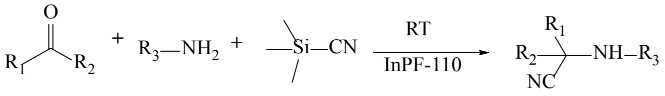

Figure 8 Streker type reaction of ketones in presence of InPF-110 [32].

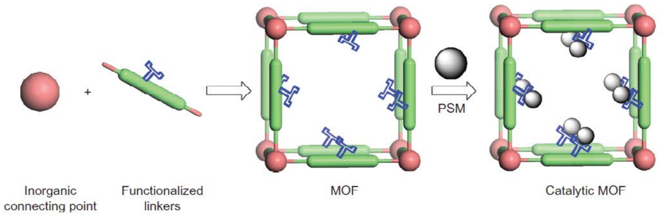

Figure 9 Representation of a homochiral MOF and its post synthetic modification (PSM) to give a catalytically active MOF. Printed with permission from Ma et al. [35].

In another example of PSM based MOFs, Fei et al. [37], used the Zr (VI)-based UIO-67 framework for crosslinking with 2,2'-bipyredine to form UiO-67-bpydc/bpdc MOF, as 2,2'-Bippyredene-5,5'-dicarboxylic acid is one of the most widely used bidentate chelators in transition metal coordination chemistry **(Figure 10)**. The resulting product is a new robust catalytic MOF with open 2,2'-bipyridine chelating sites in the framework, which readily forms complex with $PdCl_{2,}$ as an efficient catalyst. The quantitative metalation with palladium is achieved to attach the Pd(bpy)Cl_2 species on the struts of the MOFs with high crystallinity and porosity, thus exhibiting efficient, heterogeneous and recyclable catalysis of Suzuki-Miyaura cross-coupling reaction of 4-bromotoluene and phenylboronic acid with 89% conversion at 95°C in 16 h.

Further, Roy et al. [38], also demonstrated the Suzuki-Miyura cross-coupling of aryl halide and phenyl boronic acid in water by using Pd (0) NPs grafted at the surface of a Co-containing MOF, with greater than 60% conversion. This catalyst was further extended for the Sonogashira cross-coupling reaction of iodobenzene and phenyl acetylene with 35-90% conversion as shown in **Figure 11**.

Similarly, enantioselective Rh and Ru-functionalized MOF which was three times active over homogenous catalyst was reported by Falkowski et al. [39] Here, porous Zr-MOF based on a 2,2'-bis(diphenyl-phosphino)-1,1'-binaphthyl (BINAP))-derived dicarboxylate linker was synthesized and post-synthetically metalated with Ru and Rh for enantioselective catalyst for asymmetric organic transformations, including addition of aryl and alkyl groups to α,β-unsaturated ketones and hydrogenation of substituted alkene and carbonyl compounds with more than 99% conversion **(Figure 12)**.

Manna et al. [40] reported the hydrogenation of 1-octene in 16 h with 100% yield using post metalated sal-Fe-MOF which was a porous Zr-based metal-organic framework of UiO topology bridged with salicylaldimine derived dicarboxylate ligand and

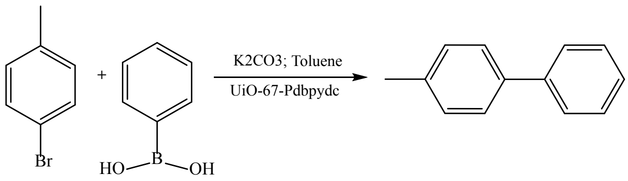

Figure 10 Suzuki-Miyaura coupling reaction of 4-bromotoluene and phenylboronic acid [37].

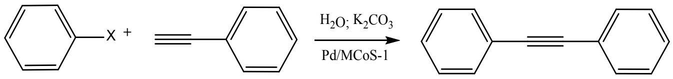

Figure 11 Suzuki-Miyaura cross-coupling reaction of aryl halides with phenyl boronic acid [38].

Table 2 Summary of known post synthetic modified MOF catalysts for organic transformations. (Bpydc=2,2´-bipyridine-5,5´-dicarboxylic acid; bpdc=4,4´-biphenyldicarboxylic acid; CoS=Cobalt Salicylate; BINAP=2,2´-bis(diphenyl-phosphino)-1,1´-binaphthyl; bpy-2,2´bipyridine-5,5´-dicarboxylic acid; sal=salicylaldimine; BPV=5,5'-bis(carboxyethenyl)-2,2'-bipyridine; mBPV=5,5'-bis (methoxy-carbonylethenyl)-2,2'-bipyridine; PT=3,8-bis(4-carboxyphenyl)phenanthroline; mPT=3,8-bis(4-methoxycarbonylphenyl)phenanthroline).

