

# Bifunctional MOFs in Heterogeneous Catalysis

Srinivasan Natarajan\* and Krishna Manna

Cite This: *ACS Org. Inorg. Au* 2024, 4, 59–90

Read Online

ACCESS |

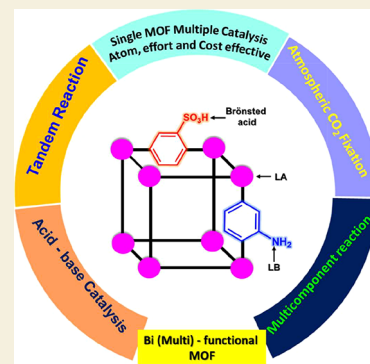
Metrics &amp; More

Article Recommendations

Supporting Information

**ABSTRACT:** The ever-increasing landscape of heterogeneous catalysis, pure and applied, utilizes many different catalysts. Academic insights along with many industrial adaptations paved the way for the growth. In designing a catalyst, it is desirable to have *a priori* knowledge of what structure needs to be targeted to help in achieving the goal. When focusing on catalysis, one needs to cope with a vast corpus of knowledge and information. The overwhelming desire to exploit catalysis toward commercial ends is irresistible. In today's world, one of the requirements of developing a new catalyst is to address the environmental concerns. The well-established heterogeneous catalysts have microporous structures (<25 Å), which find use in many industrial processes. The metal–organic framework (MOF) compounds, being pursued vigorously during the last two decades, have similar microporosity with well-defined pores and channels. The MOFs possess large surface area and assemble to delicate structural and compositional variations either during the preparation or through postsynthetic modifications (PSMs). The MOFs, in fact, offer excellent scope as simple Lewis acidic, Brønsted acidic, Lewis basic, and more importantly bifunctional (acidic as well as basic) agents for carrying out catalysis. The many advances that happened over the years in biology helped in the design of many good biocatalysts. The tools and techniques (advanced preparative approaches coupled with computational insights), on the other hand, have helped in generating interesting and good inorganic catalysts. In this review, the recent advances in bifunctional catalysis employing MOFs are presented. In doing so, we have concentrated on the developments that happened during the past decade or so.

**KEYWORDS:** Metal–organic frameworks, Lewis acid catalysis, Lewis basic catalysis, Bifunctional catalysis, Multifunctional catalysis, Tandem reactions, Deacetalization–Knoevenagel condensation reactions, CO<sub>2</sub> fixation reactions, Nanoparticle supported MOFs



## 1. INTRODUCTION

Catalysis has been so widely woven into the fabric of life that the practice and pursuit of the subject transcends across different disciplines of science and engineering. The canvas of catalysis has been large and continuously growing over the years. It may be noted that there has been considerable success in discovering newer catalysts compared to obtaining greater insights over the known ones.<sup>1–3</sup>

For carrying out efficient catalysis and understanding the catalytic process, two different strategies exist toward the design of solid catalysts. In one approach, the individual steps for the overall reaction are considered and optimized, and the second approach focuses on the location of the active site within the structure. For one of the goals of preparing new compounds that could be potential catalysts, one needs to look for maximum surface area, precise catalytic reaction centers, and good activity, selectivity, and durability. The desiderata of designing a new catalyst need to encompass the following: (i) to be able to operate under mild conditions that are environmentally benign; (ii) reasonable freedom from restrictions imposed by diffusional considerations of molecules (reactants and products); (iii) possession of well-defined and specially separated reaction centers; and (iv) the scope to probe the mechanistic understanding of the catalytic action.

In the area of catalysis, the idea that the catalyst possesses bifunctional or multifunctional character is a desired property. There have been studies toward the multifunctional behavior of catalysts, especially those involving zeolites and mesoporous compounds.<sup>4</sup> It is becoming clear that in seeking to create compounds with good surface areas and catalytic activity one needs to have solids that have pore diameters in the microporous region (~20 Å).

Aluminosilicate zeolites have been the backbone of the study of catalysts and the science of catalysis over many decades. These compounds possess porosity in the microporous range of 4–20 Å. The discovery of metal–organic frameworks (MOFs) in the late 90s and its subsequent developments appear have caught the imagination of the catalyst community.<sup>5–10</sup> The attractive features of many MOF compounds toward catalysis are as follows: (i) they permit free flow of reactants and products through the channels

**Received:** July 18, 2023  
**Revised:** October 18, 2023  
**Accepted:** October 19, 2023  
**Published:** November 11, 2023

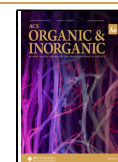


Table 1. MOFs with Different Lewis Acidic Functionalities and Their Utilities toward Catalysis<sup>a</sup>

Sr. No.	MOF Compound	Lewis acidic metal site	Labile solvent	Catalytic reaction	Ref
1	Zr <sub>6</sub> -fBDC and Zr <sub>6</sub> -fBPDC	Zr <sup>4+</sup>	H <sub>2</sub> O	Arene C–H Iodination	258
2	Zr <sub>6</sub> OTf-BTB	Zr <sup>4+</sup>	-	Povarov Reactions	259
3	[Zn <sub>2</sub> (TBIB) <sub>2</sub> (HTCPB) <sub>2</sub> ] <sub>2</sub> ·9DMF·19H <sub>2</sub> O	Zn <sup>2+</sup>	-	Cycloaddition of CO <sub>2</sub> Friedländer Reaction	260
4	MOF-525, PCN-222 and PCN-224	Zr <sup>2+</sup> , Mn <sup>2+</sup> , Zn <sup>2+</sup>	-	Cycloaddition of CO <sub>2</sub>	261
5	M-NU-1008	M = Zr <sup>4+</sup> , Hf, Th, Ce <sup>3+</sup>	H <sub>2</sub> O	Cycloaddition of CO <sub>2</sub>	262
6	ZIF-8	Zn <sup>2+</sup>	-	Epoxide Hydroxylation	263
7	Tb(BTC)(H <sub>2</sub> O) <sub>3</sub> (DMF) <sub>1,1</sub>	Tb <sup>3+</sup>	H <sub>2</sub> O, DMF	Synthesis of β-Aminoalcohols	264
8	Er(BTC)(H <sub>2</sub> O)·(DMF) <sub>1,1</sub>	Er <sup>3+</sup>	H <sub>2</sub> O, DMF	Hantzsch Coupling and Tetrahydro-4H-Chromene Synthesis	265
9	[Ba <sub>2</sub> (BDPO)(H <sub>2</sub> O)]·DMA	Ba <sup>2+</sup>	H <sub>2</sub> O	Cycloaddition of CO <sub>2</sub>	266
10	NH <sub>2</sub> -MIL-101/PAN	Cr <sup>3+</sup>	-	Friedel–Crafts Acylation of Anisole Esterification reaction	267
11	Cu(II)-MOF	Cu <sup>2+</sup>	H <sub>2</sub> O	Cycloaddition of CO <sub>2</sub>	268
12	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (OAc) <sub>2,4</sub> [M(P <sup>N</sup> N <sup>N</sup> P)X] <sub>2,4</sub> [M = Pd, Pt]	Zr <sup>4+</sup> , Pd(I), Pt(I)	-	Hydroamination of <i>o</i> -Alkynyl Aniline	269
13	[Zn <sub>2</sub> (iso) <sub>2</sub> (bpy) <sub>2</sub> ]	Zn <sup>2+</sup>	DMF	Cycloaddition of CO <sub>2</sub>	270
14	[Zn(BPBA)Cl]·5H <sub>2</sub> O	Zn <sup>2+</sup>	H <sub>2</sub> O	Cyclization of <i>ortho</i> -Substituted Diaminonaphthalene to Naphthimidazole	58
15	Ce-doping MIL-88A(Fe)	Ce <sup>3+</sup> , Fe <sup>3+</sup>	-	Catalytic Ozonation	271
16	Pd(II)/UIO-66 (Zr), Pd(II)/MIL-101 (Cr) and Pd(II)/MOF-5 (Zn)	Pd <sup>2+</sup> , Cr <sup>3+</sup> , Zn <sup>2+</sup>	H <sub>2</sub> O	CO Esterification to Dimethyl Carbonate	272
17	UiO-66	Zr <sup>4+</sup>	H <sub>2</sub> O	Aldose Sugars to Polyhydroxyalkyl and C-Glycosyl Furans	273
18	[Cd <sub>3</sub> (BDC) <sub>3</sub> (OPP)(DMF) <sub>2</sub> ] <sub>2</sub> ·2DMA	Cd <sup>2+</sup>	DMF	Hantzsch Reaction	274
19	Cu-BTC(MOF-199)	Cu <sup>2+</sup>	-	Aerobic Oxidative Synthesis of Imines	275
20	MIL-101(Fe,Sc)	Fe <sup>3+</sup> , Sc <sup>3+</sup>	-	Glucose to 5-Hydroxymethyl Furfural	276
21	Al-ITQ-Br, Al-ITQ-NO <sub>2</sub> , L-MOF-EB L-MOF-AB	Fe <sup>3+</sup> , Al <sup>3+</sup>	-	Oxidation of Thiophenol to Diphenyldisulfide	277
22	[Eu(tctb)(H <sub>2</sub> O)]	Eu <sup>3+</sup>	H <sub>2</sub> O	Diamines to Benzimidazoles	278
23	[M <sub>6</sub> (TATAB) <sub>4</sub> (DABCO) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sub>2</sub> ·12DMF·9H <sub>2</sub> O	M = Co <sup>2+</sup> , Ni <sup>2+</sup>	H <sub>2</sub> O	Chemical Fixation of CO <sub>2</sub>	279
24	MixUMCM-1-NH <sub>2</sub>	Zn <sup>2+</sup>	-	Aldol–Tishchenko Reaction	280
25	[In <sub>3</sub> (NIPH) <sub>3</sub> (HNIPH)(OH) <sub>2</sub> ] <sub>2</sub> ·4H <sub>2</sub> O	In <sup>3+</sup>	-H <sub>2</sub> O	Multicomponent Strecker Reactions	281
26	[Mn <sub>2</sub> (TDP)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> ·3H <sub>2</sub> O·3DMF	Mn <sup>2+</sup>	-H <sub>2</sub> O	Chemical Fixation of CO <sub>2</sub>	282
27	[Cu <sub>6</sub> (TADIPA) <sub>3</sub> (DABCO)(H <sub>2</sub> O) <sub>2</sub> (DMF) <sub>2</sub> ] <sub>2</sub> ·13H <sub>2</sub> O [Cu <sub>6</sub> (TADIPA) <sub>3</sub> (H <sub>2</sub> O) <sub>6</sub> ] <sub>2</sub> ·16H <sub>2</sub> O·8DMF [H <sub>3</sub> O][Cu <sub>6</sub> (TPTA) <sub>3</sub> (DMA) <sub>4</sub> (COO)] <sub>2</sub> ·12H <sub>2</sub> O·7DMA [Cu <sub>6</sub> (C <sub>17</sub> O <sub>9</sub> N <sub>2</sub> H <sub>8</sub> ) <sub>3</sub> (C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> )(H <sub>2</sub> O) <sub>2</sub> (DMF) <sub>2</sub> ] <sub>2</sub> ·3DMF·8H <sub>2</sub> O	Cu <sup>2+</sup>	-H <sub>2</sub> O, DMF, DMA	Chemical Fixation of CO <sub>2</sub>	283
28	UiO-66-TA	Zr <sup>4+</sup>	-H <sub>2</sub> O	Hydrogenation of Cinnamaldehyde	284
29	MIL-101(Cr)-LP	Cr <sup>3+</sup>	-	Reduction of Imine	285
30	MIL-101(Cr) MOF	Cr <sup>3+</sup>	-	glucose to fructose	286
31	[Zn <sub>3</sub> (Hbtc) <sub>2</sub> (atz) <sub>2</sub> ] <sub>2</sub> ·CH <sub>3</sub> CN·2CH <sub>3</sub> OH [Co <sub>3</sub> (Hbtc) <sub>2</sub> (atz) <sub>2</sub> ] <sub>2</sub> ·H <sub>2</sub> O·2DMF	Zn <sup>2+</sup> Co <sup>2+</sup>	-	Coupling of CO <sub>2</sub> and Epoxides	287
32	[Zn(bix)] <sub>2</sub> [V <sub>2</sub> O <sub>6</sub> ](V-Zn-MOF)	Zn <sup>2+</sup>	-	Cyanosilylation Reaction of Aldehydes	288
33	[Dy <sub>3</sub> (data) <sub>3</sub> ·2DMF]·DMF	Dy <sup>3+</sup>	DMF	Chemical Fixation of CO <sub>2</sub>	155
34	Cu-MOF	Cu <sup>2+</sup>	-	Catalytic CO <sub>2</sub> Fixation	289
35	[Cd(bpp)(L)(H <sub>2</sub> O)]·DMF	Cd <sup>2+</sup>	-H <sub>2</sub> O	Strecker Reaction	290
36	Cr-UiO-66-CAT	Zr <sup>4+</sup>	-	Oxidation of Alcohols to Ketones	85

<sup>a</sup>H<sub>2</sub>fBDC = 2,3,5,6-tetrafluoro-1,4-benzenedicarboxylic acid; H<sub>2</sub>fBPDC = 2,2',3,3',5,5',6,6'-octafluoro-4,4'-biphenyldicarboxylic acid; TBIB = 1,3,5-tri(1*H*-benzo[*d*]imidazol-1-yl)benzene); H<sub>3</sub>TCBPB = 1,3,5-tris(4'-carboxyphenyl)benzene; BTC = 1,3,5-benzenetricarboxylate; DMF = *N,N*-dimethylformamide; PAN = polyacrylonitrile; P<sup>N</sup>N<sup>N</sup>P = 2,6-(HNPAr<sub>2</sub>)<sub>2</sub>C<sub>3</sub>H<sub>3</sub>N; Ar = *p*-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub><sup>-</sup>; X = Cl<sup>-</sup>, I<sup>-</sup>; iso = isophthalic acid; bpy = 4,4'-dipyridyl; BPBA = 3,5-bis(4-oxo-4*H*-pyridin-1-yl)-benzoate; OPP = *N,N'*-(oxybis(4,1-phenylene))bis(1-(pyridin-4-yl)methanimine); H<sub>2</sub>BDC = terephthalic acid; H<sub>3</sub>tctb = tris(*p*-carboxylic acid)tridurylborane; H<sub>3</sub>TATAB = 4,4',4''-s-triazine-1,3,5-triyl-tri-*p*-aminobenzoic acid; DABCO = 1,4-diazabicyclo[2.2.2]octane; BDC = 1,4-benzenedicarboxylate; ABDC = 2-amino-1,4-benzenedicarboxylate, btb = 4,4',4''-benzene-1,3,5-triyl-trisbenzoic acid; H<sub>2</sub>NIPH = 5-nitroisophthalic acid; H<sub>4</sub>TPTA = 1,1',3',1''-terphenyl-3,3'',5,5'-tetracarboxylic acid; H<sub>4</sub>CBDA = 5,5'-(carbonylbis(azanediyl)) diisophthalic acid; TA = terephthalic acid; LP = Lewis pair; bix = 1,4-bis(imidazole-1-ylmethyl)benzene; 2,5-data = 2,5-diamino-terephthalate; H<sub>2</sub>L = 5-(1-oxo-2,3-dihydro-1*H*-inden-2-yl)isophthalic acid; H<sub>2</sub>L = 4,4'-(dimethylsilanediyl)bis-benzoic acid; bpp = 1,3-bis(4-pyridyl)propane.

(pores) and cages; (ii) they have spatially distributed distinct catalytic sites; and (iii) they create the possibility for performing shape-selective, enantioselective, and regioselective

reactions. The MOFs offer ease of synthesis coupled with a diverse range of compositional variations, which would be desirable toward heterogeneous catalysis. The MOFs offer the

following advantages: (i) The MOF structures are flexible (breathable) and expand and contract by external stimuli;<sup>11–14</sup> (ii) the metal as well as the ligand that forms the structures can be replaced by postsynthetic modifications to render them attractive toward many physical and chemical properties;<sup>15–21</sup> (iii) the organic ligands are amenable for manipulations to create specific functionality in the compounds, which would be desirable toward organocatalysis;<sup>22–30</sup> and (iv) MOFs can provide hydrophilic and hydrophobic environments which can be exploited toward specific catalysis.<sup>31–35</sup>

There have been many catalytic studies that were carried out employing MOFs. In most of the studies, the metal sites were always exploited for their Lewis-acidic behavior.<sup>24,36–38</sup> Most of the earlier attempts toward catalysis employing MOFs were predominantly Lewis acid catalysis only.<sup>39–42</sup> Brønsted acid catalysis was also attempted employing MOFs.<sup>43,44</sup> Over the years it has been shown that the organic ligands in MOFs also catalyze many reactions, especially acting as a Lewis base.<sup>45–48</sup> As the MOFs possess both the Lewis acidic as well as basic centers, bifunctional catalysis was attempted.<sup>49–52</sup>

The bifunctional MOFs offer advantages toward studying the cascade reactions. The cascade/domino/tandem reactions<sup>53,54</sup> utilize at least two consecutive reactions and involve different chemical functionality available within the compound. The cascade process involves a set of reactions where the product(s) of the reaction(s) is consumed in a subsequent reaction. In these reactions, the isolation of intermediates is not required and the reaction(s) proceeds in a stepwise manner. The cascade reaction requires different catalytically active sites distributed over a large surface area and in a periodic manner. The MOFs with their large surface area with good pore size distribution and availability of functional groups would be ideally suited for such reactions.<sup>55–57</sup>

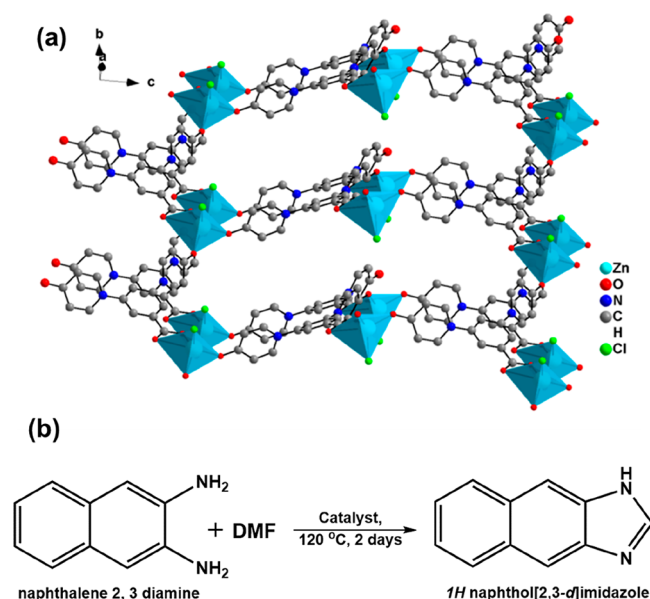
In this review, we focus on the recent developments on MOFs that offer multifunctionality toward heterogeneous catalysis. We have specifically given closer attention to the developments toward catalytic reactions that have been performed employing MOFs during the past decade or so. In this task, there may be a few oversights, which are not intentional.

## 2. GENERATION OF FUNCTIONALITY IN MOFS

Most of the MOF compounds possess Lewis acidity due to the metal centers—the strength of the acidity depends on the size of the metal ions, the oxidation state, and its coordination preferences. In addition to this, it may be possible to create acidity in MOFs by suitable postsynthetic modifications. Here, we outline a few such scenarios:

### 2.1. Lewis Acid Functionality

The acidity can be classified as Brønsted acid or Lewis acid—the former is the stronger acid compared to the latter. The MOFs that were explored toward acid catalysis are tabulated in Table 1. Lewis acidity in MOFs generally refers to an accessible metal site, with a low coordination number, which is also known as a coordinatively unsaturated metal site (CU). The coordinatively unsaturated metal sites can be achieved *in situ* by the removal of labile ligands bonded to the metal, which usually are the solvent molecules. A Zn MOF, {[Zn(BPBN)-Cl]·SH<sub>2</sub>O}<sub>n</sub> (BPBN = 3,5-bis(4-oxo-4H-pyridin-1-yl)-benzotrinitrile) (Figure 1a) has been synthesized and has been utilized for the synthesis of naphthimidazole from 2,3-diaminonaphthalene and DMF at 120 °C with good yield (Figure 1b). The



**Figure 1.** (a) 3D structure of the [Zn(BPBN)Cl]·SH<sub>2</sub>O MOF. (b) Synthesis of naphthimidazole in the presence of heterogeneous catalyst. Reproduced with permission from ref 58. Copyright 2020 Elsevier.

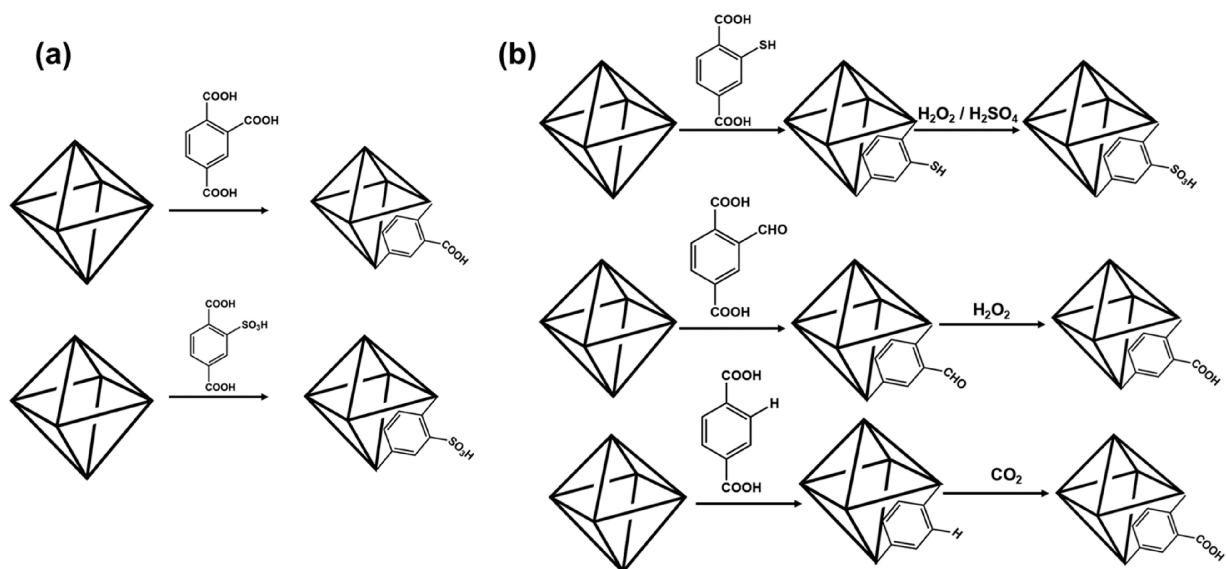
tetrahedrally coordinated Zn center acts as Lewis acid site and facilitates this reaction.<sup>58</sup> UiO-66 (UiO = University of Oslo) is one of the MOFs which was studied toward the Lewis acid catalytic reaction. Zr-MOFs provide unsaturated metal sites, which could be exploited as Lewis acid centers in catalytic reactions. The open metal sites generally act as electron pair acceptors and accelerate the reaction process.<sup>59</sup> Most of the earlier studies exploiting the Lewis acid functionality concentrated on cyanosilylation of imines.<sup>60</sup> These are typically low temperature reactions, and in most cases the yield is >95%. Recently, lanthanide centers were explored as possible Lewis acid catalytic centers in the compound, [La<sub>2/3</sub>(qptca)<sub>1/2</sub>] (qptca = 1,1':4',1'':4'',1''':4'''-quinquephenyl)-2,2'',2''',5''-tetracarboxylic acid), toward the Friedel–Crafts reaction. The alkylation of indole and pyrrole with  $\beta$ -nitrostyrene with a wide substrate scope gave the desired product with high yield and recyclability.<sup>61</sup>

As an example of unusual Lewis acidity in MOFs, the example of easily modifiable nature of the ligand was exploited in preparing Pd-mono(thiocatecholato) units inside the MOF UiO-66.<sup>85</sup> This modified MOF exhibited excellent regioselectivity toward the sp<sup>2</sup> carbon, oxidation of alcohols to ketones, etc.<sup>85,86</sup> A more interesting approach is to replace the ligand, which expands the MOF, allowing for enhanced catalytic activity.<sup>83</sup> In this work, C<sub>2</sub> symmetry ligands were exchanged for C<sub>3</sub> symmetric, which causes defects in the overall structure, paving the way for better Lewis acid activity.<sup>87</sup>

### 2.2. Brønsted Acid Functionality

In the traditional framework compounds of aluminosilicate zeolites, metal phosphates, etc. Brønsted acidity was generated by manipulating the structure by having elements of different valencies.<sup>88–90</sup> The charge compensating protons have been found to have strong Brønsted acid character. In MOFs, such a possibility is difficult to achieve, as the framework contains metal centers with fixed valences and organic ligands. There are examples of MOF compounds where elements of mixed

Scheme 1. Schematic Showing How the Additional Functionality Is Used in Generating Brønsted Acidity in MOFs: (a) Direct Synthesis; (b) via Postsynthetic Modification