Host MOF	Metal	Resulting MOF	Reaction(s)	Reactant	Conversion	Ref.
UiO-67-bpydc	Pd	UiO-67-Pdbpydc0.5/ bpdc0.5	Suzuki–Miyaura cross-coupling	Phenylboronic acid and 4-bromotoluene	89%	[37]
MCoS-1	Pd	Pd/MCoS-1	Suzuki–Miyaura cross-coupling	Aryl halides and Phenylboronic acid	60-98%	[38]
BINAP-MOF	Ru Rh	Ru-BINAP Rh-BINAP	Asymmetric addition Hydrogenation	Arylboronic Acids β-Keto Esters	99% 97%	[39]
bpy-UiO	Ir Pd	bpy-UiO-Ir bpy-UiO-Pd	Borylation; Ortho-silylation Dehydrogenation	Arenes Benzylicsilyl ethers Cyclohexenones	83% 83% 80%	[41]
[Sal-MOF]	Fe	sal-Fe-MOF	Hydrogenation	1-Octene	92%	[40]
BPV-MOF, mBPV-MOF	Ir	BPV-MOF-Ir, mBPV-MOF-Ir	Hydrosilylation	Aldehydes/Ketones	100%	[42]
mPT-MOF	Ir	mPT-MOF-Ir	Dehydrosilylation/dehydrogenative cyclization	N-Methylbenzyl Amines	100%	

postsynthetic metalation with iron (II) chloride. Impressively, the obtained sal-Fe-MOF displayed very high turnover numbers of up to 145000 and shows an amazing more than 15 times of reusability by recycling the catalyst. Similarly, Wenbin Lin's group used post synthetic metalation approach for the synthesis of bipyridyl-containing MOF, bpy-UiO, which further post metalated with Iridium and palladium resulting in bpy-UiO-Ir and bpy-UiO-Pd MOFs respectively. The bpy-UiO-Ir is a highly active catalyst for both borylation of aromatic C-H bonds and *O*-silylation of benzilicsilyl ethers with at least three orders of magnitude higher reactivity when compared to a homogeneous control reaction. More than 80% dehydrogenation of substituted cyclohexanones was carried out in the presence of the bpy-UiO-Pd catalyst **(Figure 13)** [41]. An impressive feature of this work is that, the bpy-UiO-Ir was recycled and reused 20 times for the borylation reaction without loss of catalytic activity. In another report, the same group synthesized a series of robust and porous bipyridyl- and phenanthroline-based MOFs of UiO topology using a dicarboxylate linker and their post synthetic metalation with Iridium resulting in the BPV-MOF-Ir, mBPV-MOF-Ir and mPT-MOF-Ir [42]. The obtained catalysts are highly active catalysts for tandem hydrosilylation of aryl ketones and aldehydes (100% conversion) followed by dehydrogenative ortho-silylation of benzylicsilyl ethers as well as C–H borylation of arenes with 100% conversion. Here, mBPV-MOF-Ir exhibited high Turnover number (TONs) of up to 17000 for C–H borylation reactions and was recycled and reused without degradation for more than 15 times. The mPT-MOF-Ir showed impressive catalytic activity in tandem dehydrosilylation / dehydrogenative cyclization of N-methylbenzyl amines to azasilolanes in the absence of a hydrogen acceptor. The accompanying distinctiveness of these MOF-Ir catalysts is that they are significantly more active (up to 95 times) and stable than their homogeneous counterparts.

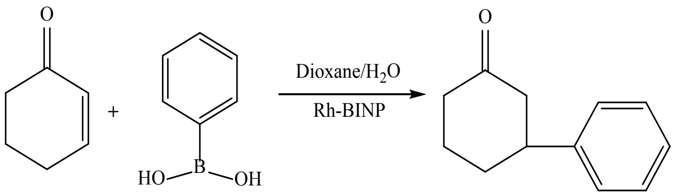

Figure 12 Asymmetric addition of aryl boronic acid to 2-cyclohexenone [39].

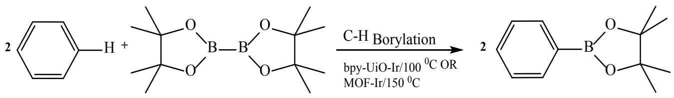

Figure 13 C-H borylation of arenes using Bpy-UiO-Ir and MOF-Ir as catalysts [41,42].

MOF derived catalysis

Metal nanoparticles (NPs) have attracted significant attention due to their high efficiency in the organic catalytic reactions like hydrogenation, dehydrogenation, oxidation, C-C cross coupling, Suzuki-Miyura coupling reactions etc. However, in many cases, the unstable and morphological or structural changes of small NPs under reaction conditions reduce the catalytic efficiency of the metal based catalysts [43,44]. Researchers have solved this problem by embedding the NPs in the cage or channel of porous materials or by fabricating a composite catalyst with new nanomaterials like mesoporous silica, graphene, MOS$_x$, and metal-organic frameworks [45-48]. Due to their promising mechanical and chemical stability and large surface area, the carbonaceous materials, such as active carbons, carbon nanotubes and graphene have been used as efficient support materials for preparing heterogeneous catalysts. The embedded NPs in carbon catalysts easily block the micro pores of the active carbon which results in diminished catalytic conversions as the NPs hinder the diffusion of reactants. Also physically attached NPs with the carbon undergo leaching during the reaction which significantly reduced the catalytic activity. Recently, MOFs have been utilized as precursors/templates for synthesis of porous NPs supported carbon structures, as they exhibit mesoporosity, recyclability and seperability [49-50]. To date, much progress has been achieved in deriving high performance catalyst materials from MOFs. One of the best examples of MOF derived catalysts is the porous metal embedded carbon derived from direct carbonization of the MOF in reducing environments [51-55]. Direct carbonization produces a hierarchical porous carbon structure with pore structure retained from the MOF along with active metal atoms embedded at the nodes **(Figure 14)**.

To overcome the significant challenges to develop the low cost noble metal nanocatalyst with high catalytic activity and selectivity, convenient separation and reusability, Zhang et al. [56] synthesized a newer magnetically separable gold (Au/MPC) and palladium (Pd/MPC) NPs based porous carbon composite derived from Fe-MIL-88A. The MOF derived nanocatalysts which possess large surface area, mesopores and super para-magnetism for easy separation and convenient recovery for reusability. The obtained Au/MPC and Pd/MPCs were successfully used for the efficient (100% conversion) reduction of 4-nitrophenol to 4-aminophenol with the rate constant of $k=1 \times 10^{-2}$ and 1.2×10^{-2} respectively. Ma et al. [57] reported the one-step pyrolysis of ZIF-67, produced N-doped porous carbon incorporating well-dispersed Co/CoO NPs as an excellent catalyst with magnetic separability and reusability. Catalyst possesses chemoselectivity for the tandem dehydrogenation of ammonia borane and hydrogenation of nitro compounds at room temperature with 86-100% yield. In their study Dong et al. [58,59] carried out Suzuki-Miyura coupling reactions with high catalytic efficiency yield ranging from 90-99% of aryl halide with phenylboronic acid using MOF-5-derived nanoporous carbon immobilized with Palladium NPs. This work highlights the development of efficient heterogeneous catalyst using MOF-Derived porous carbon as hosts for ultrafine metal nanoparticles.

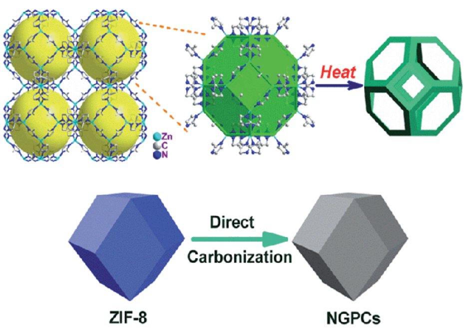

Figure 14 Schematic representation of graphitized nanoporous carbons synthesis from MOF driven template synthesis. The ZIF-8 parent model of cage-type pore structure (top) and rhombic dodecahedral morphology (bottom) converted into carbon with retaining its morphology was represented here. Printed with permission from Zhang et al. [51].

Though MOFs served as heterogeneous catalysts for more than a decade, over the past few years, the research advanced further because of many new kinds of MOF chemistry development which showed higher thermal and chemical stability. Enhanced stability aspect of MOFs facilitated post synthesis modification to derive MOFs with enhanced catalytic performance. Thus, with imminent prospective in tunability, flexibility and stability in MOFs, definitely take these materials into next generation catalysis for industrial applications. Also, the porous structure of MOF with spatial presence of metallic centers provided a new platform for the development of porous carbon materials (with embedded metal nanocluster) as efficient heterogeneous catalysts.

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