Table 2. MOFs with Brønsted Acidity and the Associated Catalysis<sup>a</sup>

Sr. No.	MOF	Brønsted acidic site	Catalytic reaction	Ref
1	PTACMIL-101(Al)-NH <sub>2</sub>	H <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ] <sub>n</sub> H <sub>2</sub> O	Glucose Dehydration to 5-Hydroxymethylfurfural	62
2	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> @Zr-MOF	-SO <sub>3</sub> H	Levulinic Acid to $\gamma$ -Valerolactone	63
3	[(CH <sub>2</sub> COOH) <sub>2</sub> IM]HSO <sub>4</sub> @H-UiO-66	[(CH <sub>2</sub> COOH) <sub>2</sub> IM]HSO <sub>4</sub>	Biodiesel Synthesis	64
4	PO <sub>4</sub> /NU(eq) and PO <sub>4</sub> /NU(half)	-PO <sub>4</sub>	Glucose to 5-Hydroxymethylfurfural	65
5	MIL-101(Cr)-SO <sub>3</sub> H	-SO <sub>3</sub> H	Cross-Dehydrogenative Coupling of C–H Bonds	66
6	CoFe <sub>2</sub> O <sub>4</sub> /MIL-88B(Fe)-NH <sub>2</sub> /(Py-Ps)PMo	-SO <sub>3</sub> H	Transesterification	67
7	MIL-101(Cr)-NH-CO-Pr-COOH	-COOH	Synthesis of Quinazolin-(4H)-1-one	68
8	MOF-808-SO <sub>4</sub>	-SO <sub>4</sub>	Dimerization of Isobutene (2-Methyl-1-propene)	69
9	[Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>5,6</sub> (C <sub>9</sub> H <sub>3</sub> O <sub>6</sub> ) <sub>2</sub> (HCOO) <sub>0.18</sub> (SO <sub>4</sub> ) <sub>2.1</sub> ](H <sub>2</sub> O) <sub>2</sub>	-OH	Isobutene Dimerization	70
10	Hf-MOF-808	$\mu^3$ -OH	Meerwein–Ponndorf–Verley Reduction Styrene Oxide Ring-Opening $\alpha$ -Pinene Oxide Isomerization	71
11	MIL-100(Cr) and MIL-100(Fe)	-H <sub>2</sub> O-CO	Acetalization of Benzaldehyde with Methanol	72
12	PCN-222(Ni)-SO <sub>4</sub>	SO <sub>4</sub> <sup>2-</sup>	Tandem Semisynthesis of Artemisinin	73
13	Zr-MOF-808-S	OH <sup>-</sup> /H <sub>2</sub> O	Glycerol Dehydration	74
14	Al-MIL-53-RSO <sub>3</sub> HAL-MIL-53-ArSO <sub>3</sub> H	-SO <sub>3</sub> H	[4 + 2] Cycloaddition Reaction	75
15	UiO-66 (Zr, Hf), Zr-BTC	$\mu_3$ -OH	Cycloaddition Reaction	76
16	MIL-100(Fe) (Lys-PM <sub>2</sub> )	Lys-PM <sub>2</sub>	Conversion of Glucose to Levulinic Acid	77
17	[BSO <sub>3</sub> HMIIm][HSO <sub>4</sub> ](IRMOF-3)	[BSO <sub>3</sub> HMIIm][HSO <sub>4</sub> ]	Bligh–Dyer Method for Biodiesel Production	78
18	MIL-101(Cr)-SO <sub>3</sub> H	-SO <sub>3</sub> H	Methanolysis of Styrene Oxide	79
19	Cr <sub>3</sub> ( $\mu_3$ -O)(H <sub>2</sub> O) <sub>3</sub> (NDC(SO <sub>3</sub> H <sub>5/6</sub> ) <sub>2</sub> ) <sub>3</sub> (BUT-8(Cr)-SO <sub>3</sub> H)	-SO <sub>3</sub> H	Esterification Reaction	80
20	MIL-IMAc-Br <sup>-</sup>	Br <sup>-</sup>	Cycloaddition of CO <sub>2</sub>	81
21	(H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub> ) (POM@MOF)	H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	Glucose into 5-Hydroxymethylfurfural	82
22	MIL-(Cr)-101-SO <sub>3</sub> H	SO <sub>3</sub> H	Catalytic Conversion of Glucose	83
23	UiO-66(SO <sub>3</sub> H) <sub>2</sub>	SO <sub>3</sub> H	Synthesis of Dihydro-2-oxypyrrrole Derivatives	84

<sup>a</sup>PTA = phosphotungstic acid; Py-Ps = pyridine with 1,3-propanesultone; H<sub>4</sub>TADIPA = 5-5'-(1H-1,2,4-triazole-3,5-diyl) diisophthalic acid; Lys = lysine functionalized phosphotungstic acid; [BSO<sub>3</sub>HMIIm][HSO<sub>4</sub>] = 1-butylsulfonate-3-methylimidazolium bisulfate; NDC(SO<sub>3</sub>H)<sub>2</sub><sup>2-</sup> = 4,8-disulfonaphthalene-2,6-dicarboxylate; IMAc = 1H-imidazole-1-acetic acid.

valency exist as part of the structure.<sup>91,92</sup> The Brønsted acidity in many MOFs, however, appears to arise out of the nonbonded acidic groups of the ligands (Scheme 1).<sup>43,72</sup> The MOFs, thus, provide the versatility of having both the Lewis acidic as well as Brønsted acidic functionality within the same MOF.<sup>68,93–95</sup> The many catalytic reactions that have been carried out employing Brønsted acid functionality in MOFs are listed in Table 2. In MIL-(Cr)-101-SO<sub>3</sub>H, the Cr<sup>3+</sup>

ions act as a Lewis acidic and the -SO<sub>3</sub>H groups act as the Brønsted acidic centers for the catalytic conversion of glucose.<sup>83</sup>

The acidic stability of the MOFs was exploited in generating new Brønsted acidity through postsynthetic modifications in UiO-66(SH)<sub>2</sub>.<sup>96</sup> In this study, UiO-66(SH)<sub>2</sub> was modified by treatment with H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> to form UiO-66(SO<sub>3</sub>H)<sub>2</sub>,

Table 3. MOFs with Different Basic Functionalities and Their Utility toward Catalysis<sup>a</sup>

Sr. No.	MOF Compound	Ligand responsible for basicity	Catalytic reaction	Ref
1	[Cd(C <sub>16</sub> H <sub>10</sub> N <sub>2</sub> O <sub>8</sub> S)(H <sub>2</sub> O)]	-NH	Knoevenagel Condensation	110
2	[(Nd <sub>2</sub> (TATMA) <sub>2</sub> ·4DMF·4H <sub>2</sub> O)] <sub>n</sub>	-N	Knoevenagel Condensation	111
3	[H <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> [Zn <sub>4</sub> (L) <sub>1,5</sub> (ad) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> ·4DMF	-NH <sub>2</sub>	Knoevenagel Condensation	112
4	{[Zn <sub>2</sub> (D-CAM) <sub>2</sub> (L)]·MeOH·2H <sub>2</sub> O} <sub>n</sub>	-NH	Ring-Opening of Spiro-Epoxyoxindoles	113
5	Co <sub>2</sub> (bdda) <sub>1,5</sub> (OAc) <sub>1</sub> ·5H <sub>2</sub> O	-NH	Henry Reactions	114
6	[Zn(OBA)(BPDB) <sub>0,5</sub> ] <sub>n</sub> ·2DMF	-N	Knoevenagel Condensation	115
7	[Y <sub>3</sub> (μ <sub>3</sub> -O) <sub>2</sub> (μ <sub>3</sub> -OH)(H <sub>2</sub> O) <sub>2</sub> (BTCTBA) <sub>2</sub> ] <sub>2</sub> ·2[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ] <sub>2</sub> ·5DMF·C <sub>6</sub> H <sub>5</sub> Cl·4H <sub>2</sub> O	C=O–N–H	Knoevenagel Condensation	116
8	[Zn <sub>2</sub> (hfpbb) <sub>2</sub> (4-bpdh)]·0.5DMF and [Zn <sub>2</sub> (hfpbb) <sub>2</sub> (4-bpdb)]·2DMF	-N=N-	Knoevenagel Condensation	117
9	UiO-67-BPY@UiO-66	-N <sub>bpy</sub>	Knoevenagel Condensation	118
10	[Zn <sub>2</sub> (3-tpom)(L) <sub>2</sub> ] <sub>2</sub> ·2H <sub>2</sub> O	-O	Strecker Reaction	119
11	[Cu <sub>2</sub> (L)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> ·(3DMF)(4H <sub>2</sub> O)	-N	Henry Reactions	120
12	[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup> ] <sub>2</sub> [Zn <sub>3</sub> ((μ <sub>3</sub> -O))(L) <sub>2</sub> (H <sub>2</sub> O)]·4DMF·2H <sub>2</sub> O	-NH <sub>2</sub>	Chemical Fixation of CO <sub>2</sub>	121
13	[Cu <sub>2</sub> (L)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> ·(5DMF)(4H <sub>2</sub> O)	-NH <sub>2</sub>	Biginelli Reactions	122
14	[CoL(H <sub>2</sub> O) <sub>3</sub> ] <sub>2</sub> ·2NO <sub>3</sub>	-N	Knoevenagel Condensation	123
15	UiO-67@Fe	-N <sub>bpy</sub>	Morita–Baylis–Hillman Reaction	124
16	ZIF-8, ZIF-67	-N <sub>im</sub>	Knoevenagel Condensation	125
17	MIL-125-NH <sub>2</sub>	-NH <sub>2</sub>	Plasticizers Syntheses	126
18	SB-Cu1	-N	N-Arylation	127
19	NH <sub>2</sub> cCo-PYI1 and NH <sub>2</sub> cCo-PYI2	-NH <sub>2</sub>	Aldol and Knoevenagel Condensations	128

<sup>a</sup>Nic = nicotinamide; pic = picrate; H<sub>3</sub>dcp = 3,5-pyrazoledicarboxylic acid; DMA = *N,N*-dimethylacetamide; ad = adenine; H<sub>4</sub>L = 5,5'-(1,3,6,8-tetraoxobenzo phenanthroline-2,7-diy)bis-1,3-benzenedicarboxylic acid; H<sub>3</sub>TATMA = 4,4,4'-s-triazine-1,3,5-triyltri-*m*-aminobenzoate; L = *N'*-(pyridin-4-ylmethylene)isonicotinohydrazide; bdda: 4,4'-[benzene-1,4-diy]bis(methylidenenitrilo) dibenzoic acid; H<sub>3</sub>BTCTBA = 4,4',4'-[1,3,5-benzenetriyltris(carbonylimino)]trisbenzoic acid; 4-bpdb = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene; 4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene; H<sub>2</sub>L = dicarboxylic acid 4,4'-(dimethylsilanediy)bis-benzoic acid; 3-tpom = tetrakis(3-pyridyloxymethylene)methane; H<sub>4</sub>L = 5,5'-(piperazine-1,4-diy)diisophthalic acid; L = 4-(trifluoromethyl)aniline, 1-bromo-3,5-dimethylbenzene; L = tris(4-(4*H*-1,2,4-triazol-4-yl)phenyl)amine; PYI = pyrrolidine-2-yl-imidazole.

which was later found to be a good catalyst for synthesis of dihydro-2-oxypyrrole derivatives.<sup>84</sup>

### 2.3. Basic Functionalities in MOFs

It has been well established that Lewis acidities are much easier to generate in MOFs. In many of the traditional framework compounds, the basic functionality is generated when the extra-framework protons are the Brønsted acid sites and the framework oxygens and their conjugate form the basic sites.<sup>97,98</sup> In addition, alkali and alkaline earth exchanged zeolites are also designated as basic.

An easier approach toward the generation of Lewis basicity is feasible in MOFs compared to the traditional framework of zeolites and aluminophosphates. In this approach, the functionality of organic ligands plays an important role in creating the basicity to the structure. More importantly the Lewis basic sites are spatially separated and, in a sense, can be considered as a single basic site, similar to the acid site, which many researchers have exploited.<sup>99,100</sup>

Thus, in MOFs the -NH<sub>2</sub> group plays a crucial role as the Lewis basic site. In addition, researchers have also used nonbonded carboxyl (-COO<sup>-</sup>) and similar units as Lewis bases.<sup>101</sup> The Lewis basic sites in MOFs and their utility toward catalysis are listed in Table 3. For example, IRMOF-1 (commonly known as MOF-5) is constructed from the Zn<sup>2+</sup> ions and ligand BDC, while replacement of BDC with NH<sub>2</sub>-BDC yields IRMOF-3, which exhibits Lewis basic behavior toward the Knoevenagel condensation reaction.<sup>102,103</sup> A range of metals viz., Zn,<sup>47</sup> Zr,<sup>104</sup> Al,<sup>105</sup> Ti,<sup>106</sup> and Cu<sup>107</sup> were employed for the preparation of MOFs with NH<sub>2</sub>-BDC, which were found to be useful in base catalyzed Knoevenagel

condensation reactions. ZIFs (zeolite imidazolate frameworks), which were formed by assembling Zn metal and imidazole linker, provide high stability, high surface area as well as sufficient basicity, arising out of the N atoms of the imidazole have been exploited toward base catalysis.<sup>108</sup> Such ZIF compounds were also found to be good catalysts toward Knoevenagel condensation reaction at room temperature with ~99% yield.<sup>109</sup>

### 3. MULTIFUNCTIONAL CATALYTIC CENTERS IN MOFS

From the above descriptions, it is clear that forming bifunctional catalytic sites in MOFs is facile. The metal sites can provide the Lewis acidity, and the Lewis basic sites can be generated from the carboxylate units, specific functional groups in the ligand. The acid–base pair can be spatially well separated and in the precise location to facilitate bifunctional catalysis.<sup>45,129–131</sup> The bifunctionality available in MOFs can be utilized in multiple ways: (i) in organic reactions involving multiple steps without separation and purification of the intermediates in each step;<sup>132</sup> (ii) in catalyzing multiple reactions simultaneously involving more than one reaction pathway; (iii) in promoting tandem catalysis involving reactions that proceed sequentially; and (iv) in catalyzing acid–base reactions. The bifunctionality in MOFs toward catalysis can be achieved by the following: (i) coordinatively unsaturated metal sites for Lewis acid functionality along with a suitable ligand that offers Lewis basic functionality; (ii) use of multifunctional ligands either during the formation of the MOFs or through postsynthetic modifications; and (iii)

Table 4. MOFs with Bi-/Multifunctionality and Their Use in Catalysis<sup>a</sup>

Sr. No.	MOF Compound	Reactive site	Catalytic reaction	Ref
1	MIL-101(Cr)-N(CH <sub>2</sub> PO <sub>3</sub> H <sub>2</sub> ) <sub>2</sub>	Cr(III) Phosphonates, -NH <sub>2</sub>	Synthesis of N-Amino-2-Pyridone and Pyrano [2,3-c] Pyrazole Derivatives	139
2	[Zn <sub>2</sub> (TCA)(BIB) <sub>2.5</sub> ](NO <sub>3</sub> )	Zn (II), N <sub>TCA</sub>	Cycloaddition of CO <sub>2</sub>	140
3	[Mn <sub>2</sub> (DPP)(H <sub>2</sub> O) <sub>3</sub> ].6H <sub>2</sub> O	Mn (II), -N <sub>pyridine</sub>	Cycloaddition of CO <sub>2</sub>	141
4	[Zn(1,4-NDCA)(3-BPDB) <sub>0.5</sub> ](DMF)(MeOH) [Cd <sub>4</sub> (1,4-NDCA) <sub>4</sub> (3-BPDB) <sub>4</sub> ].2(DMF)	Zn(II)Cd(II), -N=N-	Friedländer Reaction	142
5	[M <sub>3</sub> (5-CFIA) <sub>2</sub> (8H <sub>2</sub> O)].H <sub>2</sub> O	Cd(II), Mn(II), -NH	Michael Addition Aldol Condensation $\beta$ -Enamination Reactions	143
6	[Zn(HL) <sub>2</sub> ]	Zn (II), -N <sub>triazole</sub>	Knoevenagel Condensation	50
7	[Zn <sub>15</sub> (L-NH <sub>2</sub> ) <sub>6</sub> (HL-NH <sub>2</sub> ) <sub>6</sub> (LNA) <sub>4</sub> (HLNA) <sub>2</sub> ( $\mu_3$ -OH) <sub>2</sub> ]	Zn(II), -NH <sub>2</sub>	Knoevenagel Condensation	144
8	SulP1/SulP2-MOF-808(Hf)	Hf(IV), Phosphonate	Reductive Amination and Hydroaminomthylation Reactions	145
9	ED/MIL-101(Cr)	Cr (III), -NH <sub>2</sub>	Hantzsch Condensation Reaction	146
10	Zn-Bp-BTC MOF	Zn(II), -N <sub>bipyridine</sub>	Knoevenagel Condensation Multicomponent Reaction Benzimidazole Synthesis	147
11	Lysine - (Zr)MOF-808	Zr(IV), -NH <sub>2</sub>	Henry Condensation and Friedel/Crafts Type Alkylation	148
12	C <sub>32</sub> H <sub>40</sub> Fe <sub>2</sub> N <sub>2</sub> S <sub>4</sub> Zn	Zn(II), -NH <sub>2</sub>	One Pot Synthesis of Chromene and Imidazopyrimidine Derivatives	149
13	Co/Ni <sub>2</sub> (BTC)(OH)(4-TPT) <sub>2</sub> (H <sub>2</sub> O).(DMA) <sub>0.5</sub> (H <sub>2</sub> O) <sub>2</sub>	Co(II)Ni(II), N <sub>pyridyl</sub>	Oxidation-Knoevenagel Cascade Reaction	150
14	Cu <sub>3</sub> TATAT	Cu(II), -NH, N	Aerobic Oxidation/Knoevenagel Condensation	151
15	Hf/Zr MOF-808	Hf(IV)Zr(IV) Defective -OH	Tandem N-Alkylation of Amines with Benzyl Alcohol	152
16	PMoV <sub>2</sub> @DETA-MIL-101	Cr(III)PMoV <sub>2</sub> , -NH <sub>2</sub>	Aerobic Oxidation-Knoevenagel One-Pot Reaction	153
17	CuI@UiO-67-IM	CuI	One-Pot Azide-Alkyne Cycloaddition	154
18	[Dy <sub>3</sub> (data) <sub>3</sub> .2DMF].DMF, NH <sub>2</sub> .TMU-73	Dy(III), -NH <sub>2</sub>	Solvent-Free Conversion of CO <sub>2</sub> to Cyclic Carbonates	155
19	Co-NDTz and Co-NDPhTz	Co(II), -N <sub>tetrazole</sub>	Tandem Oxidation and CO <sub>2</sub> Conversion Reactions	156
20	[Cu <sub>2</sub> Br <sub>2</sub> (pypz)] <sub>n</sub> .nH <sub>2</sub> O	Cu(II), Br <sup>-</sup>	Homocoupling of Arylboronic Acids and Epoxidation of Olefins	157
21	[Cd(PBA)(DMF)].DMF	Cd(II), -NH	Cyanosilylation and Hydroboration	158
22	Ni-DDIA	Ni(II)-COOH	Biginelli Reaction	94
23	MIL-101(Cr)-NH-CO-Pr-COOH	Cr(III)-COOH	Synthesis of Quinazolin-(4H)-1-one Derivatives	68
24	MIL-101(Cr)-SO <sub>3</sub> H	Cr(III)-SO <sub>3</sub> H	Hydrogenation of Imines	159
25	Arg <sub>2</sub> PTA/ZIF-8	Zn <sup>2+</sup> , -N <sub>imidazole</sub>	Production of Biodiesel from Insect Lipid	160

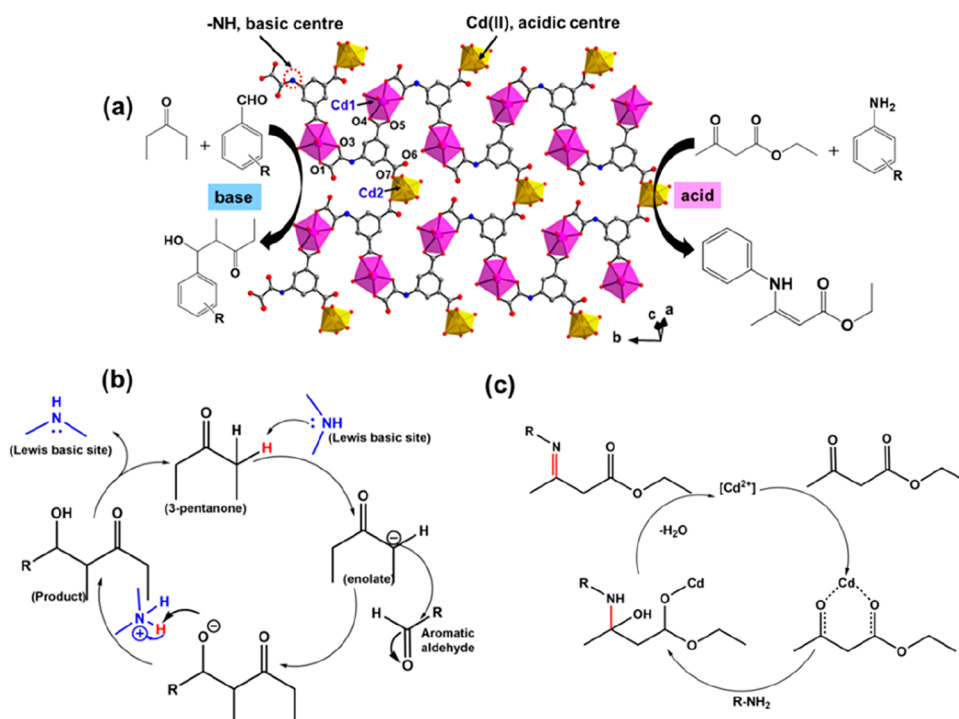
<sup>a</sup>Abbreviations: data = 2,5-data = 2,5-diamino-terephthalate; MA = melamine; ED = ethylene diamine; DPP = 2,6-di(2,4-dicarboxyphenyl)-4-(pyridine-4-yl)pyridine; H<sub>8</sub>L = tetraphenylsilane tetrakis-4-phosphonic acid; H<sub>3</sub>TCA = tricarboxy triphenyl amine; BIB = 1,3-bis(imidazol-1-ylmethyl)benzene; H<sub>4</sub>L = 2,6-di(2,4-dicarboxyphenyl)-4-(pyridine-4-yl)pyridine; Bp = 4,4'-bipyridine; BTC = 1,3,5-benzene tricarboxylate; H<sub>2</sub>L<sub>NA</sub> = 2,6-naphthalenedicarboxylic acid; H<sub>2</sub>L-NH<sub>2</sub> = 2,2'-diamino[1,1'-biphenyl]-4,4'-dicarboxylic acid; CSMCRI-10 = Central Salt & Marine Chemicals Research Institute; BuPh<sub>3</sub>P = (4-bromobutyl)triphenylphosphonium bromide; SIPA = 5-sulfoisophthalic acid; ABPY = 4,4'-azopyridine; 5-CFIA = 5-(carboxyformamido)isophthalic acid; BDC = 1,4-benzenedicarboxylate; A = acid; B = base; (BINDIH<sub>4</sub>) = N,N'-bis(5-isophthalic acid)naphthalenediimide; DATRZ = 3,5-diamino-1,2,4-triazole; pypz = bis[3,5-dimethyl-4-(4'-pyridyl)pyrazol-1-yl] methane; PBA = 5-(4-pyridin-3-yl-benzoylamino)isophthalic acid; H<sub>2</sub>NDTz = 2,6-naphthaleneditetrazole; H<sub>2</sub>NDPhTz = 2,6-bis(4-(1H-tetrazol-5-yl)phenyl)naphthalene; Arg = Arginine.

incorporation of metal nanoparticles within the MOF structure (Scheme S1). These techniques are popular in generating bifunctional MOF compounds, and there are other techniques that may also be utilized to generate bifunctionality in MOFs. The number of MOF compounds with bifunctionality has grown rapidly in recent years. This is not surprising, as the initial efforts during the development of MOFs were toward establishing newer framework compounds and exploring their physical properties.<sup>133–136</sup> The emphasis on the utility of MOFs toward catalysis involving both the acidic as well as basic functionalities is summarized in Table 4. In addition to preparing MOFs with bifunctionality by careful choice of the ligands, it is also possible to generate bifunctionality by carrying out postsynthetic modifications. Examples of bi- or

multifunctionality through postsynthetic modifications (PSMs) have been known.<sup>137,138</sup> The PSM allows better control on the structure and fine-tuning of the functionality toward a particular catalytic activity.

### 3.1. Examples of Catalysis Involving Acidic and Basic Centers

As listed in Table 4, there have been a number of studies involving bifunctionality in MOFs. In this section, we focus on a few select examples that characterize the bifunctionality in a MOF compound. The examples utilize both the acidic as well as basic functionality toward catalysis, but these reactions are carried out independently and not as tandem catalytic reactions. The tandem catalytic studies are dealt with separately.



**Figure 2.** (a) View of the structure of the MOF  $[Cd_3(C_{10}H_4O_7N_1)_2(8H_2O)] \cdot H_2O$  with Cd centers (Lewis acidic) and an -NH moiety (Lewis basic). (b) Schematic of the possible reaction pathway for the base catalyzed aldol condensation reaction. (c) Schematic of the acid catalyzed enamine formation involving the Cd center. Reproduced with permission from ref 143. Copyright 2023 American Chemical Society.

The MOF  $[M_3(C_{10}H_4O_7N_1)_2(8H_2O)] \cdot H_2O$  ( $M = Cd, Mn$ ), was explored toward the formation of the  $\beta$ -enaminoester (Lewis acid catalyzed), and the -NH moiety present in the ligand was exploited toward the Claisen–Schmidt reactions (Lewis base catalyzed) (Figure 2a).<sup>143</sup> The Claisen–Schmidt reaction is a classic base catalyzed aldol condensation reaction involving an aromatic aldehyde and a ketone forming conjugated  $\beta$ -hydroxy carbonyl compounds. The uncoordinated -NH group acts as the basic center and catalyzes the Claisen–Schmidt reaction (Figure 2b). The formation of  $\beta$ -enaminoesters is acid catalyzed, and the  $Cd^{2+}$  center acts as the Lewis acidic center and catalyzes the reaction between ethyl acetoacetate and aniline (Figure 2c).<sup>143</sup> A two-dimensional (2D) MOF,  $[Cd(PBA)(DMF)] \cdot DMF$  (Cd-PBA), ( $H_2PBA = 5$ -(4-pyridin-3-yl-benzoylamino)-isophthalic acid), was found to be a catalyst for the base catalyzed (the N from the pyridine acts as the base center) Knoevenagel condensation reaction and the Lewis acid catalyzed (Cd centers) cyanosilylation of various aldehydes with trimethylsilyl cyanide.<sup>158</sup>

There are many reports in the literature where only one of the functional groups (usually the Lewis basic functionality) was investigated toward catalytic studies. As mentioned earlier, in all the MOFs, the metal centers always act as Lewis acid centers. In most of the cases, it appears that the reaction of choice for the Lewis base catalyzed reaction is the Knoevenagel condensation (Table 3).

### 3.2. Tandem/Cascade Reaction

The chemical industries, generally, look to eliminate the number of steps in a chemical reaction process. Another impediment in many reactions is the need to isolate intermediates for further processing. Tandem/cascade reactions provide a possible alternative to reduce the need to isolate the intermediates and in that way also reduce the

number of steps.<sup>161,162</sup> To carry out such tandem reactions, it is necessary to have different catalytically active centers, preferably distributed uniformly, across the surface of the compound. It is even more important if the reaction requires both the acidic as well as basic functionalities. There is a need to replace multistep as well as salt forming chemical reactions. The approach that provides some success is the tandem reaction, where multiple reactions are combined in a sequential way to yield a single product. This approach is also known as “one-pot”, “domino”, and cascade reactions.<sup>53</sup> There are many advantages in employing “tandem” reactions: (i) good atom economy; (ii) reduction of the formation of chemical wastes; (iii) reduction in the consumption of energy; (iv) no need to isolate any intermediates; etc. The tandem catalyses are known as concurrent tandem catalysis (CTC)<sup>53,163</sup> and auto tandem catalysis (ATC).<sup>164</sup> One of the important criteria in carrying out the tandem catalytic reactions is the compatibility of the catalyst toward the reactants, intermediates, and solvents. In addition, it is preferable to have the catalytically active centers separated spatially and in a periodic manner. It would be an added advantage if the catalyst can also host both acidic as well as basic catalytic centers. From the arguments as well as the descriptions above, the MOFs have positioned themselves to be an excellent candidate to investigate the multistep tandem/cascade reactions. The many cascade reactions that have been carried out using MOFs are summarized in Table 5. In this section, we provide select examples of such reactions. The reaction that was most studied as tandem reactions in MOFs is the deacetalization (acid catalyzed) followed by Knoevenagel condensation (base catalyzed).

**3.2.1. Deacetalization–Knoevenagel Tandem Reaction.** The functionalization of Cr-MIL-101, with amino and sulfo groups, through postsynthetic modifications, allowed the one-pot deacetalization–Knoevenagel tandem reaction.<sup>165</sup> The

Table 5. Summary of Tandem Deacetalization–Knoevenagel Reaction Employing Bifunctional MOFs<sup>44</sup>

Sr. No.	MOF compound	Reactive site	Reactants	Products	Reaction conditions	Ref
1	Yb-BDC-NH <sub>2</sub> Dy-BDC-NH <sub>2</sub> Sm-BDC-NH <sub>2</sub>	Yb <sup>3+</sup> , Dy <sup>3+</sup> , Sm <sup>3+</sup> , -NH <sub>2</sub>	BDA and MN	2-benzylidenemalononitrile	DMSO-d <sub>6</sub> (2 mL), catalyst (100 mg), 50 °C, 24 h	291
2	3.1% Ru/Uio-66	Ru <sup>2+</sup> , Zn <sup>2+</sup>	BA and MN	2-benzylidenemalononitrile	toluene (1.5 mL), O <sub>2</sub> 1 atm, 100 °C	292
3	HNUST-8	Cu <sup>2+</sup> , acylamide	BDA and MN	2-benzylidenemalononitrile	DMSO, 50 °C, 48 h, 0.5 mol % HNUST-8	293
4	HNUST-6	Cu <sup>2+</sup> , acylamide	BDA and MN	2-benzylidenemalononitrile	0.5 mol % catalyst, DMSO, 50 °C, 48 h	294
5	[Zn <sub>5</sub> (L) <sub>4</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sub>n</sub> ·8n(DMF)·4n(H <sub>2</sub> O)	Zn <sup>2+</sup> , -NH	BDA and MN	2-benzylidenemalononitrile	1 mol % of catalyst 1 or 2, DMF (0.5 mL), 80 °C, 3 h	295
6	Cz-MOF-253-800	Al <sup>3+</sup> , N	BD and MN	2-benzylidenemalononitrile	2 mL of toluene, and 5 mg of Pd/Cz-MOF-253-800, 80 °C, 17 h, 150 psi H <sub>2</sub>	296
7	ZIF-8, UiO-66(Zr)-NH <sub>2</sub> , MIL-101(Cr)-NH <sub>2</sub>	Zn <sup>2+</sup> , O <sup>2-</sup> , N <sup>-</sup> , -OH, -NH <sub>2</sub>	BDA and MN	2-benzylidenemalononitrile	100 °C, 3 h in the Pickering emulsions consisting of water (3 mL)–toluene (2 mL) MOFs (50 mg)	297
8	GSMCRL-15	Cd <sup>2+</sup> , -N=N-NH <sub>2</sub>	BDA and MN	2-benzylidenemalononitrile	2 mol % catalyst, 4 h, 60 °C, solvent free	298
9	H-ZIF-8/Au@mSiO <sub>2</sub>	Au, Zn <sup>2+</sup> , -N-	p-nitro BD and MN	2-(4-nitrobenzylidene) malononitrile	catalyst (30 mg) and 2.0 mL tetrahydrofuran at 30 °C for 0.5 h	299
10	Hf-Uio-66-N <sub>2</sub> H <sub>3</sub>	Hf, N <sub>2</sub> H <sub>3</sub>	BD, MN	2-benzylidenemalononitrile	ethanol (0.3 mL), catalyst (20 mg), RT, 4 h	300
11	NUC-29	Cd <sup>2+</sup> , N <sub>pyridine</sub>	BDA, MN	2-benzylidenemalononitrile	1.0 mol % based on the {Cd} center, DMSO 50 mL, 5 h, 70 °C	301
12	NUC - 53	Zn <sup>2+</sup> , N <sub>pyridine</sub>	BDA, MN	2-benzylidenemalononitrile	0.3 mol %, DMSO 3 mL, 6h, 70 °C	302
13	Uio-67-(NH <sub>2</sub> ) <sub>2</sub>	Zr <sup>4+</sup> , -NH <sub>2</sub>	BDA, MN	2-benzylidenemalononitrile	ethanol (0.3 mL) and catalyst (15 mg) 10 h, 60 °C	303
14	IRA900(αOH)-MIL-101(Al)-NH <sub>2</sub>	Al <sup>3+</sup> , -NH <sub>2</sub>	BDA, MN	2-benzylidenemalononitrile	solvent free, catalyst 0.3 g, 5 h at 110 °C	304
15	Cu(ABDC)(DMF)	Cu <sup>2+</sup> , -NH <sub>2</sub>	BDA, MN	2-benzylidenemalononitrile	d <sub>5</sub> -acetone, 0.1 mol % catalyst, 24 h, 60 °C	305
16	Zr <sub>12</sub> BDC-NH <sub>2</sub>	Zr <sup>4+</sup> , -NH <sub>2</sub>	BDA, MN	2-benzylidenemalononitrile	CDCl <sub>3</sub> (1.5 mL), catalyst, 55 °C, 24 h, 100 mg	306
17	MIL-101(Cr)@PMF	Cr <sup>3+</sup> , -NH-NH <sub>2</sub>	BDA, MN	2-benzylidenemalononitrile	30 mg catalyst, 12 h, 4 mL ethanol, 65 °C	307
18	[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>3</sub> ] <sub>2</sub> [BaZn(TDP)(H <sub>2</sub> O)]·DMF·5H <sub>2</sub> O, (NUC-51)	Zn <sup>2+</sup> , Ba <sup>2+</sup> , -COOH, N <sub>pyridine</sub>	BDA, MN	2-benzylidenemalononitrile	1.0 mol % catalyst, 5 mL (DMSO) 4 h 70 °C	308
19	(Me <sub>2</sub> NH <sub>2</sub> )[InZn(TDP)(OH) <sub>2</sub> ]·4DMF·4H <sub>2</sub> O (NUC-42)	Zn <sup>2+</sup> , In <sup>3+</sup> , -COOH, N <sub>pyridine</sub>	BDA, MN	2-benzylidenemalononitrile	DMSO, 5 mL, 8h, 60 °C, 1 mol % catalyst	309
20	MIL-101(Cr)@MOF-867	Cr <sup>3+</sup> , Zn <sup>2+</sup> , -C≡N	BDA, MN	2-benzylidenemalononitrile	20 mg, 70 °C, 12 h, DMSO (4 mL)	310

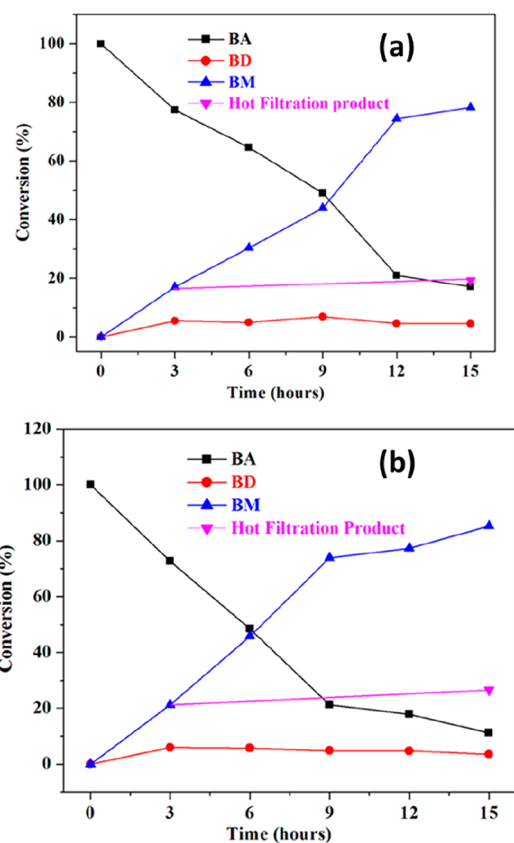
<sup>a</sup>Abbreviations: BA = benzyl alcohol, MN = malononitrile; BDC-NH<sub>2</sub> = 2-aminobenzenedicarboxylate; BDA = benzaldehyde dimethyl acetal; PDBAD = 4',4''-((pyridine-3,5-dicarbonyl)bis-(azanediy))bis[1,1'-biphenyl]-3,5-dicarboxylic acid; MOPBB = (5-methoxy-isophthaloyl)-bis(azanediy))disophthalic acid; 1,4-BDC = 1,4-benzene dicarboxylate; BD = benzaldehyde; H<sub>3</sub>TCA = 4,4',4'-tri-carboxytriphenylamine; DPA = (E)-1,2-di(pyridin-4-yl)diazene; 2-Melm = 2-methylimidazole; 2-H<sub>2</sub>BDC-N<sub>2</sub>H<sub>3</sub> = hydrazinyl-1,4-benzenedicarboxylic acid; H<sub>6</sub>TDP = 2,4,6-tris(2,4-dicarboxyphenyl)pyridine; ABDC = 2,2'-diamino-[1,1'-biphenyl]-4,4'-dicarboxylic acid; PMF = polymelamine formaldehyde.



general mechanistic pathway involves the acidic (Cr or  $\text{SO}_3\text{H}$ ) center to polarize the oxygen atom of the benzaldehyde dimethyl acetal to form benzaldehyde, which also increases the electrophilicity of the C center. The basic site helps in the nucleophile attack on the  $\text{-C=O}$  carbon, aiding the formation of the final product. The main outcome of this study appears to be the formation of the ammonium functionality, through proton transfer from the sulfonic acid to the amino group, which acts as the catalytic site. This approach of forming a zwitterionic form in a MOF could be an important development and would pave the way forward to carry out tandem reactions.<sup>165</sup> The use of 5-sulfoisophthalic acid as the primary linker and 4,4'-azopyridine (I) and 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (II) as the secondary linkers along with  $\text{Cd}^{2+}$  ions resulted in two different MOFs.<sup>166</sup> Both the compounds were explored toward the one-pot tandem deacetalization–Knoevenagel condensation reactions due to the presence of Lewis acidic (Cd metal centers) as well as basic (azine, free pyridine, and uncoordinated sulfo oxygens) sites. This highlight of the study is in identifying the formation of aldehyde (Lewis acidic) as slower compared to the Knoevenagel reaction (Lewis basic). In the tandem reaction, the aldehyde formed by the Lewis acid catalysis was immediately consumed in the subsequent Knoevenagel reaction, which facilitates the forward reaction due to Le Chatelier's principle.<sup>166</sup> A detailed time dependent study clearly outlines the relative merits of the Lewis acidic as well as basic sites in the two-component stepwise cascade reaction (Figure 3).

The direct synthesis route was adapted in the preparation of PCN-700, where the Brønsted acidity was achieved by introducing  $\text{H}_2\text{TPDC}(\text{COOH})_2$  [(1,1',4',1''-terphenyl)-2,2'',4,4''-tetracarboxylic acid] and the basicity by introducing  $\text{H}_2\text{BDC-NH}_2$  (2-aminoterephthalic acid) in the framework (Figure 4).<sup>167</sup> The modified compound, PCN-700-AB, was found to be a good catalyst toward the one-pot tandem reaction of benzaldehyde dimethyl acetal into benzylidene malononitrile. The spatial distribution of the acidic and basic sites in PCN-700-AB was found to effectively catalyze this cascade reaction. When the acidic sites were blocked by making an ester- $\text{CH}_3$  group in the same MOF, PCN-MB (Figure S1), the tandem reaction yields were poorer.<sup>167</sup> This clearly establishes the need to have both the acidic as well as the basic functionalities in the same compound for this reaction. A general scheme for this tandem reaction is given in Scheme 2.

**3.2.2. Other Tandem Reactions.** Though the deacetalization–Knoevenagel reaction was the dominant cascade reaction investigated over many MOFs, there are other tandem reactions that have been explored as well (Table 6). For example, Cr-MOF (MIL-101-Cr) ( $\text{Cr}_3(\text{F})(\text{H}_2\text{O})_2\text{O}[(\text{O}_2\text{C})\text{-C}_6\text{H}_4(\text{CO}_2)]_3$ ) was modified by PSM to generate MIL-101- $\text{SO}_3\text{H-NH}_2$ , which was found to be a good catalyst toward the one-pot tandem catalytic reaction.<sup>168,169</sup> The modified MOF was prepared through a postsynthetic route by sulfonation of the framework with chlorosulfonic acid in dichloromethane.<sup>170</sup> This compound was found to exhibit catalytic activity toward a three-component condensation reaction between aromatic aldehydes, resorcinol, and malononitrile in aqueous medium, forming 2-amino-4H chromene by the Knoevenagel condensation reaction followed by the Michael reaction (Figure S2).<sup>170</sup> The unmodified MOF, MIL-101-Cr, was found to give a lower yield of the desired product, and increased acidity by

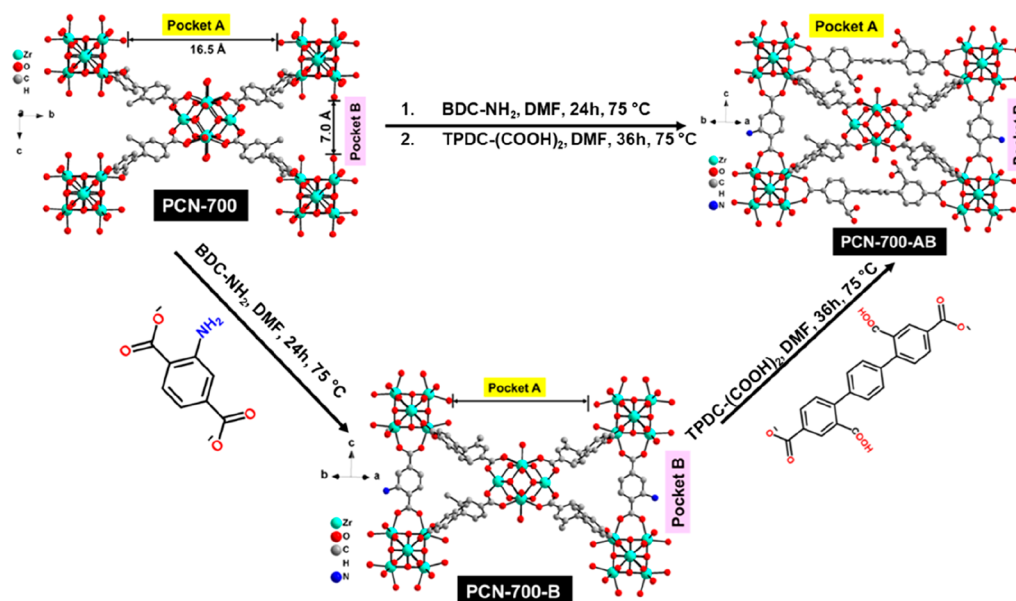


**Figure 3.** Kinetic study for the one-pot tandem deacetalization–Knoevenagel reaction with I (a) and II (b) as a heterogeneous catalyst (solvent-free condition). Adapted with permission from ref 166. Copyright 2018 American Chemical Society.

grafting  $\text{-SO}_3\text{H}$  to the framework gave improved catalytic activity for the overall reaction (Scheme S2).

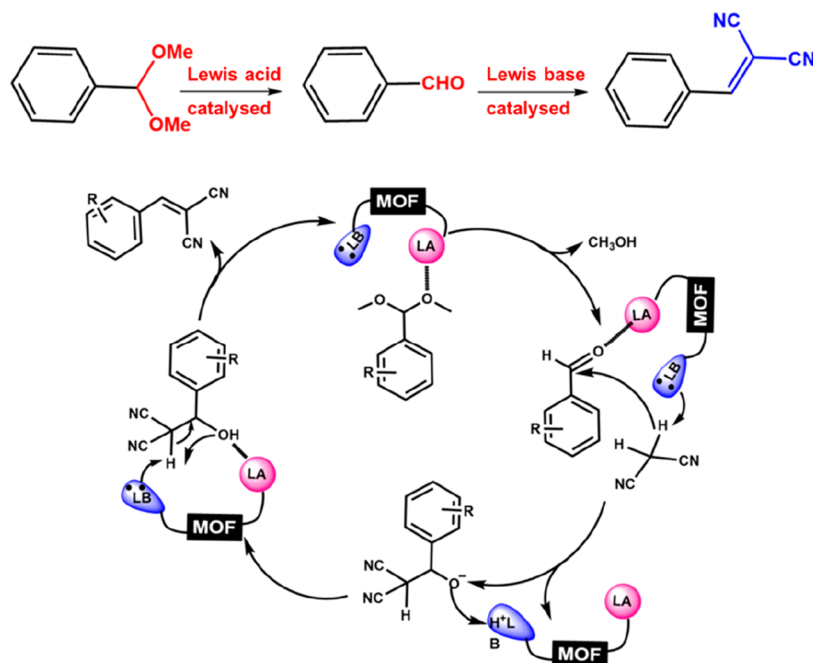
The MOF  $\text{Hf}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{HCO}_2)_6((\text{O}_2\text{C})_3\text{C}_6\text{H}_3)_{6/3}$ , [MOF-808(Hf)], (Figure 5a) was modified postsynthetically to give rise to a bifunctional catalyst for the reductive amination of ketones. The compound MOF-808(Hf) was exchanged to incorporate sulfonated phenylphosphines without oxidation to give a ligand attached with the MOF (Figure 5b). This ligand (SulP1-/MOF-808(Hf), Figure 5b) complexes with Ir and Rh to give a bifunctional catalyst (SulP1-/MOF-808(Hf–Ir)), containing both the metal–phosphine complexes and the Lewis acidic framework (Hf metal sites). The metalated MOF is a good example of having possible a homogeneous catalyst anchored over a heterogeneous host, which helps in the tandem reductive amination and hydro aminomethylation reactions. The catalytic tandem reaction of functionalized acetophenones with benzyl amine derivatives under 50 bar of  $\text{H}_2$  at 90 °C gave the product *N*-(cyclopentylmethyl)aniline with good yield (>90%). The formation of the product involves Lewis acid catalysis of the aldehyde addition to the amines, forming the corresponding imines, which are reduced further by the Ir/Rh centers (Figure 5c).<sup>145</sup> This work is reminiscent of the anchoring of chiral homogeneous noble metal catalysts within mesoporous MCM-41 toward superior performance in allylic amination and other reactions.<sup>2</sup>

A chromium MOF, OMS-MIL-101(Cr) (OMS = open metal site), was reacted with ethylene diamine, which creates basic centers in addition to the Cr acidic centers (Figure



**Figure 4.** Structures of PCN-700, PCN-700-B, and PCN-700-AB. Hydrogen atoms are omitted for clarity. Reproduced with permission under a Creative Commons CC-BY 3.0 from ref 167. Copyright 2019 CCS Chemistry.

### Scheme 2. Mechanism of the Deacetalization–Knoevenagel Condensation Reaction<sup>a</sup>



<sup>a</sup>LA = Lewis acidic site; LB = Lewis basic site.

6a).<sup>146</sup> This catalyst was useful toward multicomponent Hantzsch reactions. The condensation between aromatic aldehydes, dimedone,  $\beta$ -ketoesters, and ammonium acetate gave the product polyhydroquinoline with good yield (>98%) (Figure 6b).<sup>146</sup> The mechanism proceeds via the activation of the aryl halides over the acidic  $\text{Cr}^{3+}$  sites, and the  $-\text{NH}_2$  group helps in activating the  $\beta$ -ketoesters.<sup>146</sup> The grafting of lysine (2,6-diamino-hexanoic acid) to (Zr)MOF-808 allowed exploration of the multifunctionality by carrying out two sequential reactions: (i) Henry condensation (base catalyzed) and (ii) Friedel/Crafts type alkylation (acid catalyzed) in one-pot solvent-free conditions.<sup>148</sup> In this cascade reaction, both

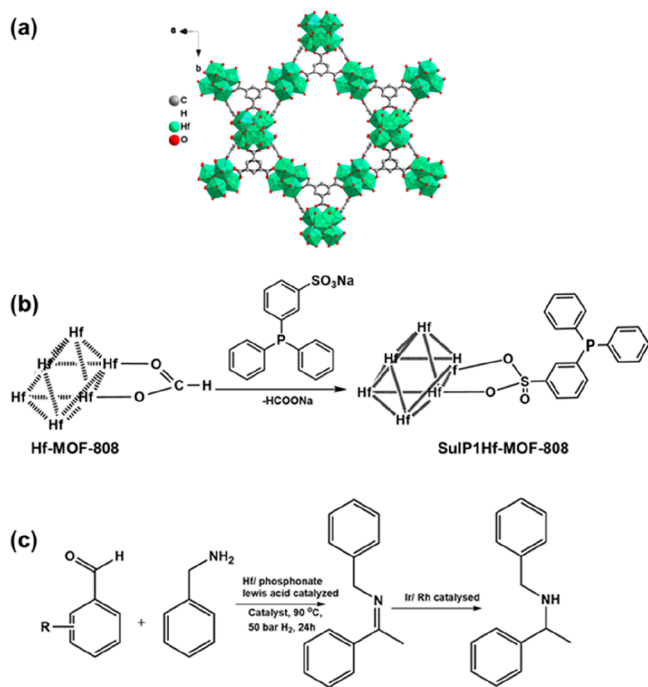
grafted basic sites (aliphatic amino groups) and framework acid sites (coordinatively unsaturated Zr sites) were employed.

A detailed kinetic study indicated that the former step is slower than the later (Figure S3). The combination of naphthalene dicarboxylic acid as the primary ligand and 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (3-BPDB) as the secondary ligand gave three-dimensional structures of Zn and Cd. The Lewis acid character (Zn/Cd center) was employed toward the condensation of amino benzaldehyde and ketones (Friedländer reaction). The Lewis basic character ( $-\text{N}=\text{N}-$ ) was used for the three-component condensation that involves Knoevenagel and Michael reactions.<sup>142</sup> In this study, a cascade

Table 6. Summary of Other Cascade Reactions Employing Bifunctional MOFs<sup>44</sup>

Reaction name	Sr. No.	MOF compound	Reactive site	Reactants	Product	Conditions	Ref
Multicomponent Hanstch Reaction	1	OMS-MIL-101(Cr)	Cr, NH <sub>3</sub>	aromatic aldehydes, dimedone, β-ketoesters ammonium acetate	methyl 2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate	4 mol % of cat, EtOH	146
Chromene Synthesis	2	MIL-101(Cr)-N(CH <sub>3</sub> PO <sub>3</sub> H <sub>2</sub> ) <sub>2</sub>	Cr -NH <sub>2</sub> , -PO <sub>3</sub> -OH, O <sup>-</sup>	ethyl cyanoacetate or ethyl acetoacetate, hydrazine hydrate, malononitrile, aldehydes	N-amino-2-pyridone and pyrano [2,3-c] pyrazole	5–10 mol % cat.	139
	3	Zn-Bp-BTC MOF	N, O <sup>-</sup> , -OH	benzaldehyde, malononitrile, and active methylene dimedone	2-amino-4H-chromene	0.06 mmol cat, ethanol	147
Henry Condensation–Friedel Craft Alkylation	4	zinc(II)-L1/L2/L3/L4	Zn, -NH <sub>2</sub>	aldehyde malononitrile 1,3-diketone	chromene	EtOH (2 mL), RT, 2 h, air	149
Oxidation–Knoevenagel Cascade Reaction	5	(Zn)MOF-808	Zr, lysine	benzaldehyde, nitromethane, indole	1-(2-nitro-1-phenylethyl)-1H-indene	2.5 mg cat, 30 °C	148
	6	M <sub>2</sub> (BTC)(OH)(4-TPT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (DMA) 0.5(H <sub>2</sub> O)	Co, Ni, N	benzyl alcohol malononitrile	benzylidene	0.25 mmol % cat, air, 400 μL CH <sub>3</sub> CN, n-dodecane, 12 h, 353 K	150
	7	Ni <sub>2</sub> (BTC) <sub>2</sub> (4-TPT) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ·1.5H <sub>2</sub> O	Cu, N	benzyl alcohol malononitrile	benzylidene	8 mol % cat, TEMPO (0.5 equiv), 5 mL CH <sub>3</sub> CN, 75 °C, 1 atm O <sub>2</sub> , 12 h	151
	8	H <sub>3</sub> PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> @MIL-101	Mo, V, Cr	benzyl alcohol malononitrile	benzylidene	0.5 mol % cat, toluene (1 mL) O <sub>2</sub> , sealed, 120 °C, 24 h	153
Oxidation–imine Formation	9	SulPIMOF-808(Hf)-Ir/Rh	Rh/IrPO <sub>3</sub> , Hf	ketone, benzyl amine	N-(cyclopentylmethyl)aniline	1.5 mol % catalyst in 5 mL toluene under 50 bar of H <sub>2</sub> at 90 °C for 24 h	145
Knoevenagel Condensation–hydrogenation	10	Zr/Hf-MOF-808	Zr/Hf, defect -OH	aniline, benzyl alcohols	N,1-diphenylmethanimine	T = 120 °C, 0.6 mmol of catalyst and o-xylene as solvent, 2 h	152
	11	IY-SO <sub>3</sub> H/Rh@S-ZIF-8	-SO <sub>3</sub> H, Zn, N	p-nitrobenzaldehyde, malononitrile	2-(4-aminobenzylidene) malononitrile	toluene (5 mL), 30 °C, 2 h; 2 MPa H <sub>2</sub> , 80 °C, 12 h	221

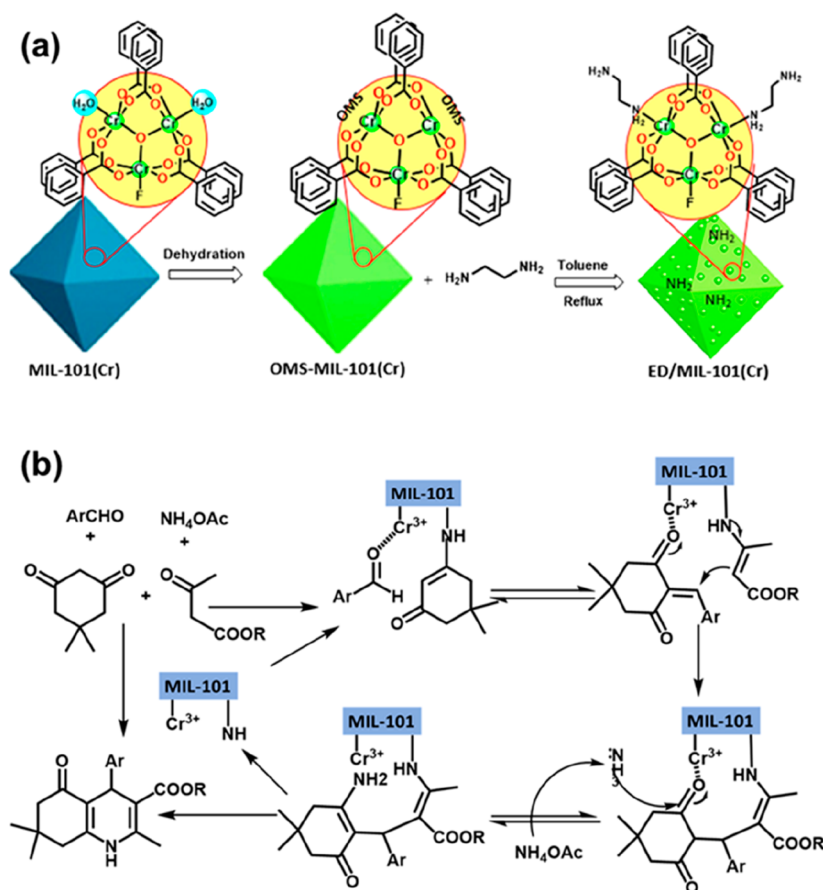
<sup>a</sup>PDEAEMA = poly[(2-diethylamino)ethyl methacrylate]; IY = Integrated yolk; H<sub>6</sub>TATAT = 5,5',5''-(1,3,5-triazine-2,4,6-triyl)tris(azanediy)trisophthalate; AP = 2-aminopyridine; BTC = 1,3,5-benzene tricarboxylate; Bp = 4,4'-bipyridine; N-ferrocenylmethyl-N-butyl dithiocarbamate (L1); N-ferrocenylmethyl-N-ethylmorpholine dithiocarbamate (L2); N-ferrocenylmethyl-N-2-(diethylamino)-ethylamine dithiocarbamate (L3); N-4-methoxybenzyl-N-3-methylpyridyl dithiocarbamate (L4).



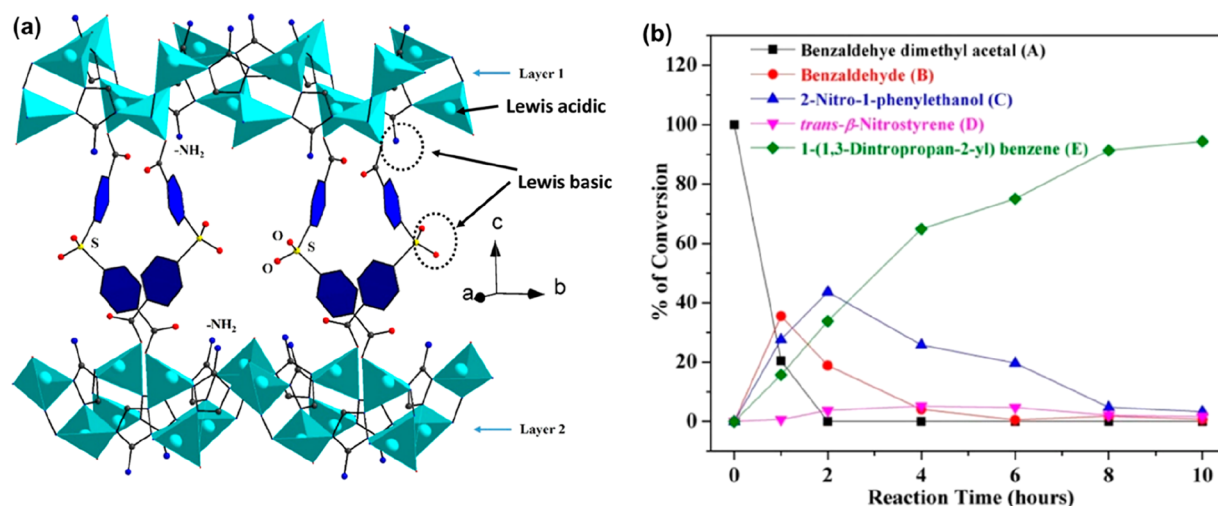
**Figure 5.** (a) Structure of MOF-808. (b) Schematic of the postsynthetic exchange of sulfonated phosphines for formate groups on MOF-808(Hf). (c) Scheme for the reductive amination reaction. Reproduced with permission from ref 145. Copyright 2018 John Wiley and Sons.

reaction of two distinct base catalyzed mechanisms has been investigated. Anchoring CuI over modified UiO-67 was found to be a good catalyst for the azide–alkyne cycloaddition reaction.<sup>154</sup> The mechanism involves mediated alkyne interactions followed by the azide reaction forming the triazole derivatives. It is a different approach, as metal salts have been anchored over the MOFs instead of simple metal nanoparticles.

In a recent work, for the first time, a 4-step cascade reaction was carried out using the same strategy of spatially separated Lewis acid and base functionality in  $[\text{Zn}_2(\text{SDBA})(3\text{-ATZ})]$  (SDBA = 4,4'-sulfonyldibenzoic acid; 3-ATZ = 3-amino 1,2,4-triazole) (Figure 7a).<sup>171</sup> The different steps that were studied involve deacetalization (Lewis acid catalyzed), Henry, and Michael reactions (Lewis base catalyzed) (Scheme 3). This reaction was possible due to the presence of additional basic sites in the MOFs (primary amine,  $\text{-NH}_2$ , and sulfonyl oxygen atoms). The four-step reaction consists of the following: the first reaction is the formation of an aldehyde (B) from the benzaldehyde dimethyl acetal (A) (Lewis acid catalyzed); the second reaction is between the nitroalkane and the aldehyde, forming (Henry reaction) 2-nitro-1-phenyl ethanol (C) (Lewis base catalyzed); the third reaction is the dehydration of (C) to give trans  $\beta$ -nitrostyrene (D) (Lewis base catalyzed); and finally reaction between nitromethane and (D) gives (1,3-dinitropropan-2-yl)benzene (E) (Scheme 3). The time dependent study clearly indicates that the dehydration of 2-nitro-1-phenyl ethanol to trans- $\beta$ -nitrostyrene was the rate

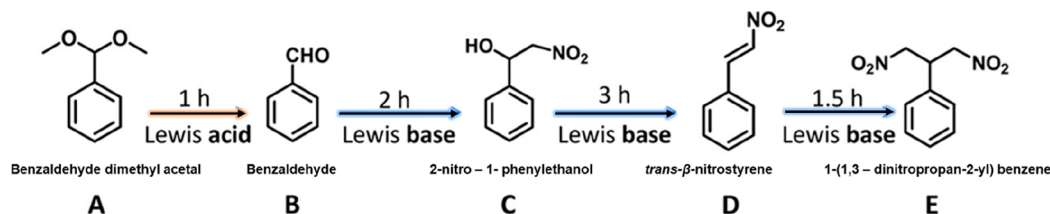


**Figure 6.** (a) Schematic illustration for the preparation of ED/MIL-101(Cr). (b) Plausible mechanism for MIL-101(Cr)- $\text{NH}_2$  catalysis of the Hantzsch reaction. Reproduced with permission from ref 146. Copyright 2018 John Wiley and Sons.

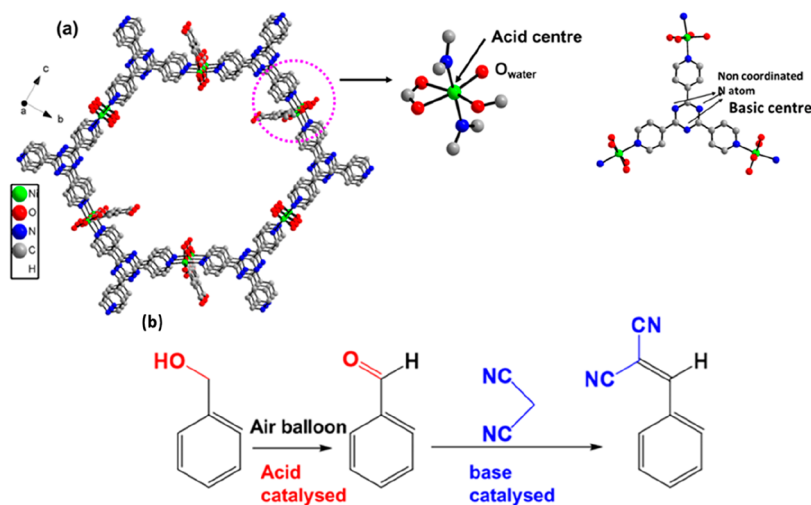


**Figure 7.** (a, b) Connectivity between the Zn-ATZ layers through the acid ligand (SDBA) in I and II. (c, d) Time dependent study of the one-pot tandem four-step deacetalization–Henry–Michael reactions for I and II. Reprinted with permission from ref 171. Copyright 2023 American Chemical Society.

### Scheme 3. Summary of the Four-Step Cascade Reaction Involving the Deacetalization–Henry–Michael Reaction<sup>4</sup>



<sup>4</sup>Reproduced with permission from ref 171. Copyright 2023 American Chemical Society.



**Figure 8.** (a) Structure of MOF highlighting the acidic and basic centers. (b) Schematic of the oxidation–Knoevenagel condensation reaction. Reproduced with permission from ref 150. Copyright 2021 Royal Society of Chemistry.

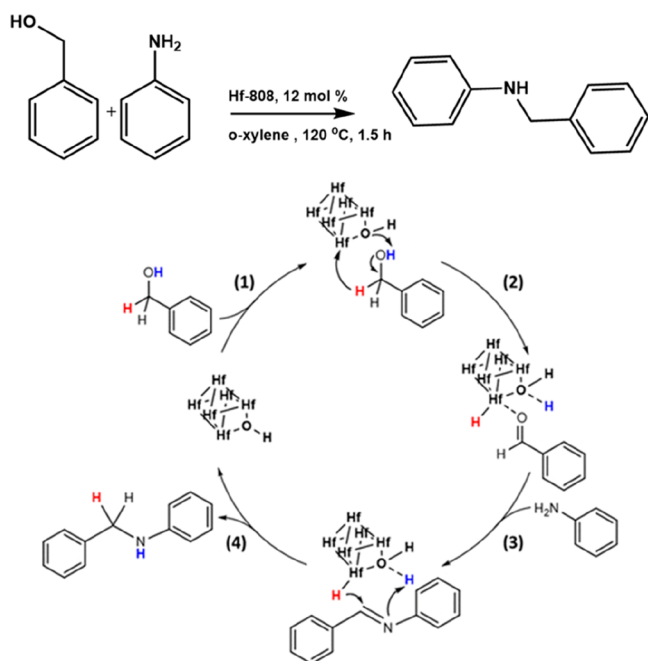
limiting step and that the Le Chatelier's principle was in action for the reaction to proceed in the forward reaction. It is clearly a good example where the bifunctionality of the MOF was exploited toward a cascade reaction that involved multiple steps. The number of steps (3) in the base catalyzed reactions is more compared to that of the acid catalyzed one in this cascade reaction. The presence of the primary -NH<sub>2</sub> group, which is a strong base, helped in this reaction<sup>171</sup> (Figure 7b).

**3.2.3. Oxidation–Knoevenagel/Amination Cascade Reaction.** The compounds M(BTC)(OH)(4-TPT)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(DMA)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2</sub> (H<sub>3</sub>BTC = 1,3,5-tribenzoic acid; 4-TPT = 2,4,6-tris(4-pyridyl)-1,3,5-triazine; M = Co, Ni) and Ni<sub>3</sub>(BTC)<sub>2</sub>(4-TPT)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>·1.5H<sub>2</sub>O have terminal H<sub>2</sub>O molecules coordinated to the metal centers (Co/Ni) which can be removed by heating (Figure 8a).<sup>150</sup> This creates an open coordination site at the metal center, which can act as Lewis acidic center. The secondary ligand 4-TPT can be the Lewis

basic center. The compounds were found to be good catalysts for the oxidation of benzyl alcohol to benzaldehyde (acid catalyzed) followed by reaction with malonitrile to give benzilidene malonitrile (base catalyzed) (Figure 8b).<sup>150</sup> A similar reaction was also carried out over the Cu<sub>3</sub>TATAT MOF (H<sub>6</sub>TATAT = 5,5',5''-(1,3,5-triazine-2,4,6-triyl) tris-(azanediyl)triisophthalate) compound.<sup>151</sup>

The use of Zr/Hf-MOF-808 toward the synthesis of secondary amines was established by reacting anilines and benzyl alcohols. This reaction does not require any additional base and/or external H<sub>2</sub>.<sup>152</sup> The reaction proceeds through the deprotonation of the alcohol by the metal center followed by the dehydrogenation to form benzaldehyde, which reacts with the amino group of the aniline, forming the final benzylaniline product (Scheme 4). There are some important observations

**Scheme 4. Possible Mechanism for the *N*-Alkylation Reaction of Aniline with Benzyl Alcohol to Form the *N*-Benzylaniline Product<sup>a</sup>**

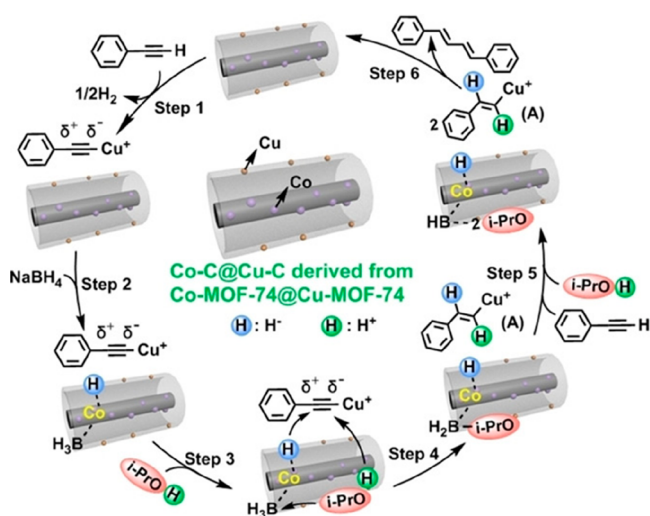


<sup>a</sup>Adapted with permission under a Creative Commons (CC BY 4.0) from ref 152. Copyright 2021 American Chemical Society.

in this reaction. The presence of a defective -OH group in the Hf-cluster metal center enhances the acidity and helps in the formation of benzaldehyde in the first step. The captured proton at the defective -OH group site also aids in the formation of the final product by reacting with the imine nitrogen formed through the condensation of the aldehyde and amine (Scheme 4). This is an interesting strategy where the proton is captured initially and later released during the final step to give the desired product.

The encapsulation of polyoxometalate H<sub>3</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> (PMoV<sub>2</sub>) into the cages of an alkylamine-modified MIL-101 was employed for the aerobic oxidation–Knoevenagel one-pot tandem reaction (Scheme S3). The main observation in this reaction is that it does not use any noble metals for the aerobic oxidation of the alcohols.<sup>153</sup>

**Scheme 5. Co-MOF-74@Cu-MOF-74 Derived Bifunctional Co-C@Cu-C for One-Pot Production of 1,4-Diphenyl-1,3-butadiene from Phenylacetylene<sup>a</sup>**



<sup>a</sup>Reprinted with permission from ref 209. Copyright 2020 John Wiley and Sons.

### 3.3. Anchoring Metal Nanoparticles toward Catalysis

The development of metal nanoparticles during the 90s and the associated advancements in nanoscience provide an important opportunity to explore multifunctionality in MOFs.<sup>172–174</sup> It may be noted that the use of well distributed supported metal catalysis (e.g., Pd or Pt in Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, zeolites, and mesoporous silica) is one of the earlier examples of bifunctional catalysts.<sup>175–177</sup> Many of the supported catalysts are useful toward the “spillover” reactions involving hydrogen.<sup>178</sup> The noble metal and the support influence the electronic state of the metal along with its precise morphology. Today, it has been possible to prepare noble metal nanoparticles with controlled sizes and shapes,<sup>179–182</sup> which may be of importance in heterogeneous catalysis. The noble metal nanoparticles can be stabilized by anchoring the particles through suitable functional groups—most notably the thiol (-SH) functionality. The usefulness of noble metal centers for diverse catalytic reactions has been known over many decades.<sup>183–187</sup> Many of these earlier reactions are homogeneous catalytic reactions, where the recyclability of the catalyst would be difficult. In recent years, it has been possible to prepare atom precise metal nanoclusters and assemble them into extended structures.<sup>188–192</sup> In addition, the ease of functionalizing the ligands that can be used in the preparation of MOFs opens up an interesting possibility toward anchoring metal nanoparticles at precise locations within the MOFs. The MOFs provide reasonable thermal and chemical stability and pore and channel sizes which can be gainfully employed to explore the usefulness of metal nanoparticles toward catalytic reactions. This approach would be similar to carrying out the homogeneous reactions within heterogeneous surroundings. Catalytic reactions of this nature were attempted by anchoring organometallic complexes directly into the mesoporous compounds, notably on MCM-41 and related ones.<sup>193–195</sup>

Most of the MOFs possess Lewis acidity, and the functional ligand provides the necessary additional reactive center (either Bronsted acidic or basic). These MOFs are already bifunctional and the anchoring of metal nanoparticles adds to the

Table 7. Nanoparticle Loaded MOFs and Their Utility in Catalysis<sup>a</sup>

Sr. No.	MOF compound	Reactive site	Nanoparticle	Catalytic reaction	Ref
1	Au@ZIF-8	Zn <sup>2+</sup> /-N <sub>im</sub>	Au	hydrogenation of n-hexene	311
2	nFe <sub>3</sub> O <sub>4</sub> @Pd/ZIF-8@ZIF-8	Zn <sup>2+</sup> /-N <sub>im</sub>	Fe <sub>3</sub> O <sub>4</sub> /Pd	hydrogenation of styrene	312
3	UiO-66-biguanidine/Pd	Zr <sup>4+</sup> /-NH <sub>2</sub>	Pd	Suzuki–Miyaura coupling	313
4	Ag@UiO-66-SH	Zr <sup>4+</sup> /-NH <sub>2</sub>	Ag	three-component A <sup>3</sup> coupling	314
5	AgPd@MIL-125-NH <sub>2</sub> -PDA	Cr <sup>3+</sup> /-NH <sub>2</sub>	Ag-Pd	Suzuki coupling reaction hydrogenation of aldehyde	315
6	MOF-Pd NPs	Cu <sup>2+</sup> /-NH <sub>2</sub>	Pd	aerobic oxidation of benzyl alcohol	316
7	Pt@UiO-66-NH <sub>2</sub>	Zr <sup>4+</sup> /-NH <sub>2</sub>	Pt	synthesis of nitrones	173
8	Au-NP/Ni-Cu MOF	Ni <sup>2+</sup> /Cu <sup>2+</sup>	Au	chemical degradation of Rhodamine B	317
9	Au@Cu(II)-MOF	Cu <sup>2+</sup> /-N	Au	oxidation–condensation reactions	198
10	Co–MOF-74@Cu–MOF-74	Co <sup>2+</sup> /Cu <sup>2+</sup>	CoCu	1, 4-diphenyl-1,3-butadiene from phenylacetylene	209
11	Pd(0)@UiO-68-AP	Zr <sup>4+</sup> /-N	Pd	oxidation–Knoevenagel condensation	215
12	Au/NH <sub>2</sub> –UiO-66	Zr <sup>4+</sup> /-NH <sub>2</sub>	Au	tandem reaction	216
13	Pd-Au@Mn(II)-MOF	Mn(II)/N	Pd-Au	alcohol to imines	217
14	Al-ITQ-SO <sub>3</sub> H/Pd	Al(III), SO <sub>3</sub> H	Pd	oxidation–acetalization	219
15	IY-SO <sub>3</sub> H/Rh@S-ZIF-8	Zn(II)SO <sub>3</sub> H	Rh	Knoevenagel condensation–hydrogenation reaction	221
16	Pd@UiO-66(Hf)	Hf(IV)	Pd	Hantzsch reaction	318
17	Pd@NH <sub>2</sub> -UiO-66	Zr(IV)/-NH <sub>2</sub>	Pd	Suzuki coupling/asymmetric aldol condensation	224
18	Ni@ZrOF	Zr(IV)/-NH <sub>2</sub>	Ni	chemical fixation of CO <sub>2</sub>	319
19	Au@[Zn <sub>14</sub> (L) <sub>6</sub> (O) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]	Zn(II)	Au	chemical fixation of CO <sub>2</sub>	249
20	Ag(I)@MOF-NHC	Zn(II)/-N	Ag	chemical fixation of CO <sub>2</sub>	250
21	Pt@MOF-S, Pt@UiO-66, Pt@UiO-66-NH <sub>2</sub>	Zr(IV)/-NH <sub>2</sub>	Pt	biomass valorization	320
22	[Zn(4-bpdh)] <sub>3</sub> DMF	-N	Pd	Sonogashira coupling reaction	321
23	Ag/UiO-66	Zr <sup>4+</sup>	Ag	3,4-dihydropyrimidin-2(1H)-one synthesis	322
24	Au/MOF-199	Cu <sup>2+</sup>	Au	A <sup>3</sup> -coupling reaction	323
25	metal/UiO-66	Zr <sup>4+</sup>	Pt, Pd, Ru	oxidation of volatile organic compound	324
26	Pd(0)@UiO-68-AP	Zr, -NH	Pd	oxidation–Knoevenagel cascade reaction	215
27	Au@NH <sub>2</sub> -UiO-66	Zr, -NH <sub>2</sub>	Au	oxidation–Knoevenagel cascade reaction	216
28	Pd-Au@Mn(II)-MOF	Mn, N <sub>pyr</sub>	Pd, Au	oxidation–imine/acetal formation cascade reaction	217
29	Pd@MIL-101	Cr, N	Pd	oxidation–imine/acetal formation cascade reaction	218
30	Pd@Al-MOF	Al, -SO <sub>3</sub> H	Pd	oxidation–imine/acetal formation cascade reaction	219
31	Pd@PDEAEMA-g-UiO-66	Zr, -NH <sub>2</sub>	Pd	Knoevenagel condensation–hydrogenation	220
32	Pd/MIL-101-SO <sub>3</sub> H	-SO <sub>3</sub> H	Pd	hydrogenation esterification cascade reaction	222
33	Pd@UiO-66(Hf)	Zr	Pd	hydrogenation esterification cascade reaction	223

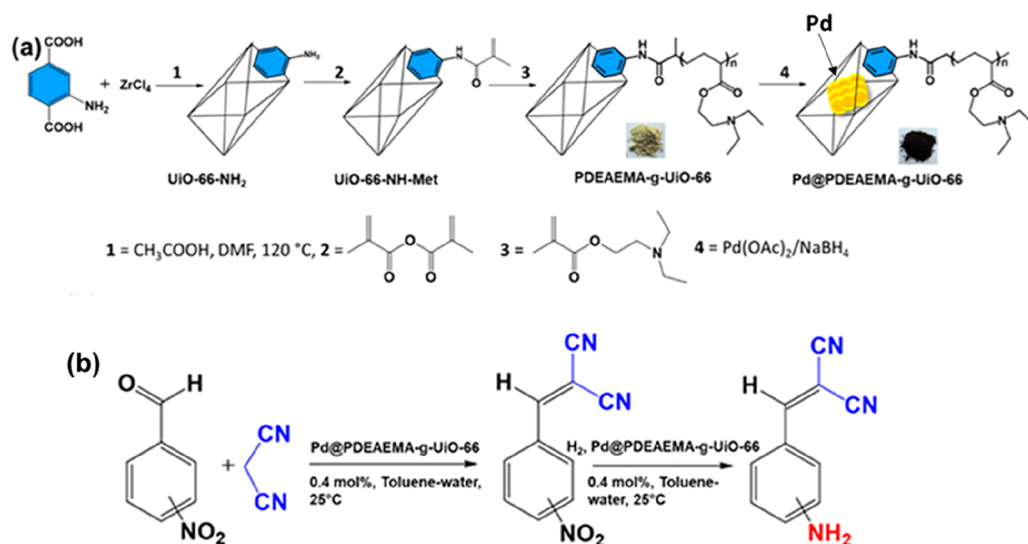
<sup>a</sup>OPNs = organic polymer networks; PDA = polydopamine; AP = aminopyridine; NHC = N-heterocyclic carbene; 4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene.

existing functionality. The main advantages of anchoring the metal nanoparticles are their small (nano) size and the availability of periodically placed metals over the surface of the MOFs, which would be useful toward many heterogeneous catalytic reactions. Much of the earlier work on such type of nanoparticle anchored MOFs was termed “ship in a bottle” catalysts.<sup>196,197</sup> The usefulness of this approach was shown by anchoring Au nanoparticles in a MOF, Au@Cu(II)-MOF, toward a tandem oxidation–Knoevenagel condensation reaction that involves the conversion of benzyl alcohol to benzylidene malononitrile with good yield, conversion, and selectivity.<sup>198</sup> Similarly, Pd@Ni-MOF was shown to be a good catalyst toward Suzuki coupling of aryl chlorides.<sup>199</sup> It is notable that many reactions involving Suzuki coupling are carried out by employing aryl bromides and iodides and that the presence of Pd nanoparticles uniformly distributed in a heterogeneous environment (Pd@Ni-MOF) converts the aryl chlorides with good yield as well as recyclability.<sup>199</sup> Many studies of this nature have been known in the literature.<sup>200–205</sup> The important nanoparticle loaded MOFs and their utility in heterogeneous catalytic studies are listed in Table 7.

As discussed above, anchoring of noble metal particles supported over the MOFs was found to be dominant in many

catalytic reactions. There have been attempts at synthesizing 3d metal nanoparticles, at the expense of the MOF framework, by anchoring them over carbonized MOFs.<sup>206–208</sup> It has been shown that MOFs when heated in an inert atmosphere (Ar atmosphere) or under vacuum at elevated temperatures form carbon with the metals distributed over the carbon. This carbonization process, in general, results in the formation of different forms of carbon such as amorphous carbon, graphitized carbon, or a mixture of both. Depending on the composition of the MOFs, the resulting metal nanoparticles can be either single nanoparticles or bimetallic nanoparticles supported over the amorphous carbon. It has been known that amorphous carbon can act as a good support toward many catalytic reactions.<sup>209–214</sup> The bimetallics supported over the carbonized MOFs can be exploited toward catalytic reactions where the differences in the catalytic activity of the different metals would be important.

This strategy was employed toward the preparation of Co-Cu bimetallic nanoparticles supported on carbon (Co-C@Cu-C) by pyrolyzing Co/Cu-MOF-74.<sup>209</sup> This bimetallic catalyst was found to be a good catalyst for the conversion of phenylacetylene to 1,4-diphenyl-1,3-butadiene. This reaction involves C–C coupling as well as hydrogenation reactions, and



**Figure 9.** (a) Schematic of synthesis of Pd@PDEAEMA-g-UiO-66 through PSM. Yellow balls: Pd nanoparticles. (b) Knoevenagel condensation followed by hydrogenation cascade reactions over the Pd@PDEAEMA-g-UiO-66 catalyst. Reproduced with permission from ref 220. Copyright 2017 American Chemical Society.

the reaction proceeds over the Co centers. The possible mechanism for this cascade reaction is given in Scheme 5. Phenylacetylene is initially activated by metallic Cu NPs, forming Cu<sup>+</sup>-phenylacetylide complex on the surface of Cu NPs. The metallic Co NPs in Co-C@Cu-C help in the dissociation of NaBH<sub>4</sub> to form Co-BH<sub>3</sub> and CoH, which act as the active species for the hydrogenation of the phenylacetylene. The proposed mechanism also involves the migration the hydrides on Co nanoparticles to diffuse to interact with the adsorbed Cu<sup>+</sup>-phenylacetylide complex. The remaining hydrides in BH<sub>3</sub>(*i*-PrO)<sup>−</sup> dissociate over the metallic Co NPs, which helps in the spillover of hydrogen to react with the adsorbed Cu<sup>+</sup>-phenylacetylide complex. The *in situ* formed complex between CuI-phenylacetylide dimerizes to form 1, 4-diphenyl-1,3-butadiene.

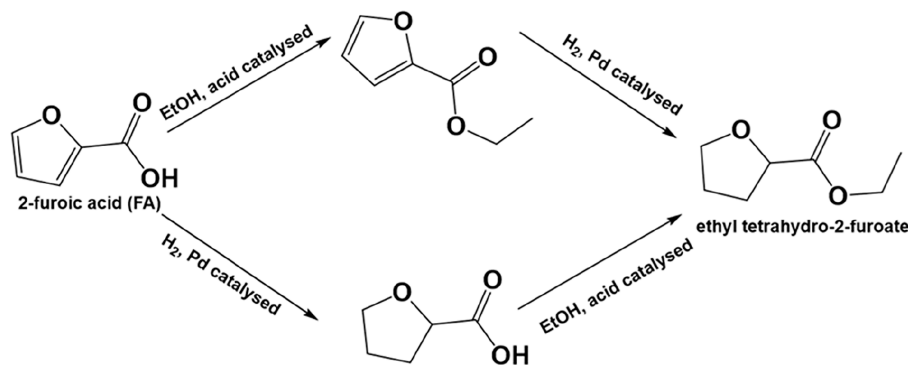
The pyrolysis of a cobalt MOF, [Co(C<sub>14</sub>H<sub>8</sub>O<sub>6</sub>)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)·2H<sub>2</sub>O]·(C<sub>3</sub>H<sub>7</sub>NO), results in Co supported on amorphous/graphitized carbon. The Co nanoparticles were shown to be a good green catalyst for the selective reduction of nitroarenes to amines in the presence of the hydrazine as a hydrogen source.<sup>199</sup> The Co metal particles supported on the carbon matrix help in the decomposition of hydrazine to produce the hydrogen *in situ*. The hydrogen spillover helps in the reduction of nitroaromatics to the aniline derivatives. The examples clearly support the spillover effect in employing metal nanoparticles toward hydrogenation reactions. A mixed precursor containing Cu, Co, and Ni introduced into MIL-101 was reduced *in situ* with NH<sub>3</sub>BH<sub>3</sub> to give Cu@Co@Ni NPs inside MIL-101 pores. The compound Cu@Co@Ni/MOF catalyzes nitroarene hydrogenation in the presence of NH<sub>3</sub>BH<sub>3</sub>, which supplies the necessary hydrogen for the reaction.<sup>204</sup>

**3.3.1. Cascade Reactions Involving Anchored Nanoparticles.** A bifunctional Pd(0)@UiO-68-AP catalyst, prepared using the postsynthetic approach, catalyzes aerobic oxidation of benzyl alcohol by the Pd NPs followed by reaction with malononitrile via the Knoevenagel condensation, forming benzylidene malononitrile.<sup>215</sup> The oxidation of the benzyl alcohol is promoted by the Pd catalyst whereas the Knoevenagel condensation is facilitated by the basic nitrogen

center.<sup>215</sup> A similar reaction was also carried out employing Au nanoparticles anchored over NH<sub>2</sub>-UiO-66,<sup>216</sup> for the selective oxidation of primary alcohols in tandem with Knoevenagel condensation reactions. A Mn(II) MOF, (MnL<sub>2</sub>)·2CH<sub>3</sub>OH (L = 4,4,4-trifluoro-1-(4-(pyridin-4-yl)phenyl)butane-1,3-dione), with Pd-Au bimetallic alloy nanoparticles (Pd-Au@Mn(II)-MOF) was employed as a bifunctional heterogeneous catalyst for the one-pot tandem synthesis of imines from benzyl alcohols and aniline (Figure S4). The oxidation reaction was catalyzed by nanoparticles, and the imine formation was due to the N-containing ligand.<sup>217</sup> Similar reactions have also been carried out with Pd nanoparticles (NPs) encapsulated in MIL-101.<sup>218</sup> An aluminum MOF, Al-ITQ-SH, having thiol units was used to anchor Pd nanoparticles, and the thiol moieties were converted into sulfonic groups (Brønsted acid).<sup>219</sup> This compound catalyzes a one-pot, two-step oxidation-acetalization reaction where the oxidation of benzyl alcohol into benzaldehyde under an O<sub>2</sub> atmosphere was catalyzed by Pd nanoparticles, followed by the acetalization of aldehydes employing the Brønsted acid functionality. A Pd NP loaded and pH-switchable polymer-grafted UiO-66-MOF, Pd@PDEAEMA-g-UiO-66, (PDEAEMA = poly[(2-diethylamino)ethyl methacrylate]), was employed toward a biphasic Knoevenagel condensation–hydrogenation cascade reaction using different atmospheres (Figure 9a). The Knoevenagel condensation step was carried out under air atmosphere, whereas the hydrogenation reaction was carried out in hydrogen atmosphere (Figure 9b).<sup>220</sup>

A bifunctional composite compound with a macro-/microporous ZIF-8 shell and rhodium nanoparticles anchored over sulfonated cross-linked polystyrene was prepared to carry out the Knoevenagel–hydrogenation reaction.<sup>221</sup> The reactants containing the aldehyde and malononitrile in toluene solvent under a pressure of hydrogen (2 MPa) gave the benzylidene malononitrile product in near ~100% yield. The composite catalyst was found to be robust with negligible leaching of the anchored Rh nanoparticles.<sup>221</sup> Another reaction that utilizes nanoparticle supported over MOFs is the hydrogenation–esterification reaction. The hydrogenation is catalyzed by the noble metal nanoparticles, and the



Scheme 6. Scheme of the Cascade Reaction Process from FA to ETF<sup>a</sup>

<sup>a</sup>Reproduced with permission from ref 222. Copyright 2019 Royal Society of Chemistry.

esterification reaction is catalyzed by the acidic sites. The compound MIL-101-SO<sub>3</sub>H was appended with Pd nanoparticles to give Pd/MIL-101-SO<sub>3</sub>H.<sup>222</sup> This compound was active to convert furoic acid (FA) (biomass derived) into value chemicals such as ethyl tetrahydro-2-furoate (ETF). The FA was esterified with ethanol, forming ethyl furoate (EF), which was hydrogenated to give ETF (yield = 100%, selectivity >99%) (Scheme 6). A similar reaction has also been attempted over Pd@UiO-66(Hf).<sup>223</sup>

The use of bifunctionality was shown elegantly by adding an L-proline functionality to -NH<sub>2</sub>-UiO-66, which also had Pd nanoparticles through PSM. This modified MOF was shown to be a chiral catalyst toward Suzuki coupling (Pd centered) followed by asymmetric aldol condensation (N centered). The reaction between 1,4-bromobenzaldehyde and phenylboronic acid in EtOH–H<sub>2</sub>O was catalyzed by Pd@NH<sub>2</sub>-UiO-66(pro) and K<sub>2</sub>CO<sub>3</sub> at 80 °C.<sup>224</sup>

As described above, the overall activity of the MOFs has been enhanced by having the nanoparticles. Though most of the studies concentrated on noble metals, there have been efforts toward other transition metals as well. As can be noted, in most of the cases one finds a good synergistic and cooperative effect between the metal nanoparticles and the overall functionality of the MOFs. The reactions, in a way, replicate many of the well-established and known organometallic catalyses in these compounds. This effort paves the way for carrying out homogeneous catalysis under a heterogeneous environment. It is likely that many other reactions would also be attempted in the future to reap the benefits of having well dispersed nanomaterials in bifunctional MOFs. This approach really makes the MOF compounds truly multifunctional.

### 3.4. Fixation of Atmospheric CO<sub>2</sub>

One of the important issues of concern is the control of CO<sub>2</sub> in the atmosphere. CO<sub>2</sub> has been designated as an important greenhouse gas, and it is desirable to convert it to other useful chemicals.<sup>225–230</sup> There have been attempts to convert the CO<sub>2</sub> under atmospheric conditions, both through the catalytic route<sup>231–233</sup> as well as electrochemically.<sup>234–236</sup> The intense research, over the years, has involved conversion of CO<sub>2</sub> into cyclic carbonate, carboxylation, reductive N-functionalization of various amines with CO<sub>2</sub> to furnish N-formyl compounds, and carboxylative cyclization of propargyl amines and alcohols.<sup>237–241</sup> In many of these attempts, organometallic compounds, nanoparticle grafted compounds, and others have been explored.<sup>242</sup> There have been considerable efforts toward

fixing CO<sub>2</sub> at atmospheric pressures employing MOFs, notably bifunctional ones. Some of the important studies toward the fixation of CO<sub>2</sub> employing MOFs are listed in Table 8.

Tetra(4-pyridyl)porphyrin (H<sub>2</sub>TPyP) was employed along with 4,4'-oxybis(benzoic acid) (H<sub>2</sub>OBA) to form a 2D compound, [Zn<sub>2</sub>(C<sub>40</sub>H<sub>24</sub>N<sub>8</sub>)<sub>0.5</sub>(C<sub>14</sub>H<sub>8</sub>O<sub>5</sub>)(DMA)](DMA)-(H<sub>2</sub>O)<sub>6</sub>.<sup>243</sup> The Zn<sup>2+</sup> ions were ion-exchanged with the Cu<sup>2+</sup> in a postsynthetic modification, and the Cu compound was employed for the cyclic carbonate formation reaction with tetra-*n*-*tert*-butylammonium bromide (TBAB) as a cocatalyst, which gave cyclic carbonates with high yield.<sup>243</sup>

A plausible reaction mechanism for the cycloaddition of CO<sub>2</sub> to cyclic carbonates using bifunctional MOFs is given in Scheme 7. The zirconium-phosphonate MOF Zr(H<sub>4</sub>L) (H<sub>8</sub>L = tetraphenylsilane tetrakis-4-phosphonic acid) was shown to be a good catalyst toward the CO<sub>2</sub>/epoxide coupling reaction. The presence of a Brønsted acid (protonated phosphonate) along with the Lewis acidic (Zr metal) functionality helped in catalyzing the reaction forming cyclic carbonates (Figure S5).<sup>244</sup> A copper MOF, [Cu(2,5-BPTA)(bpy)(H<sub>2</sub>O)] (2,5-BPTA = 2,5-bis(prop-2-yn-1-yloxy)terephthalic acid and bpy = 4,4'-bipyridine, Figure 10a), was shown to catalyze CO<sub>2</sub> to cyclic carbonates in the presence of TBAB as a cocatalyst.<sup>245</sup> The Cu<sup>2+</sup> ions acts as the Lewis acid centers to polarize the epoxide oxygen and increase the electrophilicity of the carbon. The Br<sup>-</sup> from the TBAB helps in the ring opening of the epoxides. The Cu<sup>2+</sup> acts as the center for the subsequent binding of CO<sub>2</sub> with the ring opened epoxide along with the elimination of the Br<sup>-</sup> by ring closing, forming the cyclic carbonates (Figure 10b).<sup>245</sup> As noted in Table 8, the number of examples of the conversion of CO<sub>2</sub> to cyclic carbonates are many. It appears that the presence of stronger acidic sites along with basic sites helps toward catalyzing this reaction. Lanthanide MOFs (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb; NTB = 4,4',4''-nitriлотribenzoic acid; NMP = *N*-methylpyrrolidone) have also been shown to effectively catalyze the CO<sub>2</sub> conversion.<sup>246</sup> The compounds catalyze the reaction between CO<sub>2</sub> and epichlorohydrin in the presence of *n*-Bu<sub>4</sub>NBr as the cocatalyst with a yield of 97%.<sup>246</sup>

In many of the cycloadditions of CO<sub>2</sub> to epoxide, a cocatalyst is generally employed. The role of the cocatalysts such as TBAB, in the cycloaddition of CO<sub>2</sub>, is to enhance the catalytic activity by participating during the ring opening step. A zeolitic imidazole framework-78 (ZIF-78) was found to be a good catalyst (Figure 11) toward the CO<sub>2</sub>/propylene oxide (PO) cycloaddition, forming propylene carbonate (PC) in the

Table 8. Summary of Atmospheric CO<sub>2</sub> Fixation over MOFs<sup>a</sup>

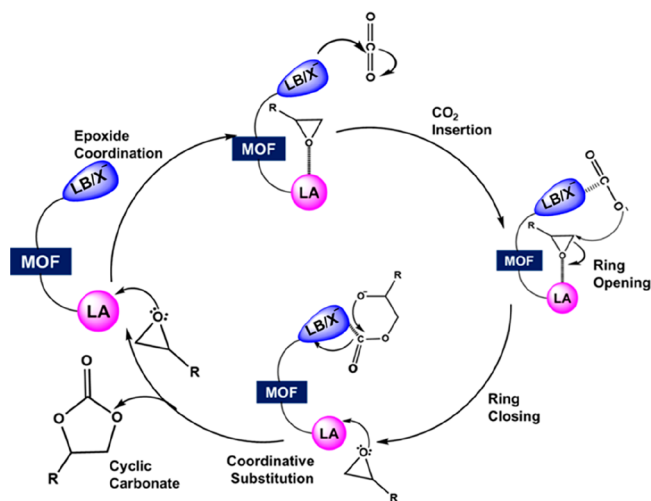
Sr. No.	MOF	Reactive site	Reactant	Product	Reaction conditions	Ref
1	(I <sup>-</sup> )Meim-UiO-66	Zr <sup>4+</sup> , I <sup>-</sup>	ECH	4-(chloromethyl)-1,3-dioxolan-2-one	0.1 MPa, 120 °C, 24 h	248
2	MIL-IL(A) MIL-IL(B)	Cr <sup>3+</sup> , Br <sup>-</sup>	SO	4-phenyl-1,3-dioxolan-2-one	2 MPa, 110 °C, 2 h	325
3	MIL-IMAc-Br <sup>-</sup>	Cu <sup>2+</sup> .COOH, Br <sup>-</sup>	ECH	4-(chloromethyl)-1,3-dioxolan-2-one	0.5 MPa, 60 °C, 24 h	81
4	Mg-MOF-74  Co-MOF-74	Mg <sup>2+</sup> , Co <sup>2+</sup> , OH	SO	4-phenyl-1,3-dioxolan-2-one	2 MPa, 100 °C, 4 h	326, 327
5	UiO-66-NH <sub>2</sub>	Zr <sup>4+</sup> , NH <sub>2</sub>	SO	4-phenyl-1,3-dioxolan-2-one	2.0 MPa, 100 °C, 4 h	328
6	BIT-101 BIT-102 BIT-103	Zn <sup>2+</sup> , COO	PO	4-methyl-1,3-dioxolan-2-one	3 MPa, 160 °C, 24 h	329
7	1-NH <sub>2</sub>	CONH, NH <sub>2</sub>	ECH, PO	4-(chloromethyl)-1,3-dioxolan-2-one-4-methyl-1,3-dioxolan-2-one	0.1 MPa, 90 °C, 50 h, 3 MPa, 100 °C, 6 h	330
8	UMCM-1-NH <sub>2</sub>	Zn <sub>4</sub> O, NH <sub>2</sub>	PO	4-methyl-1,3-dioxolan-2-one	1.2 MPa, 120 °C, 24 h	331
9	Zn-TATAB	Zn <sup>2+</sup> , NH	ECH	4-(chloromethyl)-1,3-dioxolan-2-one	1 atm, 100 °C, 16 h	332
10	Co/Ni-TATAB	Co <sup>2+</sup> , Ni <sup>2+</sup> , NH	ECH/ECH	4-(chloromethyl)-1,3-dioxolan-2-one	1 bar, 80 °C, 15 h	279
11	Zn-BTC-2MeIm	Zn <sup>2+</sup> , 2MeIm	ECH, PO	4-(chloromethyl)-1,3-dioxolan-2-one	3.0 MPa, 100 °C, 6 h	333
12	Co(tp)(bpy) MOF-508a	Co <sup>2+</sup> , Zn <sup>2+</sup> , free pyridine N	ECH	4-(chloromethyl)-1,3-dioxolan-2-one	1 MPa, 100 °C, 8 h	334
13	(Me <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> [Zn <sub>8</sub> (Ad) <sub>4</sub> (DABA) <sub>6</sub> O] <sub>n</sub> ·7DMF	Zn <sup>2+</sup> , Ad, and NH <sub>2</sub>	ECH	4-(chloromethyl)-1,3-dioxolan-2-one	1 bar, 100 °C, 24 h	335
14	ZIF-8	Zn <sup>2+</sup> , Im	ECH	4-(chloromethyl)-1,3-dioxolan-2-one	7 bar, 100 °C, 4 h	336
15	ZIF-90	Zn <sup>2+</sup> , CHO	PO	4-methyl-1,3-dioxolan-2-one	2 MPa, 120 °C, 8 h	337
16	CZ-ZIF	Zn <sup>2+</sup> /Co <sup>2+</sup> , HmIm	ECHPO	4-(chloromethyl)-1,3-dioxolan-2-one	7 bar, 100 °C, 4 h	338
17	ZIF-67	Co <sup>2+</sup> , HmIm	ECHPO	4-(chloromethyl)-1,3-dioxolan-2-one	10 bar, 120 °C, 6 h	339
18	Ti-ZIF	Ti <sup>4+</sup> , Im	SO	4-phenyl-1,3-dioxolan-2-one	1.72 bar, 100 °C, 8 h	340
19	MIL-101-P( <i>n</i> -Bu) <sub>3</sub> BrMIL-101-N( <i>n</i> -Bu) <sub>3</sub> Br	Cr <sup>3+</sup> , Br <sup>-</sup>	POPO	4-methyl-1,3-dioxolan-2-one	2.0 MPa, 80 °C, 8 h	341
20	F-ZIF-90	Zn <sup>2+</sup> , I <sup>-</sup>	AGE	4-((allyloxy)methyl)-1,3-dioxolan-2-one	1.17 MPa, 120 °C, 6 h	342
21	IL-ZIF-90	Zn <sup>2+</sup> , I <sup>-</sup>	PO	4-methyl-1,3-dioxolan-2-one	1.0 MPa, 120 °C, 3 h	343
22	ZnTCPPC(Br)Etim-UiO-66	Zn <sup>2+</sup> , Br <sup>-</sup>	AGE	4-((allyloxy)methyl)-1,3-dioxolan-2-one	1 bar, 140 °C, 14 h	344
23	Salen-Co(23%)C(Br <sup>-</sup> )Etim-UiO-66	Co <sup>3+</sup> , Br <sup>-</sup>	SO	4-phenyl-1,3-dioxolan-2-one	0.1 MPa, 120 °C, 12 h	345
24	UiO-67-IL	Zr <sup>4+</sup> , Br <sup>-</sup>	ECH	4-(chloromethyl)-1,3-dioxolan-2-one	1 atm, 90 °C, 12 h	346
25	FJI-C10	Cr <sup>3+</sup> , Br <sup>-</sup>	ECH	4-(chloromethyl)-1,3-dioxolan-2-one	1 bar, 80 °C, 12 h	347
26	IL@MIL101-SO <sub>3</sub> H(4)	Cr <sup>3+</sup> , Br <sup>-</sup>	ECH	4-(chloromethyl)-1,3-dioxolan-2-one	1 atm, 90 °C, 24 h	348
27	MIL-101-IMBr-6	Cr <sup>3+</sup> , Br <sup>-</sup>	PO	4-methyl-1,3-dioxolan-2-one	0.8 MPa, 80 °C, 4 h	349
28	IL/MIL-101-NH <sub>2</sub>	-COOH, NH <sub>2</sub>	PO	4-methyl-1,3-dioxolan-2-one	1.3 MPa, 120 °C, 1 h	350
29	polyILs@MIL-101	Cr <sup>3+</sup> , Br <sup>-</sup>	SO	4-phenyl-1,3-dioxolan-2-one	1 bar, 70 °C, 48 h	351
30	MIL-101-IP	Cr <sup>3+</sup> , Br <sup>-</sup>	PO	4-methyl-1,3-dioxolan-2-one	1 atm, 25 °C, 48 h	352
31	IL@ZIF-8(Zn/Co)	Zn <sup>2+</sup> , Co <sup>2+</sup> , Br <sup>-</sup>	SO	4-phenyl-1,3-dioxolan-2-one	1 atm, 100 °C, 24 h	353
32	F-IRMOF-3-2d F-IRMOF-3-4d F-IRMOF-3-6d	Zn <sub>4</sub> O, -NH <sub>2</sub> , I <sup>-</sup>	POPOPO	4-methyl-1,3-dioxolan-2-one	2 MPa, 140 °C, 1.5 h	354
33	F-IRMOF-3(MeI)  F-IRMOF-3(BuI)	Zn-OH, I <sup>-</sup>	AGE	4-((allyloxy)methyl)-1,3-dioxolan-2-one	1.2 MPa, 120 °C, 6 h	355
34	MIL-101-tmzOH-Br	Cr <sup>3+</sup> , OH <sup>-</sup> , Br <sup>-</sup>	ECH	4-(chloromethyl)-1,3-dioxolan-2-one	1 MPa, 80 °C, 2 h	356
35	2MeIm@Co-BTC-x	Co <sup>2+</sup> , MeIm	ECH/ECH	4-(chloromethyl)-1,3-dioxolan-2-one	3.0 MPa, 90 °C, 5 h, 3.0 MPa, 90 °C, 7 h	357
36	Cr-MIL-101-[BuPh <sub>3</sub> P]Br	Cr <sup>3+</sup> , Br <sup>-</sup>	ECH	4-(chloromethyl)-1,3-dioxolan-2-one	1 MPa, 80 °C, 2 h	358
37	[TMPyPmN(I)] <sup>4+</sup> (I <sup>-</sup> ) <sub>4</sub> @ZIF-8	Zn <sup>2+</sup> , Mn <sup>2+</sup> , I <sup>-</sup>	ECH	4-(chloromethyl)-1,3-dioxolan-2-one	1 bar, 100 °C, 36 h	359
38	[Zn(II)NMeTPyP] <sup>4+</sup> [I <sup>-</sup> ] <sub>4</sub> @PCN-224	Zn <sup>2+</sup> , I <sup>-</sup>	ECHPO	4-(chloromethyl)-1,3-dioxolan-2-one-4-methyl-1,3-dioxolan-2-one	0.8 MPa, 90 °C, 24 h	360

<sup>a</sup>Abbreviations: ECH = epichlorohydrin; PO = propylene oxide; SO = styrene oxide; AGE = allyl glycidyl ether; dhtp = 2,5-dihydroxyterephthalate; NH<sub>2</sub>-BDC = 2-aminoterephthalate; aip = 5-aminoisophthalic acid; NIP = 5-nitroisophthalic acid; L = N<sub>4</sub>N<sub>4</sub>'-di(pyridine-4-yl) biphenyl-4,4'-dicarboxamide; Im = imidazole; BTC = 1,3,5-benzene tricarboxylate; HmIm = 2-methylimidazole; ICA = imidazole 2-carboxaldehyde; TATAB = 4,4',4''-s-triazine-1,3,5-triyl-tri-*p*-aminobenzoic acid; DABCO = 1,4-diazabicyclo[2.2.2]-octane; MIL = Materials Institute Lavoisier; UiO = University of Oslo; BIT = Beijing Institute of Technology; Hip = 5-hydroxyisophthalic acid; Bpy = 4,4'-bipyridine; BTB = 1,3,5-tris(4-carboxyphenyl)benzene; DMF = *N,N'*-dimethylformamide; Ad = adeninate; DABA = 2,2'-dimethyl-4,4'-azobenzoate; 2-MeIm = 2-

Table 8. continued

methylimidazole; ZIF = zeolitic imidazolate framework; 2-F-BIM = 2-(furan-2-yl)-1H-benzo[d]imidazole; TCPP = 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin; IL = ionic liquid; ICA = imidazole-2-carboxyaldehyde; Etim = ethyl imidazolium; polyILs = poly(ionic liquids); IP = ionic polymer; MeI = methyl iodide; BuI = butyl iodide; IRMOF = isorecticular metal–organic framework; IMAc = 1H-imidazole-1-acetic acid; PCN = Porous coordination network; Zn(II)NMeTPyP = 5,10,15,20-tetrakis(1-methylpyridinium-4-yl) zinc(II) porphyrin; [(Etim-H<sub>2</sub>BDC)<sup>+</sup>(Br)] = 2-(3-ethyl-imidazol-1-yl)-terephthalic acid; ImBDC = 2-(imidazole-1-yl)terephthalate; salen-Co(III) - N,N'-bis(3-carboxylsalicylidene)-1,2-cyclohexanediamino cobalt(III) acetate; [BuPh<sub>3</sub>P]Br = 4-(bromobutyl)triphenylphosphonium bromide; MPImBr = 1-methyl-3-propylimidazolium bromide; HmIm = 2-methylimidazole; 2-Br-BDC = 2-bromoterephthalate; L = (Br) allylium-2-bp functionalized biphenyl dicarboxylic acid.

### Scheme 7. Plausible Reaction Mechanism for Cycloaddition of CO<sub>2</sub> and Epoxides Using Bifunctional MOFs<sup>a</sup>



<sup>a</sup>LA = Lewis acid; LB = Lewis base;  $\bar{X}$  = halide ions.

absence of any cocatalyst. The compound ZIF-78 exhibits a strong basic framework due to the presence of imidazolate (-N) linkers with the Zn centers providing the Lewis acidity. This reaction, however, was carried out at an elevated temperature and pressure.<sup>247</sup> The mechanism involves the formation of an adduct with propylene oxide and the Lewis acid centers, which is followed by the ring opening. The Lewis basic -NH groups attack on the O<sup>-</sup> ion, and CO<sub>2</sub> forms the cyclic carbonates (Scheme 8)

To date, several examples of heterogeneous bifunctional MOF catalysts have been established. The quaternary ammonium, phosphonium, imidazolium, triazolium, or pyridinium functionalized linkers can be successfully introduced as pendant groups on organic linkers, while preparing the MOFs.

This would eliminate the need to use the cocatalyst during the cycloaddition of CO<sub>2</sub> to carbonates. A N-containing ligand was introduced by the postsynthetic modification on UiO-66 to result in UiO-66-Py (pyridine) and UiO-67-Bpy (bipyridine) (Figure S6). N-Alkylation of the bipyridine and pyridine centers converts the neutral framework into an ionic one (R = Me, Et, nPr, iPr; X = I, Br, Cl) and gives rise to bifunctional behavior. This modified MOF catalyzes the cycloaddition of propylene oxide to CO<sub>2</sub>, with yields of ~99% (Figure S6).<sup>51</sup> A halide functionalized bifunctional imidazolium (Im) zirconium metal–organic framework (Zr-MOF), (Γ<sup>-</sup>)Meim-UiO-66, was shown to be an efficient and recyclable heterogeneous catalyst for the cycloaddition of CO<sub>2</sub> with epoxides without the use of cocatalysts (Figure S7). The presence of ionic Γ<sup>-</sup> in the structure acts as the Lewis base, and the Brønsted-acid (Zr-OH/Zr-OH<sub>2</sub>) helps in the formation of cyclic carbonate with 100% conversion of styrene oxide.<sup>248</sup>

The use of 2,6-di(1H-tetrazol-5-yl)naphthalene (H<sub>2</sub>NDTz) and 2,6-bis(4-(1H-tetrazol-5-yl)phenyl)naphthalene (H<sub>2</sub>NDPhTz) with cobalt gave two cobalt MOFs, which catalyze the epoxidation–carboxylation of styrene with CO<sub>2</sub> in tandem fashion. The control experiments revealed the synergic effect between the oxidant and the MOF, as ~4% of styrene oxide was obtained in the absence of catalyst. This work highlights the utility of nitrogen-rich heterocycles in MOFs for efficient development of bifunctional catalysts.<sup>156</sup>

In addition to utilizing the Lewis acidic and basic sites of MOFs toward CO<sub>2</sub> fixation, it has been shown that the use of metal nanoparticles also catalyzes such reactions. Gold nanoparticles anchored over the MOF [Zn<sub>14</sub>(L)<sub>6</sub>(O)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>] (L = 2,6-bis(2',5'-dicarboxylphenyl)pyridine) were employed toward the cycloaddition of CO<sub>2</sub> with epoxides with TBAB as the cocatalyst (Scheme 9).<sup>249</sup> A bifunctional catalyst having Ag(I) ions grafted onto N-heterocyclic carbene (NHC) sites in a MOF was found to be good catalyst for the efficient fixation of CO<sub>2</sub> with propargyl alcohols. The availability of catalytically

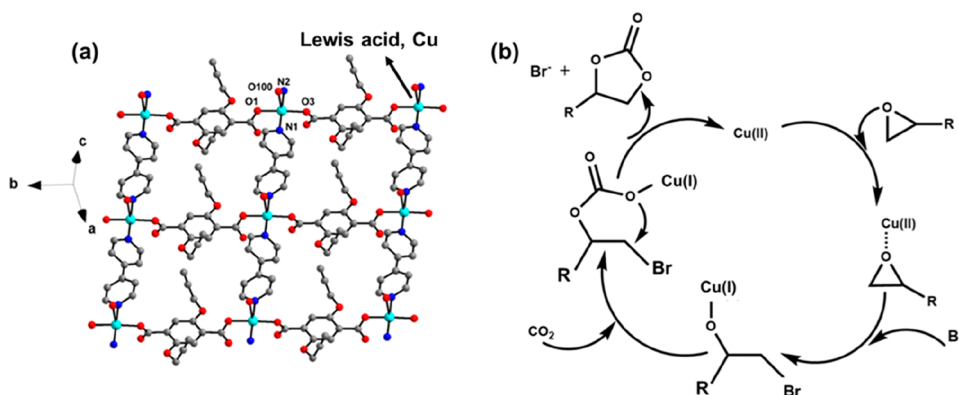
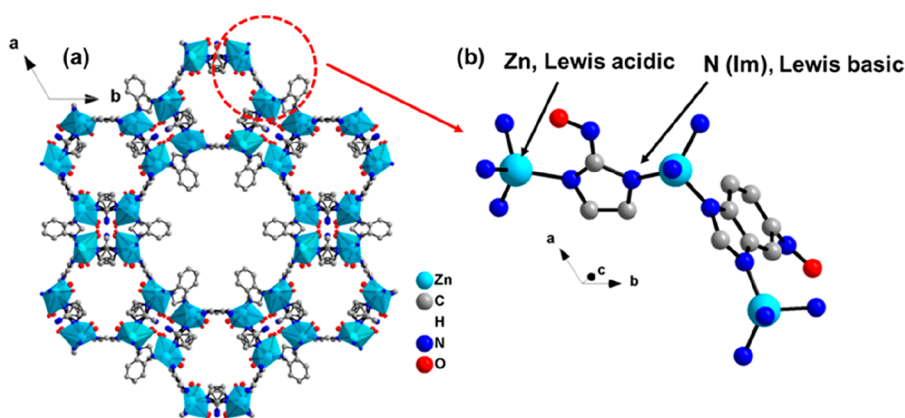
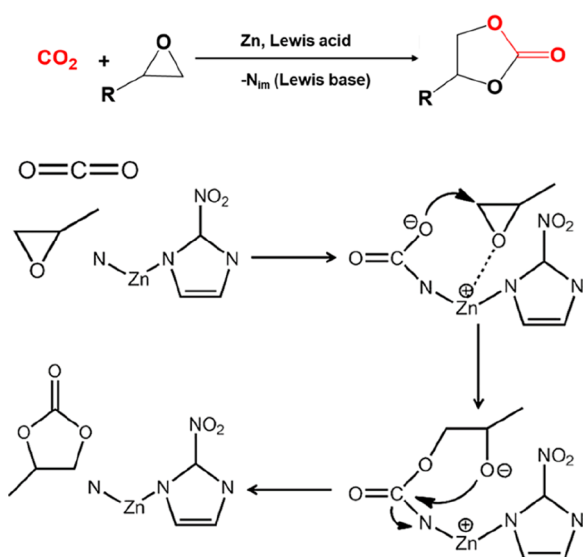


Figure 10. (a) 2D layer of the [Cu(2,5-BPTA)(bpy)(H<sub>2</sub>O)] MOF. (b) Possible mechanism for the formation of cyclic carbonate. Reproduced with permission from ref 245. Copyright 2023 American Chemical Society.



**Figure 11.** (a) Structure of ZIF-78, (b) Lewis acidic Zn center and Lewis basic N (Im) center. Reproduced with permission from ref 247. Copyright 2017 Elsevier.

**Scheme 8. Proposed Catalytic Mechanism for the CO<sub>2</sub>/PO Cycloaddition Reaction Using the ZIF-78 Heterogeneous Catalyst<sup>a</sup>**

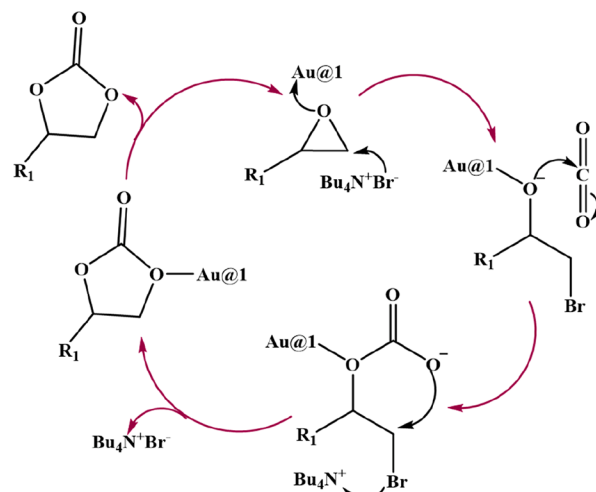


<sup>a</sup>Reproduced with permission from ref 247. Copyright 2017 Elsevier.

active alkynophilic Ag(I) and CO<sub>2</sub>-philic NHC sites in the 1D pores of the MOF helped in the fixation of CO<sub>2</sub> with propargyl alcohols (Scheme 10).<sup>250</sup> Silver nanoparticles immobilized on MOFs were shown to effectively catalyze the carboxylation of terminal alkyne with CO<sub>2</sub> to the corresponding carboxylic ester employing a porphyrin-based compound, [Zn<sub>3</sub>(C<sub>40</sub>H<sub>24</sub>N<sub>8</sub>)-(C<sub>20</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(DEF)<sub>2</sub>](DEF)<sub>3</sub> (DEF = *N,N*-diethylformamide).<sup>242</sup> In this reaction Cs<sub>2</sub>CO<sub>3</sub> acts as the cocatalyst. CO<sub>2</sub> fixation was achieved in a modified ZIF-90 compound where the carboxylate functionality provided the necessary catalytic reactive center. The catalytic activity of the modified ZIF-90-C was found to be ~100% at 50 °C for the fixation of CO<sub>2</sub> in the presence of PhSiH<sub>3</sub> as the H-donor and morpholine.<sup>238,251</sup>

The number of catalytic reactions described and discussed here is indicative of the potential that the MOFs provide as a catalyst. The examples given in this review are to highlight the utility of MOFs toward a particular reaction. For more detailed discussion about the catalytic reactions and their possible

**Scheme 9. Tentative Mechanism for CO<sub>2</sub> Cycloaddition with Epoxides<sup>a</sup>**



<sup>a</sup>TBAB = Bu<sub>4</sub>NBr. Reproduced with permission from ref 249. Copyright 2019 American Chemical Society.

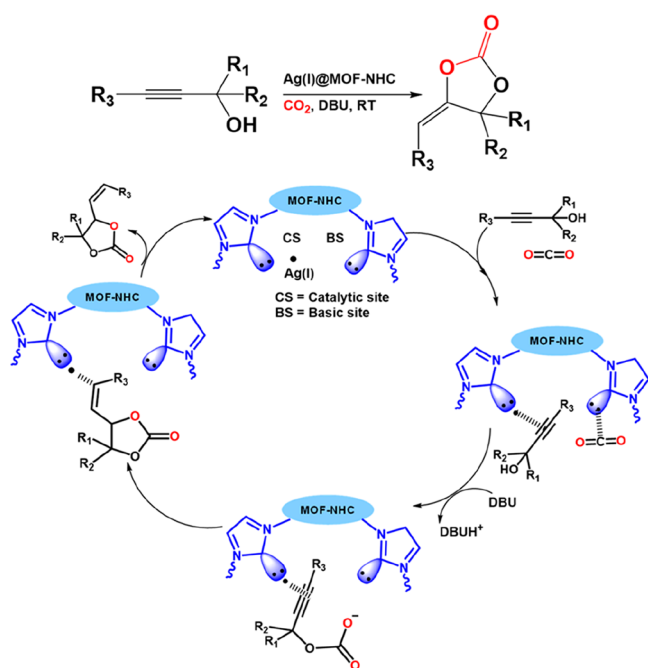
mechanism, readers may need to look at the original references.

#### 4. CONCLUDING REMARKS

The modern world is driven by the need to have clean technology where wastages are minimized. In the area of applied catalysis, the emergence of zeolites with precise and quantifiable Brønsted acidity more or less replaced the need to have corrosive ligand acids (such as HF, H<sub>2</sub>SO<sub>4</sub>, etc.) toward alkylations and isomerization of hydrocarbons.<sup>252</sup> The strategy to design new optimal catalyst, from the available knowledge of framework structures, with uniform pore/channel size having well dispersed catalytically active sites may require insights from computational design. Such an approach is likely to gain pace, and designer catalysts for a particular reaction would be feasible in the future. The flexible and ever ready synthetic chemist may be adept toward this new reality to reap the benefits. For the brighter side, as it is known in enzyme catalysis, “the placement of appropriate reactive groups in the right environment” may be enough for a designed catalyst.<sup>253</sup>

The many examples presented in this article already provide the needed enthusiasm to pursue the design strategy actively.

**Scheme 10. Proposed Mechanism for the Coupling of CO<sub>2</sub> with Propargylic Alcohol Catalyzed by Ag(I)@MOF-NHC<sup>44</sup>**



<sup>44</sup>Reproduced with permission from ref 250. Copyright 2022 Royal Society of Chemistry.

The dual functionality that provides both the acidic as well as basic sites is unique to MOFs, as these can be achieved with reasonable ease. In addition, the “ship in a bottle” type catalysts are another facet of MOF compounds, where the electronic behavior of the participating moieties can be fine-tuned to achieve better catalytic behavior. MOF catalysis can be considered to be another variant of inorganic enzyme catalysis.<sup>254</sup> Normally enzymes have a well-defined catalytic site (cavity) and molecular selectivity (shape and regio- or enantioselectivity). In MOFs, one finds the same features as exemplified in this article.

As highlighted in this article, many MOFs are useful in the synthesis of fine chemicals. The lack of stability at elevated temperatures and pressures would hinder the usage of MOFs in oil refining, petrochemical synthesis, etc. The development of MOFs as industrial catalysts needs to overcome the following requirements: (1) reproducibility and large-scale synthesis; (2) processability as extruded pellets and membranes; (3) quantifications of relative acidities; and (4) lack of quantifiable hydrophobicity and hydrophilicity. The number of MOFs that are stable and amenable to structural manipulations are limited to ZIFs, UiO, and the MIL family of compounds.<sup>255,256</sup> There is considerable scope to expand this for catalysis.

The areas where MOFs can be useful could be in converting biomass as feedstocks in the synthesis of sugars and related products.<sup>257</sup> Exploration of MOFs as supports and as composite materials also requires more attention. The structural defects that may be inherent in many MOFs need to be studied carefully, as some of the structural defects could be important for the overall catalytic activity. These are just a few of the aspects that may be worth investigating in the future so as to arrive at more robust and functional catalysts that are based on MOFs.

In addition, the use of computational approaches, especially in making newer and designer MOFs, would be beneficial. The various studies with respect to the MOF chemistry and structures indicate that they are on firm and sturdy foundations. This would be a boon for further growth in heterogeneous catalysis.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

The data underlying this study are available in the published articles and its Supporting Information.

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsorginorgau.3c00033>.

Generation of different functionality in the MOF (Scheme 1), bifunctional modification of MOF-101 (Scheme S2), synthetic process of PMoV<sub>2</sub>@DETA-MIL-101 (Scheme S3), structure of PCN-700-MB and the steps in the synthetic procedure for the conversion of PCN-700 to PCN-700-MB (Figure S1), MIL-101(Cr)-SO<sub>3</sub>H catalyzed one-pot three component condensation reaction (Figure S2), simplified model of two consecutive reactions A → B → C for the calculation of kinetic rate constants (Figure S3), synthesis of Mn(II) MOF and Pd-Au@Mn(II) MOF (Figure S4), coordination environment in Zr(H<sub>4</sub>L) with thermal ellipsoids set at 50% probability (Figure S5), syntheses of ionic UiO-67-Bpy (bipyridine) and UiO-66-Py (pyridine) (Figure S6), syntheses of Meim-UiO-66 and (Γ)Meim-UiO-66 via reticular chemistry and by a PSM method, respectively (Figure S7) (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Srinivasan Natarajan – Framework Solids Laboratory, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India; [orcid.org/0000-0002-4942-0968](https://orcid.org/0000-0002-4942-0968); Email: [snatarajan@iisc.ac.in](mailto:snatarajan@iisc.ac.in)

### Author

Krishna Manna – Framework Solids Laboratory, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsorginorgau.3c00033>

### Author Contributions

CRediT: Srinivasan Natarajan conceptualization, writing-review & editing; Krishna Manna writing-original draft.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

SN thanks the Science and Engineering research Board, (SERB) Govt. of India, for the award of a JC Bose national fellowship. SN and KM thank CSIR, Government of India, for the award of a research grant and a research fellowship.

## REFERENCES

- (1) Thomas, J. M. Turning Points in Catalysis. *Angew. Chem., Int. Ed. Engl.* **1994**, *33* (9), 913–937.
- (2) Thomas, J. M. Design, Synthesis, and in Situ Characterization of New Solid Catalysts. *Angew. Chemie Int. Ed.* **1999**, *38* (24), 3588–3628.
- (3) Yang, X.; Cao, B.; Jiang, D.; He, S.; Yuan, C.; Li, H.; Naqvi, S. R.; Wang, S. Catalytic Pyrolysis of Guaiacol on Enteromorpha-Based Biochar: A Combination of Experiments and Density Functional Theory. *Fuel Process. Technol.* **2023**, *239*, No. 107527.
- (4) Thomas, J. M.; Thomas, J. W. *Principles and Practice of Heterogeneous Catalysis*; John Wiley Sons, 2014.
- (5) James, S. L. Metal–Organic Frameworks. *Chem. Soc. Rev.* **2003**, *32* (5), 276–288.
- (6) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal–Organic Frameworks. *Science* (80–) **2013**, *341* (6149), 1230444.
- (7) Miras, H. N.; Vilà-Nadal, L.; Cronin, L. Polyoxometalate Based Open-Frameworks (POM-OFs). *Chem. Soc. Rev.* **2014**, *43* (16), 5679–5699.
- (8) Natarajan, S.; Mahata, P. Metal–Organic Framework Structures – How Closely Are They Related to Classical Inorganic Structures? *Chem. Soc. Rev.* **2009**, *38* (8), 2304–2318.
- (9) Natarajan, S.; Mandal, S. Open-Framework Structures of Transition-Metal Compounds. *Angew. Chemie Int. Ed.* **2008**, *47* (26), 4798–4828.
- (10) Zhou, H.-C.; Long, J. R.; Yaghi, O. M. Introduction to Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112* (2), 673–674.
- (11) Alhamami, M.; Doan, H.; Cheng, C. H. A Review on Breathing Behaviors of Metal–Organic-Frameworks (MOFs) for Gas Adsorption. *Materials (Basel)*. **2014**, *7* (4), 3198–3250.
- (12) Elsaidi, S. K.; Mohamed, M. H.; Banerjee, D.; Thallapally, P. K. Flexibility in Metal–Organic Frameworks: A Fundamental Understanding. *Coord. Chem. Rev.* **2018**, *358*, 125–152.
- (13) DeCoste, J. B.; Peterson, G. W. Metal–Organic Frameworks for Air Purification of Toxic Chemicals. *Chem. Rev.* **2014**, *114* (11), 5695–5727.
- (14) Thallapally, P. K.; Tian, J.; Radha Kishan, M.; Fernandez, C. A.; Dalgarno, S. J.; McGrail, P. B.; Warren, J. E.; Atwood, J. L. Flexible (Breathing) Interpenetrated Metal–Organic Frameworks for CO<sub>2</sub> Separation Applications. *J. Am. Chem. Soc.* **2008**, *130* (50), 16842–16843.
- (15) Mandal, S.; Natarajan, S.; Mani, P.; Pankajakshan, A. Post-Synthetic Modification of Metal–Organic Frameworks Toward Applications. *Adv. Funct. Mater.* **2021**, *31* (4), 2006291.
- (16) Wang, Z.; Cohen, S. M. Postsynthetic Modification of Metal–Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1315–1329.
- (17) Tanabe, K. K.; Wang, Z.; Cohen, S. M. Systematic Functionalization of a Metal–Organic Framework via a Postsynthetic Modification Approach. *J. Am. Chem. Soc.* **2008**, *130* (26), 8508–8517.
- (18) Deria, P.; Mondloch, J. E.; Karagiari, O.; Bury, W.; Hupp, J. T.; Farha, O. K. Beyond Post-Synthesis Modification: Evolution of Metal–Organic Frameworks via Building Block Replacement. *Chem. Soc. Rev.* **2014**, *43* (16), 5896–5912.
- (19) Kandiah, M.; Usseglio, S.; Svelle, S.; Olsbye, U.; Lillerud, K. P.; Tilset, M. Post-Synthetic Modification of the Metal–Organic Framework Compound UiO-66. *J. Mater. Chem.* **2010**, *20* (44), 9848–9851.
- (20) Li, J.; Huang, J.-Y.; Meng, Y.-X.; Li, L.; Zhang, L.-L.; Jiang, H.-L. Zr- and Ti-Based Metal–Organic Frameworks: Synthesis, Structures and Catalytic Applications. *Chem. Commun.* **2023**, *59* (18), 2541–2559.
- (21) Sun, Z.; Liao, Y.; Zhao, S.; Zhang, X.; Liu, Q.; Shi, X. Research Progress in Metal–Organic Frameworks (MOFs) in CO<sub>2</sub> Capture from Post-Combustion Coal-Fired Flue Gas: Characteristics, Preparation, Modification and Applications. *J. Mater. Chem. A* **2022**, *10* (10), 5174–5211.
- (22) Xu, C.; Fang, R.; Luque, R.; Chen, L.; Li, Y. Functional Metal–Organic Frameworks for Catalytic Applications. *Coord. Chem. Rev.* **2019**, *388*, 268–292.
- (23) Paz, F. A. A.; Klinowski, J.; Vilela, S. M. F.; Tome, J. P. C.; Cavaleiro, J. A. S.; Rocha, J. Ligand Design for Functional Metal–Organic Frameworks. *Chem. Soc. Rev.* **2012**, *41* (3), 1088–1110.
- (24) Chughtai, A. H.; Ahmad, N.; Younus, H. A.; Laypkov, A.; Verpoort, F. Metal–Organic Frameworks: Versatile Heterogeneous Catalysts for Efficient Catalytic Organic Transformations. *Chem. Soc. Rev.* **2015**, *44* (19), 6804–6849.
- (25) He, H.; Sun, F.; Aguila, B.; Perman, J. A.; Ma, S.; Zhu, G. A Bifunctional Metal–Organic Framework Featuring the Combination of Open Metal Sites and Lewis Basic Sites for Selective Gas Adsorption and Heterogeneous Cascade Catalysis. *J. Mater. Chem. A* **2016**, *4* (39), 15240–15246.
- (26) Gulati, S.; Vijayan, S.; Mansi, Kumar, S.; Harikumar, B.; Trivedi, M.; Varma, R. S. Recent Advances in the Application of Metal–Organic Frameworks (MOFs)-Based Nanocatalysts for Direct Conversion of Carbon Dioxide (CO<sub>2</sub>) to Value-Added Chemicals. *Coord. Chem. Rev.* **2023**, *474*, No. 214853.
- (27) Li, B.; Chrzanowski, M.; Zhang, Y.; Ma, S. Applications of Metal–Organic Frameworks Featuring Multi-Functional Sites. *Coord. Chem. Rev.* **2016**, *307*, 106–129.
- (28) Li, B.; Ma, D.; Li, Y.; Zhang, Y.; Li, G.; Shi, Z.; Feng, S.; Zaworotko, M. J.; Ma, S. Dual Functionalized Cages in Metal–Organic Frameworks via Stepwise Postsynthetic Modification. *Chem. Mater.* **2016**, *28* (13), 4781–4786.
- (29) Liu, X.; Li, J.; Li, N.; Li, B.; Bu, X.-H. Recent Advances on Metal–Organic Frameworks in the Conversion of Carbon Dioxide. *Chin. J. Chem.* **2021**, *39* (2), 440–462.
- (30) Liu, K.; Jiao, S.; Zhao, H.; Cao, F.; Ma, D. Hybridization of MOFs and Ionic POFs: A New Strategy for the Construction of Bifunctional Catalysts for CO<sub>2</sub> Cycloaddition. *Green Chem.* **2021**, *23* (4), 1766–1771.
- (31) Chen, X.; Qian, P.; Zhang, T.; Xu, Z.; Fang, C.; Xu, X.; Chen, W.; Wu, P.; Shen, Y.; Li, S.; Wu, J.; Zheng, B.; Zhang, W.; Huo, F. Catalyst Surfaces with Tunable Hydrophilicity and Hydrophobicity: Metal–Organic Frameworks toward Controllable Catalytic Selectivity. *Chem. Commun.* **2018**, *54* (32), 3936–3939.
- (32) Liu, L.; Tao, Z.-P.; Chi, H.-R.; Wang, B.; Wang, S.-M.; Han, Z.-B. The Applications and Prospects of Hydrophobic Metal–Organic Frameworks in Catalysis. *Dalt. Trans.* **2021**, *50* (1), 39–58.
- (33) Dhakshinamoorthy, A.; Asiri, A. M.; Garcia, H. Catalysis by Metal–Organic Frameworks in Water. *Chem. Commun.* **2014**, *50* (85), 12800–12814.
- (34) Li, H.-C.; Liu, W.-J.; Han, H.-X.; Yu, H.-Q. Hydrophilic Swellable Metal–Organic Framework Encapsulated Pd Nanoparticles as an Efficient Catalyst for Cr(VI) Reduction. *J. Mater. Chem. A* **2016**, *4* (30), 11680–11687.
- (35) Ding, M.; Jiang, H.-L. Improving Water Stability of Metal–Organic Frameworks by a General Surface Hydrophobic Polymerization. *CCS Chem.* **2021**, *3* (8), 2740–2748.
- (36) Yadav, A.; Kanoo, P. Metal–Organic Frameworks as Platform for Lewis-Acid-Catalyzed Organic Transformations. *Chem. – An Asian J.* **2019**, *14* (20), 3531–3551.
- (37) He, H.; Perman, J. A.; Zhu, G.; Ma, S. Metal–Organic Frameworks for CO<sub>2</sub> Chemical Transformations. *Small* **2016**, *12* (46), 6309–6324.
- (38) Ji, P.; Feng, X.; Oliveres, P.; Li, Z.; Murakami, A.; Wang, C.; Lin, W. Strongly Lewis Acidic Metal–Organic Frameworks for Continuous Flow Catalysis. *J. Am. Chem. Soc.* **2019**, *141* (37), 14878–14888.
- (39) Horike, S.; Dincă, M.; Tamaki, K.; Long, J. R. Size-Selective Lewis Acid Catalysis in a Microporous Metal–Organic Framework with Exposed Mn<sup>2+</sup> Coordination Sites. *J. Am. Chem. Soc.* **2008**, *130* (18), 5854–5855.
- (40) Alaerts, L.; Séguin, E.; Poelman, H.; Thibault-Starzyk, F.; Jacobs, P. A.; De Vos, D. E. Probing the Lewis Acidity and Catalytic Activity of the Metal–Organic Framework [Cu<sub>3</sub>(BTC)<sub>2</sub>] (BTC =

Benzene-1,3,5-Tricarboxylate). *Chem. – A Eur. J.* **2006**, *12* (28), 7353–7363.

(41) Schlichte, K.; Kratzke, T.; Kaskel, S. Improved Synthesis, Thermal Stability and Catalytic Properties of the Metal–Organic Framework Compound Cu<sub>3</sub>(BTC)<sub>2</sub>. *Microporous Mesoporous Mater.* **2004**, *73* (1), 81–88.

(42) Tanabe, K. K.; Cohen, S. M. Modular, Active, and Robust Lewis Acid Catalysts Supported on a Metal–Organic Framework. *Inorg. Chem.* **2010**, *49* (14), 6766–6774.

(43) Jiang, J.; Yaghi, O. M. Brønsted Acidity in Metal–Organic Frameworks. *Chem. Rev.* **2015**, *115* (14), 6966–6997.

(44) Li, B.; Leng, K.; Zhang, Y.; Dynes, J. J.; Wang, J.; Hu, Y.; Ma, D.; Shi, Z.; Zhu, L.; Zhang, D.; Sun, Y.; Chrzanowski, M.; Ma, S. Metal–Organic Framework Based upon the Synergy of a Brønsted Acid Framework and Lewis Acid Centers as a Highly Efficient Heterogeneous Catalyst for Fixed-Bed Reactions. *J. Am. Chem. Soc.* **2015**, *137* (12), 4243–4248.

(45) Vermoortele, F.; Ameloot, R.; Vimont, A.; Serre, C.; De Vos, D. An Amino-Modified Zr-Terephthalate Metal–Organic Framework as an Acid–Base Catalyst for Cross-Aldol Condensation. *Chem. Commun.* **2011**, *47* (5), 1521–1523.

(46) Wang, X.-S.; Liang, J.; Li, L.; Lin, Z.-J.; Bag, P. P.; Gao, S.-Y.; Huang, Y.-B.; Cao, R. An Anion Metal–Organic Framework with Lewis Basic Sites-Rich toward Charge-Exclusive Cationic Dyes Separation and Size-Selective Catalytic Reaction. *Inorg. Chem.* **2016**, *55* (5), 2641–2649.

(47) Gascon, J.; Aktay, U.; Hernandez-Alonso, M. D.; van Klink, G. P. M.; Kapteijn, F. Amino-Based Metal–Organic Frameworks as Stable Highly Active Basic Catalysts. *J. Catal.* **2009**, *261* (1), 75–87.

(48) Panchenko, V. N.; Matrosova, M. M.; Jeon, J.; Jun, J. W.; Timofeeva, M. N.; Jhung, S. H. Catalytic Behavior of Metal–Organic Frameworks in the Knoevenagel Condensation Reaction. *J. Catal.* **2014**, *316*, 251–259.

(49) Huang, Y.-B.; Liang, J.; Wang, X.-S.; Cao, R. Multifunctional Metal–Organic Framework Catalysts: Synergistic Catalysis and Tandem Reactions. *Chem. Soc. Rev.* **2017**, *46* (1), 126–157.

(50) Liu, F.; Kumar, S.; Li, S.; You, H.; Ren, P.; Zhao, L. Bifunctional Design of Stable Metal–Organic Framework Bearing Triazole–Carboxylate Mixed Ligand: Highly Efficient Heterogeneous Catalyst for Knoevenagel Condensation Reaction under Mild Conditions. *Catal. Commun.* **2020**, *142*, No. 106032.

(51) Ji, H.; Naveen, K.; Lee, W.; Kim, T. S.; Kim, D.; Cho, D.-H. Pyridinium-Functionalized Ionic Metal–Organic Frameworks Designed as Bifunctional Catalysts for CO<sub>2</sub> Fixation into Cyclic Carbonates. *ACS Appl. Mater. Interfaces* **2020**, *12* (22), 24868–24876.

(52) Hu, Y.; Zhang, J.; Huo, H.; Wang, Z.; Xu, X.; Yang, Y.; Lin, K.; Fan, R. One-Pot Synthesis of Bimetallic Metal–Organic Frameworks (MOFs) as Acid–Base Bifunctional Catalysts for Tandem Reaction. *Catal. Sci. Technol.* **2020**, *10* (2), 315–322.

(53) Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. Concurrent Tandem Catalysis. *Chem. Rev.* **2005**, *105* (3), 1001–1020.

(54) Tietze, L. F.; Beifuss, U. Sequential Transformations in Organic Chemistry: A Synthetic Strategy with a Future. *Angew. Chem., Int. Ed. Engl.* **1993**, *32* (2), 131–163.

(55) Liang, J.; Huang, Y.-B.; Cao, R. Metal–Organic Frameworks and Porous Organic Polymers for Sustainable Fixation of Carbon Dioxide into Cyclic Carbonates. *Coord. Chem. Rev.* **2019**, *378*, 32–65.

(56) Ma, D.; Li, B.; Shi, Z. Multi-Functional Sites Catalysts Based on Post-Synthetic Modification of Metal–Organic Frameworks. *Chin. Chem. Lett.* **2018**, *29* (6), 827–830.

(57) Bhattacharjee, S.; Chen, C.; Ahn, W.-S. Chromium Terephthalate Metal–Organic Framework MIL-101: Synthesis, Functionalization, and Applications for Adsorption and Catalysis. *RSC Adv.* **2014**, *4* (94), 52500–52525.

(58) Agarwal, R. A.; De, D. Selective CO<sub>2</sub> Adsorption and Lewis Acid Catalytic Activity towards Naphthimidazole Synthesis by a Zn-MOF. *Polyhedron* **2020**, *185*, No. 114584.

(59) Vermoortele, F.; Bueken, B.; Le Bars, G.; Van de Voorde, B.; Vandichel, M.; Houthoofd, K.; Vimont, A.; Daturi, M.; Waroquier, M.; Van Speybroeck, V.; Kirschhock, C.; De Vos, D. E. Synthesis Modulation as a Tool To Increase the Catalytic Activity of Metal–Organic Frameworks: The Unique Case of UiO-66(Zr). *J. Am. Chem. Soc.* **2013**, *135* (31), 11465–11468.

(60) Ohmori, O.; Fujita, M. Heterogeneous Catalysis of a Coordination Network: Cyanosilylation of Imines Catalyzed by a Cd(II)-(4,4'-Bipyridine) Square Grid Complex. *Chem. Commun.* **2004**, *14*, 1586–1587.

(61) Wu, J.-Q.; Wu, X.-Y.; Lu, J.-M.; Shi, Q.; Shao, L.-X. Highly Active La(III)-Based Metal–Organic Framework as a Heterogeneous Lewis Acid Catalyst for Friedel-Crafts Alkylation. *Chem. – A Eur. J.* **2022**, *28* (69), No. e202202441.

(62) Rahaman, M. S.; Tulaphol, S.; Hossain, M. A.; Jasinski, J. B.; Sun, N.; George, A.; Simmons, B. A.; Maihom, T.; Crocker, M.; Sathitsuksanoh, N. Cooperative Brønsted-Lewis Acid Sites Created by Phosphotungstic Acid Encapsulated Metal–Organic Frameworks for Selective Glucose Conversion to 5-Hydroxymethylfurfural. *Fuel* **2022**, *310*, No. 122459.

(63) Li, J.; Zhao, S.; Li, Z.; Liu, D.; Chi, Y.; Hu, C. Efficient Conversion of Biomass-Derived Levulinic Acid to  $\gamma$ -Valerolactone over Polyoxometalate@Zr-Based Metal–Organic Frameworks: The Synergistic Effect of Brønsted and Lewis Acidic Sites. *Inorg. Chem.* **2021**, *60* (11), 7785–7793.

(64) Ye, C.; Qi, Z.; Cai, D.; Qiu, T. Design and Synthesis of Ionic Liquid Supported Hierarchically Porous Zr Metal–Organic Framework as a Novel Brønsted–Lewis Acidic Catalyst in Biodiesel Synthesis. *Ind. Eng. Chem. Res.* **2019**, *58* (3), 1123–1132.

(65) Yabushita, M.; Li, P.; Islamoglu, T.; Kobayashi, H.; Fukuoka, A.; Farha, O. K.; Katz, A. Selective Metal–Organic Framework Catalysis of Glucose to 5-Hydroxymethylfurfural Using Phosphate-Modified NU-1000. *Ind. Eng. Chem. Res.* **2017**, *56* (25), 7141–7148.

(66) Chen, J.; Zhang, Y.; Chen, X.; Dai, S.; Bao, Z.; Yang, Q.; Ren, Q.; Zhang, Z. Cooperative Interplay of Brønsted Acid and Lewis Acid Sites in MIL-101(Cr) for Cross-Dehydrogenative Coupling of C–H Bonds. *ACS Appl. Mater. Interfaces* **2021**, *13* (9), 10845–10854.

(67) Xie, W.; Wang, H. Synthesis of Heterogenized Polyoxometalate-Based Ionic Liquids with Brønsted-Lewis Acid Sites: A Magnetically Recyclable Catalyst for Biodiesel Production from Low-Quality Oils. *J. Ind. Eng. Chem.* **2020**, *87*, 162–172.

(68) Oudi, S.; Oveisi, A. R.; Daliran, S.; Khajeh, M.; Teymouri, E. Brønsted-Lewis Dual Acid Sites in a Chromium-Based Metal–Organic Framework for Cooperative Catalysis: Highly Efficient Synthesis of Quinazolin-(4H)-1-One Derivatives. *J. Colloid Interface Sci.* **2020**, *561*, 782–792.

(69) Trickett, C. A.; Osborn Popp, T. M.; Su, J.; Yan, C.; Weisberg, J.; Huq, A.; Urban, P.; Jiang, J.; Kalmutski, M. J.; Liu, Q.; Baek, J.; Head-Gordon, M. P.; Somorjai, G. A.; Reimer, J. A.; Yaghi, O. M. Identification of the Strong Brønsted Acid Site in a Metal–Organic Framework Solid Acid Catalyst. *Nat. Chem.* **2019**, *11* (2), 170–176.

(70) Liu, P.; Redekop, E.; Gao, X.; Liu, W.-C.; Olsbye, U.; Somorjai, G. A. Oligomerization of Light Olefins Catalyzed by Brønsted-Acidic Metal–Organic Framework-808. *J. Am. Chem. Soc.* **2019**, *141* (29), 11557–11564.

(71) Rojas-Buzo, S.; Bohigues, B.; Lopes, C. W.; Meira, D. M.; Boronat, M.; Moliner, M.; Corma, A. Tailoring Lewis/Brønsted Acid Properties of MOF Nodes via Hydrothermal and Solvothermal Synthesis: Simple Approach with Exceptional Catalytic Implications. *Chem. Sci.* **2021**, *12* (29), 10106–10115.

(72) Gong, W.; Liu, Y.; Li, H.; Cui, Y. Metal–Organic Frameworks as Solid Brønsted Acid Catalysts for Advanced Organic Transformations. *Coord. Chem. Rev.* **2020**, *420*, No. 213400.

(73) Feng, L.; Wang, Y.; Yuan, S.; Wang, K.-Y.; Li, J.-L.; Day, G. S.; Qiu, D.; Cheng, L.; Chen, W.-M.; Madrahimov, S. T.; Zhou, H.-C. Porphyrinic Metal–Organic Frameworks Installed with Brønsted Acid Sites for Efficient Tandem Semisynthesis of Artemisinin. *ACS Catal.* **2019**, *9* (6), 5111–5118.

- (74) Li, X.; Huang, L.; Kochubei, A.; Huang, J.; Shen, W.; Xu, H.; Li, Q. Evolution of a Metal–Organic Framework into a Brønsted Acid Catalyst for Glycerol Dehydration to Acrolein. *ChemSusChem* **2020**, *13* (18), 5073–5079.
- (75) Li, R.; Jiang, Y.; Zhao, J.; Ramella, D.; Peng, Y.; Luan, Y. Development of a Brønsted Acid Al–MIL-53 Metal–Organic Framework Catalyst and Its Application in [4 + 2] Cycloadditions. *RSC Adv.* **2017**, *7* (55), 34591–34597.
- (76) Nguyen, L. H. T.; Nguyen, T. T. T.; Dang, M.-H. D.; Tran, P. H.; Doan, T. L. H. Heterocyclic Reaction Induced by Brønsted–Lewis Dual Acidic Hf-MOF under Microwave Irradiation. *Mol. Catal.* **2021**, *499*, No. 111291.
- (77) Qu, H.; Liu, B.; Gao, G.; Ma, Y.; Zhou, Y.; Zhou, H.; Li, L.; Li, Y.; Liu, S. Metal–Organic Framework Containing Brønsted Acidity and Lewis Acidity for Efficient Conversion Glucose to Levulinic Acid. *Fuel Process. Technol.* **2019**, *193*, 1–6.
- (78) Cheng, J.; Mao, Y.; Guo, H.; Qian, L.; Shao, Y.; Yang, W.; Park, J.-Y. Synergistic and Efficient Catalysis over Brønsted Acidic Ionic Liquid [BSO3HMIm][HSO4]–Modified Metal–Organic Framework (IRMOF-3) for Microalgal Biodiesel Production. *Fuel* **2022**, *322*, No. 124217.
- (79) Mortazavi, S.-S.; Abbasi, A.; Masteri-Farahani, M. Influence of SO3H Groups Incorporated as Brønsted Acidic Parts by Tandem Post-Synthetic Functionalization on the Catalytic Behavior of MIL-101(Cr) MOF for Methanolysis of Styrene Oxide. *Colloids Surfaces A Physicochem. Eng. Asp.* **2020**, *599*, No. 124703.
- (80) Dou, Y.; Zhang, H.; Zhou, A.; Yang, F.; Shu, L.; She, Y.; Li, J.-R. Highly Efficient Catalytic Esterification in a –SO3H-Functionalized Cr(III)-MOF. *Ind. Eng. Chem. Res.* **2018**, *57* (25), 8388–8395.
- (81) Ma, D.; Zhang, Y.; Jiao, S.; Li, J.; Liu, K.; Shi, Z. A Tri-Functional Metal–Organic Framework Heterogeneous Catalyst for Efficient Conversion of CO<sub>2</sub> under Mild and Co-Catalyst Free Conditions. *Chem. Commun.* **2019**, *55* (95), 14347–14350.
- (82) Lara-Serrano, M.; Morales-delaRosa, S.; Campos-Martin, J. M.; Abdelkader-Fernández, V. K.; Cunha-Silva, L.; Balula, S. S. One-Pot Conversion of Glucose into 5-Hydroxymethylfurfural Using MOFs and Brønsted-Acid Tandem Catalysts. *Adv. Sustain. Syst.* **2022**, *6* (5), 2100444.
- (83) Su, Y.; Chang, G.; Zhang, Z.; Xing, H.; Su, B.; Yang, Q.; Ren, Q.; Yang, Y.; Bao, Z. Catalytic Dehydration of Glucose to 5-Hydroxymethylfurfural with a Bifunctional Metal–Organic Framework. *AIChE J.* **2016**, *62* (12), 4403–4417.
- (84) Ghorbani-Vaghei, R.; Azarifar, D.; Daliran, S.; Oveisi, A. R. The UiO-66-SO<sub>3</sub>H Metal–Organic Framework as a Green Catalyst for the Facile Synthesis of Dihydro-2-Oxypyrrrole Derivatives. *RSC Adv.* **2016**, *6* (35), 29182–29189.
- (85) Fei, H.; Shin, J.; Meng, Y. S.; Adelhardt, M.; Sutter, J.; Meyer, K.; Cohen, S. M. Reusable Oxidation Catalysis Using Metal-Monocatecholato Species in a Robust Metal–Organic Framework. *J. Am. Chem. Soc.* **2014**, *136* (13), 4965–4973.
- (86) Fei, H.; Cohen, S. M. Metalation of a Thiocatechol-Functionalized Zr(IV)-Based Metal–Organic Framework for Selective C–H Functionalization. *J. Am. Chem. Soc.* **2015**, *137* (6), 2191–2194.
- (87) Liu, Y.; Li, J.-R.; Verdegaal, W. M.; Liu, T.-F.; Zhou, H.-C. Isostructural Metal–Organic Frameworks Assembled from Functionalized Diisophthalate Ligands through a Ligand-Truncation Strategy. *Chem. – A Eur. J.* **2013**, *19* (18), 5637–5643.
- (88) Rabo, J. A.; Gajda, G. J. Acid Function in Zeolites: Recent Progress. *Catal. Rev.* **1989**, *31* (4), 385–430.
- (89) Blumenfeld, A. L.; Fripiat, J. J. Characterization of Brønsted and Lewis Acidity in Zeolites by Solid-State NMR and the Recent Progress in the REDOR Technique. *Magn. Reson. Chem.* **1999**, *37* (13), S118–S125.
- (90) Weitkamp, J. Zeolites and Catalysis. *Solid State Ionics* **2000**, *131* (1), 175–188.
- (91) Masoomi, M. Y.; Morsali, A.; Dhakshinamoorthy, A.; Garcia, H. Mixed-metal MOFs: Unique Opportunities in Metal–Organic Framework (MOF) Functionality and Design. *Angew. Chem.* **2019**, *131* (43), 15330–15347.
- (92) Salama, R. S.; Manna, M. A.; Altass, H. M.; Ibrahim, A. A.; Khder, A. E.-R. S. Palladium Supported on Mixed-Metal–Organic Framework (Co–Mn-MOF-74) for Efficient Catalytic Oxidation of CO. *RSC Adv.* **2021**, *11* (8), 4318–4326.
- (93) Kalmutzki, M. J.; Hanikel, N.; Yaghi, O. M. Secondary Building Units as the Turning Point in the Development of the Reticular Chemistry of MOFs. *Sci. Adv.* **2018**, *4* (10), eaat9180.
- (94) Zhao, S.-Y.; Chen, Z.-Y.; Wei, N.; Liu, L.; Han, Z.-B. Highly Efficient Cooperative Catalysis of Single-Site Lewis Acid and Brønsted Acid in a Metal–Organic Framework for the Biginelli Reaction. *Inorg. Chem.* **2019**, *58* (12), 7657–7661.
- (95) Sun, Y.; Sun, L.; Feng, D.; Zhou, H.-C. An In Situ One-Pot Synthetic Approach towards Multivariate Zirconium MOFs. *Angew. Chemie Int. Ed.* **2016**, *55* (22), 6471–6475.
- (96) Phang, W. J.; Jo, H.; Lee, W. R.; Song, J. H.; Yoo, K.; Kim, B.; Hong, C. S. Superprotonic Conductivity of a UiO-66 Framework Functionalized with Sulfonic Acid Groups by Facile Postsynthetic Oxidation. *Angew. Chemie Int. Ed.* **2015**, *54* (17), 5142–5146.
- (97) Huang, M.; Kaliaguine, S.; Auroux, A. Lewis Basic and Lewis Acidic Sites in Zeolites. In *Studies in Surface Science and Catalysis*; Elsevier, 1995; Vol. 97, pp 311–318.
- (98) Schoonheydt, R. A.; Geerlings, P.; Pidko, E. A.; Van Santen, R. A. The Framework Basicity of Zeolites. *J. Mater. Chem.* **2012**, *22* (36), 18705–18717.
- (99) Thomas, J. M. The Ineluctable Need for in Situ Methods of Characterising Solid Catalysts as a Prerequisite to Engineering Active Sites. *Chem.—Eur. J.* **1997**, *3* (10), 1557–1562.
- (100) Thomas, J. M. On the Nature of Isolated Active Sites in Open-Structure Catalysts for the Aerial Oxidation of Alkanes. *Top. Catal.* **2001**, *15*, 85–91.
- (101) Bhadra, B. N.; Ahmed, I.; Lee, H. J.; Jung, S. H. Metal–Organic Frameworks Bearing Free Carboxylic Acids: Preparation, Modification, and Applications. *Coord. Chem. Rev.* **2022**, *450*, No. 214237.
- (102) Lee, Y.-R.; Cho, S.-M.; Ahn, W.-S.; Lee, C.-H.; Lee, K.-H.; Cho, W.-S. Facile Synthesis of an IRMOF-3 Membrane on Porous Al<sub>2</sub>O<sub>3</sub> Substrate via a Sonochemical Route. *Microporous Mesoporous Mater.* **2015**, *213*, 161–168.
- (103) Zhu, L.; Liu, X.-Q.; Jiang, H.-L.; Sun, L.-B. Metal–Organic Frameworks for Heterogeneous Basic Catalysis. *Chem. Rev.* **2017**, *117* (12), 8129–8176.
- (104) Yang, Y.; Yao, H.-F.; Xi, F.-G.; Gao, E.-Q. Amino-Functionalized Zr(IV) Metal–Organic Framework as Bifunctional Acid–Base Catalyst for Knoevenagel Condensation. *J. Mol. Catal. A Chem.* **2014**, *390*, 198–205.
- (105) Srirambalaji, R.; Hong, S.; Natarajan, R.; Yoon, M.; Hota, R.; Kim, Y.; Ho Ko, Y.; Kim, K. Tandem Catalysis with a Bifunctional Site-Isolated Lewis Acid–Brønsted Base Metal–Organic Framework, NH<sub>2</sub>-MIL-101(Al). *Chem. Commun.* **2012**, *48* (95), 11650–11652.
- (106) Sun, D.; Ye, L.; Li, Z. Visible-Light-Assisted Aerobic Photocatalytic Oxidation of Amines to Imines over NH<sub>2</sub>-MIL-125(Ti). *Appl. Catal. B Environ.* **2015**, *164*, 428–432.
- (107) Sun, L.-B.; Li, J.-R.; Park, J.; Zhou, H.-C. Cooperative Template-Directed Assembly of Mesoporous Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2012**, *134* (1), 126–129.
- (108) Lee, Y.-R.; Jang, M.-S.; Cho, H.-Y.; Kwon, H.-J.; Kim, S.; Ahn, W.-S. ZIF-8: A Comparison of Synthesis Methods. *Chem. Eng. J.* **2015**, *271*, 276–280.
- (109) Tran, U. P. N.; Le, K. K. A.; Phan, N. T. S. Expanding Applications of Metal–Organic Frameworks: Zeolite Imidazolate Framework ZIF-8 as an Efficient Heterogeneous Catalyst for the Knoevenagel Reaction. *ACS Catal.* **2011**, *1* (2), 120–127.
- (110) Kundu, T.; Manna, K.; Jana, A. K.; Natarajan, S. A Luminescent Inorganic–Organic Hybrid, [Cd(C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>O<sub>8</sub>S)-(H<sub>2</sub>O)], for the Selective and Recyclable Detection of Chromates and Dichromates in Aqueous Solution. *New J. Chem.* **2019**, *43* (33), 13263–13270.



- (111) Guo, F.; Yuan, B.; Shi, W. A Novel 2D Metal-Organic Framework with Lewis Basic Sites as a Heterogeneous Base Catalysis. *Inorg. Chem. Commun.* **2017**, *86*, 285–289.
- (112) Zhang, S.; He, H.; Sun, F.; Zhao, N.; Du, J.; Pan, Q.; Zhu, G. A Novel Adenine-Based Zinc(II) Metal-Organic Framework Featuring the Lewis Basic Sites for Heterogeneous Catalysis. *Inorg. Chem. Commun.* **2017**, *79*, 55–59.
- (113) Patel, P.; Patel, U.; Parmar, B.; Dadhania, A.; Suresh, E. Regioselective Ring-Opening of Spiro-Epoxyoxindoles by a Dual-Ligand Zinc-Based Metal–Organic Framework as an Efficient Heterogeneous Catalyst. *ACS Appl. Nano Mater.* **2022**, *5* (3), 3712–3721.
- (114) Cirujano, F. G.; Luque, R.; Dhakshinamoorthy, A. Metal-Organic Frameworks as Versatile Heterogeneous Solid Catalysts for Henry Reactions. *Molecules* **2021**, *26* (5), 1445.
- (115) Razavi, S. A. A.; Morsali, A. Function–Structure Relationship in Metal–Organic Frameworks for Mild, Green, and Fast Catalytic C–C Bond Formation. *Inorg. Chem.* **2019**, *58* (21), 14429–14439.
- (116) Qiao, J.; Zhang, B.; Yu, X.; Zou, X.; Liu, X.; Zhang, L.; Liu, Y. A Stable Y(III)-Based Amide-Functionalized Metal–Organic Framework for Propane/Methane Separation and Knoevenagel Condensation. *Inorg. Chem.* **2022**, *61* (8), 3708–3715.
- (117) Joharian, M.; Morsali, A.; Azhdari Tehrani, A.; Carlucci, L.; Proserpio, D. M. Water-Stable Fluorinated Metal–Organic Frameworks (F-MOFs) with Hydrophobic Properties as Efficient and Highly Active Heterogeneous Catalysts in Aqueous Solution. *Green Chem.* **2018**, *20* (23), 5336–5345.
- (118) Gong, Y.; Yuan, Y.; Chen, C.; Zhang, P.; Wang, J.; Khan, A.; Zhuiykov, S.; Chaemchuen, S.; Verpoort, F. Enhancing Catalytic Performance via Structure Core-Shell Metal-Organic Frameworks. *J. Catal.* **2019**, *375*, 371–379.
- (119) Gupta, V.; Mandal, S. K. A Microporous Metal–Organic Framework Catalyst for Solvent-Free Strecker Reaction and CO<sub>2</sub> Fixation at Ambient Conditions. *Inorg. Chem.* **2020**, *59* (7), 4273–4281.
- (120) Gupta, A. K.; De, D.; Bharadwaj, P. K. A NbO Type Cu(II) Metal–Organic Framework Showing Efficient Catalytic Activity in the Friedländer and Henry Reactions. *Dalt. Trans.* **2017**, *46* (24), 7782–7790.
- (121) Verma, A.; De, D.; Tomar, K.; Bharadwaj, P. K. An Amine Functionalized Metal–Organic Framework as an Effective Catalyst for Conversion of CO<sub>2</sub> and Biginelli Reactions. *Inorg. Chem.* **2017**, *56* (16), 9765–9771.
- (122) Gupta, A. K.; De, D.; Tomar, K.; Bharadwaj, P. K. A Cu(II) Metal–Organic Framework with Significant H<sub>2</sub> and CO<sub>2</sub> Storage Capacity and Heterogeneous Catalysis for the Aerobic Oxidative Amination of C(Sp<sup>3</sup>)–H Bonds and Biginelli Reactions. *Dalt. Trans.* **2018**, *47* (5), 1624–1634.
- (123) Guo, F.; Su, C.; Fan, Y.; Shi, W.; Zhang, X. Assembly of Two Self-Interpenetrating Metal–Organic Frameworks Based on a Trigonal Ligand: Syntheses, Crystal Structures, and Properties. *Inorg. Chem.* **2020**, *59* (10), 7135–7142.
- (124) Zhao, Y.; Zhu, M.; Shang, H.; Cheng, Y.; Ramella, D.; Zhu, K.; Luan, Y. UiO-67 Metal–Organic Framework Immobilized Fe<sup>3+</sup> Catalyst for Efficient Morita–Baylis–Hillman Reaction. *New J. Chem.* **2022**, *46* (7), 3199–3206.
- (125) Amarante, S. F.; Freire, M. A.; Mendes, D. T. S. L.; Freitas, L. S.; Ramos, A. L. D. Evaluation of Basic Sites of ZIFs Metal Organic Frameworks in the Knoevenagel Condensation Reaction. *Appl. Catal. A Gen.* **2017**, *548*, 47–51.
- (126) Yuan, B.; Wang, Y.; Wang, M.; Gou, G.; Li, L. Metal–organic Frameworks as Recyclable Catalysts for Efficient Esterification to Synthesize Traditional Plasticizers. *Appl. Catal. A Gen.* **2021**, *622*, No. 118212.
- (127) Bagheri, S.; Esfanidiary, N.; Yliniemi, J. Porous SB-CuI Two-Dimensional Metal-Organic Framework: The Green Catalyst towards CN Bond-Forming Reactions. *Colloids Surfaces A Physicochem. Eng. Asp.* **2022**, *637*, No. 128202.
- (128) Xing, S.; Li, J.; Niu, G.; Han, Q.; Zhang, J.; Liu, H. Chiral and Amine Groups Functionalized Polyoxometalate-Based Metal-Organic Frameworks for Synergic Catalysis in Aldol and Knoevenagel Condensations. *Mol. Catal.* **2018**, *458*, 83–88.
- (129) Boronat, M.; Climent, M. J.; Corma, A.; Iborra, S.; Montón, R.; Sabater, M. J. Bifunctional Acid–Base Ionic Liquid Organocatalysts with a Controlled Distance Between Acid and Base Sites. *Chem. – A Eur. J.* **2010**, *16* (4), 1221–1231.
- (130) Climent, M. J.; Corma, A.; Iborra, S.; Velty, A. Designing the Adequate Base Solid Catalyst with Lewis or Bronsted Basic Sites or with Acid–Base Pairs. *J. Mol. Catal. A Chem.* **2002**, *182–183*, 327–342.
- (131) Climent, M. J.; Corma, A.; Guil-López, R.; Iborra, S.; Primo, J. Use of Mesoporous MCM-41 Aluminosilicates as Catalysts in the Preparation of Fine Chemicals: A New Route for the Preparation of Jasminaldehyde with High Selectivity. *J. Catal.* **1998**, *175* (1), 70–79.
- (132) Shi, W.; Quan, Y.; Lan, G.; Ni, K.; Song, Y.; Jiang, X.; Wang, C.; Lin, W. Bifunctional Metal–Organic Layers for Tandem Catalytic Transformations Using Molecular Oxygen and Carbon Dioxide. *J. Am. Chem. Soc.* **2021**, *143* (40), 16718–16724.
- (133) Farha, O. K.; Hupp, J. T. Rational Design, Synthesis, Purification, and Activation of Metal–Organic Framework Materials. *Acc. Chem. Res.* **2010**, *43* (8), 1166–1175.
- (134) Rowsell, J. L. C.; Yaghi, O. M. Metal–Organic Frameworks: A New Class of Porous Materials. *Microporous Mesoporous Mater.* **2004**, *73* (1), 3–14.
- (135) Rosseinsky, M. J. Recent Developments in Metal–Organic Framework Chemistry: Design, Discovery, Permanent Porosity and Flexibility. *Microporous Mesoporous Mater.* **2004**, *73* (1), 15–30.
- (136) Chen, Z.; Kirlikovali, K. O.; Li, P.; Farha, O. K. Reticular Chemistry for Highly Porous Metal–Organic Frameworks: The Chemistry and Applications. *Acc. Chem. Res.* **2022**, *55* (4), 579–591.
- (137) Cohen, S. M. Postsynthetic Methods for the Functionalization of Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112* (2), 970–1000.
- (138) Stock, N.; Biswas, S. Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. *Chem. Rev.* **2012**, *112* (2), 933–969.
- (139) Babae, S.; Zarei, M.; Sepehrmansourie, H.; Zolfigol, M. A.; Rostamnia, S. Synthesis of Metal–Organic Frameworks MIL-101(Cr)-NH<sub>2</sub> Containing Phosphorous acid Functional Groups: Application for the Synthesis of N-Amino-2-Pyridone and Pyrano [2,3-c]Pyrazole Derivatives via a Cooperative Vinylogous Anomeric-Based Oxidation. *ACS Omega* **2020**, *5* (12), 6240–6249.
- (140) Yao, C.; Zhou, S.; Kang, X.; Zhao, Y.; Yan, R.; Zhang, Y.; Wen, L. A Cationic Zinc–Organic Framework with Lewis Acidic and Basic Bifunctional Sites as an Efficient Solvent-Free Catalyst: CO<sub>2</sub> Fixation and Knoevenagel Condensation Reaction. *Inorg. Chem.* **2018**, *57* (17), 11157–11164.
- (141) Xu, Z.; Zhao, Y.-Y.; Chen, L.; Zhu, C.-Y.; Li, P.; Gao, W.; Li, J.-Y.; Zhang, X.-M. Thermally Activated Bipyridyl-Based Mn-MOFs with Lewis Acid–Base Bifunctional Sites for Highly Efficient Catalytic Cycloaddition of CO<sub>2</sub> with Epoxides and Knoevenagel Condensation Reactions. *Dalt. Trans.* **2023**, *52* (12), 3671–3681.
- (142) Sarkar, A.; Mistry, S.; Natarajan, S. Friedländer, Knoevenagel, and Michael Reactions Employing the Same MOF: Synthesis, Structure, and Heterogeneous Catalytic Studies of ([Zn(1,4-NDCA)-(3-BPDB)0.5]·(DMF)(MeOH) and [Cd4(1,4-NDCA)4(3-BPDB)-4]·2(DMF)). *J. Phys. Chem. C* **2021**, *125* (49), 27230–27240.
- (143) Manna, K.; Natarajan, S. Highly Selective MOF-Based Turn-Off Luminescence Detection of Hg<sup>2+</sup> Ions in an Aqueous Medium and Its Dual Functional Catalytic Activity toward Aldol Condensation and  $\beta$ -Enamination Reactions. *Inorg. Chem.* **2023**, *62* (1), 508–519.
- (144) Huang, G.-Q.; Chen, J.; Huang, Y.-L.; Wu, K.; Luo, D.; Jin, J.-K.; Zheng, J.; Xu, S.-H.; Lu, W. Mixed-Linker Isoreticular Zn(II) Metal–Organic Frameworks as Brønsted Acid–Base Bifunctional Catalysts for Knoevenagel Condensation Reactions. *Inorg. Chem.* **2022**, *61* (21), 8339–8348.
- (145) Prasad, R. R. R.; Dawson, D. M.; Cox, P. A.; Ashbrook, S. E.; Wright, P. A.; Clarke, M. L. A Bifunctional MOF Catalyst Containing

- Metal–Phosphine and Lewis Acidic Active Sites. *Chem. – A Eur. J.* **2018**, *24* (57), 15309–15318.
- (146) Rostamnia, S.; Alamgholilloo, H.; Jafari, M. Ethylene Diamine Post-Synthesis Modification on Open Metal Site Cr-MOF to Access Efficient Bifunctional Catalyst for the Hantzsch Condensation Reaction. *Appl. Organomet. Chem.* **2018**, *32* (8), No. e4370.
- (147) Madasamy, K.; Kumaraguru, S.; Sankar, V.; Mannathan, S.; Kathiresan, M. A Zn Based Metal Organic Framework as a Heterogeneous Catalyst for C–C Bond Formation Reactions. *New J. Chem.* **2019**, *43* (9), 3793–3800.
- (148) Cirujano, F. G.; Martín, N.; Fu, G.; Jia, C.; De Vos, D. Cooperative Acid–Base Bifunctional Ordered Porous Solids in Sequential Multi-Step Reactions: MOF vs. Mesoporous Silica. *Catal. Sci. Technol.* **2020**, *10* (6), 1796–1802.
- (149) Anamika; Yadav, C. L.; Drew, M. G. B.; Kumar, K.; Singh, N. Ferrocene-Functionalized Dithiocarbamate Zinc(II) Complexes as Efficient Bifunctional Catalysts for the One-Pot Synthesis of Chromene and Imidazopyrimidine Derivatives via Knoevenagel Condensation Reaction. *Inorg. Chem.* **2021**, *60* (9), 6446–6462.
- (150) Zhang, Y.-Y.; Liu, Q.; Zhang, L.-Y.; Bao, Y.-M.; Tan, J.-Y.; Zhang, N.; Zhang, J.-Y.; Liu, Z.-J. MOFs Assembled from C3 Symmetric Ligands: Structure, Iodine Capture and Role as Bifunctional Catalysts towards the Oxidation–Knoevenagel Cascade Reaction. *Dalt. Trans.* **2021**, *50* (2), 647–659.
- (151) Miao, Z.; Luan, Y.; Qi, C.; Ramella, D. The Synthesis of a Bifunctional Copper Metal Organic Framework and Its Application in the Aerobic Oxidation/Knoevenagel Condensation Sequential Reaction. *Dalt. Trans.* **2016**, *45* (35), 13917–13924.
- (152) Bohigues, B.; Rojas-Buzo, S.; Moliner, M.; Corma, A. Coordinatively Unsaturated Hf-MOF-808 Prepared via Hydrothermal Synthesis as a Bifunctional Catalyst for the Tandem N-Alkylation of Amines with Benzyl Alcohol. *ACS Sustain. Chem. Eng.* **2021**, *9* (47), 15793–15806.
- (153) Sun, J.; Abednatanzi, S.; Chen, H.; Liu, Y.-Y.; Leus, K.; Van Der Voort, P. Bifunctional Noble-Metal-Free Catalyst for the Selective Aerobic Oxidation–Knoevenagel One-Pot Reaction: Encapsulation of Polyoxometalates into an Alkylamine-Modified MIL-101 Framework. *ACS Appl. Mater. Interfaces* **2021**, *13* (20), 23558–23566.
- (154) Hu, Y.-H.; Wang, J.-C.; Yang, S.; Li, Y.-A.; Dong, Y.-B. CuI@UiO-67-IM: A MOF-Based Bifunctional Composite Triphase-Transfer Catalyst for Sequential One-Pot Azide–Alkyne Cycloaddition in Water. *Inorg. Chem.* **2017**, *56* (14), 8341–8347.
- (155) Abazari, R.; Sanati, S.; Morsali, A.; Kirillov, A. M.; Slawin, A. M. Z.; Carpenter-Warren, C. L. Simultaneous Presence of Open Metal Sites and Amine Groups on a 3D Dy(III)-Metal–Organic Framework Catalyst for Mild and Solvent-Free Conversion of CO<sub>2</sub> to Cyclic Carbonates. *Inorg. Chem.* **2021**, *60* (3), 2056–2067.
- (156) Valverde-González, A.; Borrallo-Aniceto, M. C.; Díaz, U.; Maya, E. M.; Gándara, F.; Sánchez, F.; Iglesias, M. Nitrogen-Rich Cobalt (II) MOFs as Efficient Bifunctional Catalysts for Single or Tandem Oxidation and CO<sub>2</sub> Conversion Reactions. *J. CO<sub>2</sub> Util.* **2023**, *67*, No. 102298.
- (157) Parshamoni, S.; Telangae, J.; Sanda, S.; Konar, S. A Copper-Based Metal–Organic Framework Acts as a Bifunctional Catalyst for the Homocoupling of Arylboronic Acids and Epoxidation of Olefins. *Chem. – An Asian J.* **2016**, *11* (4), 540–547.
- (158) Hu, L.; Hao, G.-X.; Luo, H.-D.; Ke, C.-X.; Shi, G.; Lin, J.; Lin, X.-M.; Qazi, U. Y.; Cai, Y.-P. Bifunctional 2D Cd(II)-Based Metal–Organic Framework as Efficient Heterogeneous Catalyst for the Formation of C–C Bond. *Cryst. Growth Des.* **2018**, *18* (5), 2883–2889.
- (159) Chen, J.; Zhang, Z.; Bao, Z.; Su, Y.; Xing, H.; Yang, Q.; Ren, Q. Functionalized Metal–Organic Framework as a Biomimetic Heterogeneous Catalyst for Transfer Hydrogenation of Imines. *ACS Appl. Mater. Interfaces* **2017**, *9* (11), 9772–9777.
- (160) Feng, W.; Tie, X.; Duan, X.; Yan, S.; Fang, S.; Sun, P.; Gan, L.; Wang, T. Covalent Immobilization of Phosphotungstic Acid and Amino Acid on Metal–Organic Frameworks with Different Structures: Acid–Base Bifunctional Heterogeneous Catalyst for the Production of Biodiesel from Insect Lipid. *Renew. Energy* **2023**, *210*, 26–39.
- (161) Behr, A.; Vorholt, A. J.; Ostrowski, K. A.; Seidensticker, T. Towards Resource Efficient Chemistry: Tandem Reactions with Renewables. *Green Chem.* **2014**, *16* (3), 982–1006.
- (162) Vilches-Herrera, M.; Domke, L.; Börner, A. Isomerization–Hydroformylation Tandem Reactions. *ACS Catal.* **2014**, *4* (6), 1706–1724.
- (163) Zieliński, G. K.; Grell, K. Tandem Catalysis Utilizing Olefin Metathesis Reactions. *Chem.–Eur. J.* **2016**, *22* (28), 9440–9454.
- (164) Wang, J.; Yang, T.; Chen, H.; Xu, Y.-N.; Yu, L.-F.; Liu, T.; Tang, J.; Yi, Z.; Yang, C.-G.; Xue, W.; Yang, F. The Synthesis and Antistaphylococcal Activity of 9, 13-Disubstituted Berberine Derivatives. *Eur. J. Med. Chem.* **2017**, *127*, 424–433.
- (165) Liu, H.; Xi, F.-G.; Sun, W.; Yang, N.-N.; Gao, E.-Q. Amino- and Sulfo-Bifunctionalized Metal–Organic Frameworks: One-Pot Tandem Catalysis and the Catalytic Sites. *Inorg. Chem.* **2016**, *55* (12), 5753–5755.
- (166) Mistry, S.; Sarkar, A.; Natarajan, S. New Bifunctional Metal–Organic Frameworks and Their Utilization in One-Pot Tandem Catalytic Reactions. *Cryst. Growth Des.* **2019**, *19* (2), 747–755.
- (167) Hu, X.-J.; Li, Z.-X.; Xue, H.; Huang, X.; Cao, R.; Liu, T.-F. Designing a Bifunctional Brønsted Acid–Base Heterogeneous Catalyst Through Precise Installation of Ligands on Metal–Organic Frameworks. *CCS Chem.* **2020**, *2* (1), 616–622.
- (168) Li, B.; Zhang, Y.; Ma, D.; Li, L.; Li, G.; Li, G.; Shi, Z.; Feng, S. A Strategy toward Constructing a Bifunctionalized MOF Catalyst: Post-Synthetic Modification of MOFs on Organic Ligands and Coordinatively Unsaturated Metal Sites. *Chem. Commun.* **2012**, *48* (49), 6151–6153.
- (169) Lee, Y.-R.; Chung, Y.-M.; Ahn, W.-S. A New Site-Isolated Acid–Base Bifunctional Metal–Organic Framework for One-Pot Tandem Reaction. *RSC Adv.* **2014**, *4* (44), 23064–23067.
- (170) Saikia, M.; Saikia, L. Sulfonic Acid-Functionalized MIL-101(Cr) as a Highly Efficient Heterogeneous Catalyst for One-Pot Synthesis of 2-Amino-4H-Chromenes in Aqueous Medium. *RSC Adv.* **2016**, *6* (19), 15846–15853.
- (171) Sarkar, A.; Mistry, S.; Bhattacharya, S.; Natarajan, S. Multistep Cascade Catalytic Reactions Employing Bifunctional Framework Compounds. *Inorg. Chem.* **2023**, *62*, 11142.
- (172) Luo, S.; Zeng, Z.; Zeng, G.; Liu, Z.; Xiao, R.; Chen, M.; Tang, L.; Tang, W.; Lai, C.; Cheng, M.; Shao, B.; Liang, Q.; Wang, H.; Jiang, D. Metal Organic Frameworks as Robust Host of Palladium Nanoparticles in Heterogeneous Catalysis: Synthesis, Application, and Prospect. *ACS Appl. Mater. Interfaces* **2019**, *11* (36), 32579–32598.
- (173) Li, X.; Zhang, B.; Tang, L.; Goh, T. W.; Qi, S.; Volkov, A.; Pei, Y.; Qi, Z.; Tsung, C.-K.; Stanley, L.; Huang, W. Cooperative Multifunctional Catalysts for Nitrone Synthesis: Platinum Nanoclusters in Amine-Functionalized Metal–Organic Frameworks. *Angew. Chemie Int. Ed.* **2017**, *56* (51), 16371–16375.
- (174) Dhakshinamoorthy, A.; Asiri, A. M.; Garcia, H. Metal Organic Frameworks as Versatile Hosts of Au Nanoparticles in Heterogeneous Catalysis. *ACS Catal.* **2017**, *7* (4), 2896–2919.
- (175) Luo, W.; Cao, W.; Bruijninx, P. C. A.; Lin, L.; Wang, A.; Zhang, T. Zeolite-Supported Metal Catalysts for Selective Hydrodeoxygenation of Biomass-Derived Platform Molecules. *Green Chem.* **2019**, *21* (14), 3744–3768.
- (176) Bailie, J. E.; Hutchings, G. J.; O’Leary, S. Supported Catalysts. *Encycl. Mater. Sci. Technol.* **2001**, 8986–8990.
- (177) Parker, G. J. Guided-Wave Optical Communications: Materials. *Encycl. Mater. Sci. Technol.* **2001**, 3703–3707.
- (178) Xiong, M.; Gao, Z.; Qin, Y. Spillover in Heterogeneous Catalysis: New Insights and Opportunities. *ACS Catal.* **2021**, *11* (5), 3159–3172.
- (179) Rao, C. N. R.; Kulkarni, G. U.; Thomas, P. J.; Edwards, P. P. Metal Nanoparticles and Their Assemblies. *Chem. Soc. Rev.* **2000**, *29* (1), 27–35.

- (180) Rajumon, M. K.; Prabhakaran, K.; Rao, C. N. R. Adsorption of Oxygen on (100), (110) and (111) Surfaces of Ag, Cu and Ni: An Electron Spectroscopic Study. *Surf. Sci.* **1990**, *233* (1), L237–L242.
- (181) Lingampalli, S. R.; Ayyub, M. M.; Magesh, G.; Rao, C. N. R. Photocatalytic Reduction of CO<sub>2</sub> by Employing ZnO/Ag<sub>1</sub>-XCu<sub>x</sub>/CdS and Related Heterostructures. *Chem. Phys. Lett.* **2018**, *691*, 28–32.
- (182) Ayyappan, S.; Gopalan, R. S.; Subbanna, G. N.; Rao, C. N. R. Nanoparticles of Ag, Au, Pd, and Cu Produced by Alcohol Reduction of the Salts. *J. Mater. Res.* **1997**, *12* (2), 398–401.
- (183) Osborn, J. A.; Wilkinson, G.; Mrowca, J. J. Tris-(Triphenylphosphine)Halorhodium(I). *Inorganic Syntheses; Inorganic Syntheses*; 1967; pp 67–71.
- (184) Knowles, W. S. Asymmetric Hydrogenations (Nobel Lecture). *Angew. Chemie Int. Ed.* **2002**, *41* (12), 1998–2007.
- (185) Fihri, A.; Bouhrara, M.; Nekoueshahraki, B.; Basset, J.-M.; Polshettiwar, V. Nanocatalysts for Suzuki Cross-Coupling Reactions. *Chem. Soc. Rev.* **2011**, *40* (10), 5181–5203.
- (186) Bodkin, J. A.; McLeod, M. D. The Sharpless Asymmetric Aminohydroxylation. *J. Chem. Soc. Perkin Trans. 1* **2002**, No. 24, 2733–2746.
- (187) Hoyle, C. E.; Bowman, C. N. Thiol–Ene Click Chemistry. *Angew. Chemie Int. Ed.* **2010**, *49* (9), 1540–1573.
- (188) Mukherjee, S.; Das, A.; Das, A. K.; Sheriff, A.; Sunny, K.; Nair, A. S.; Bhandary, S.; Bhowal, R.; Chopra, D.; Pathak, B.; Yamazoe, S.; Mandal, S. Single Cu Atom Doping on Au<sub>11</sub> Nanocluster: Its Implication toward Selectivity in C–C Coupling Reaction. *Chem. Mater.* **2023**, *35* (4), 1659–1666.
- (189) Mukherjee, S.; Jayakumar, D.; Mandal, S. Insight into the Size Evolution Transformation Process of the Fcc-Based Au<sub>28</sub>(SR)<sub>20</sub> Nanocluster. *J. Phys. Chem. C* **2021**, *125* (22), 12149–12154.
- (190) Pradeep, T.; Anshup. Noble Metal Nanoparticles for Water Purification: A Critical Review. *Thin Solid Films* **2009**, *517* (24), 6441–6478.
- (191) Tom, R. T.; Nair, A. S.; Singh, N.; Aslam, M.; Nagendra, C. L.; Philip, R.; Vijayamohan, K.; Pradeep, T. Freely Dispersible Au@TiO<sub>2</sub>, Au@ZrO<sub>2</sub>, Ag@TiO<sub>2</sub>, and Ag@ZrO<sub>2</sub> Core–Shell Nanoparticles: One-Step Synthesis, Characterization, Spectroscopy, and Optical Limiting Properties. *Langmuir* **2003**, *19* (8), 3439–3445.
- (192) Jain, P.; Pradeep, T. Potential of Silver Nanoparticle-Coated Polyurethane Foam as an Antibacterial Water Filter. *Biotechnol. Bioeng.* **2005**, *90* (1), 59–63.
- (193) Maschmeyer, T.; Rey, F.; Sankar, G.; Thomas, J. M. Heterogeneous Catalysts Obtained by Grafting Metallocene Complexes onto Mesoporous Silica. *Nature* **1995**, *378* (6553), 159–162.
- (194) Chen, J.; Li, Q.; Xu, R.; Xiao, F. Distinguishing the Silanol Groups in the Mesoporous Molecular Sieve MCM-41. *Angew. Chem., Int. Ed. Engl.* **1996**, *34* (23–24), 2694–2696.
- (195) Oldroyd, R. D.; Thomas, J. M.; Maschmeyer, T.; MacFaul, P. A.; Snelgrove, D. W.; Ingold, K. U.; Wayner, D. D. M. The Titanium (IV)-Catalyzed Epoxidation of Alkenes by Tert-Alkyl Hydroperoxides. *Angew. Chem., Int. Ed. Engl.* **1996**, *35* (23–24), 2787–2790.
- (196) Ploetz, E.; Engelke, H.; Lächelt, U.; Wuttke, S. The Chemistry of Reticular Framework Nanoparticles: MOF, ZIF, and COF Materials. *Adv. Funct. Mater.* **2020**, *30* (41), 1909062.
- (197) Wang, T.; Gao, L.; Hou, J.; Herou, S. J. A.; Griffiths, J. T.; Li, W.; Dong, J.; Gao, S.; Titirici, M.-M.; Kumar, R. V.; Cheetham, A. K.; Bao, X.; Fu, Q.; Smoukov, S. K. Rational Approach to Guest Confinement inside MOF Cavities for Low-Temperature Catalysis. *Nat. Commun.* **2019**, *10* (1), 1340.
- (198) Wang, J.-S.; Jin, F.-Z.; Ma, H.-C.; Li, X.-B.; Liu, M.-Y.; Kan, J.-L.; Chen, G.-J.; Dong, Y.-B. Au@Cu(II)-MOF: Highly Efficient Bifunctional Heterogeneous Catalyst for Successive Oxidation–Condensation Reactions. *Inorg. Chem.* **2016**, *55* (13), 6685–6691.
- (199) Manna, K.; Suresh Kumar, B.; Maity, T.; Natarajan, S. C–C Coupling of Aryl Chlorides and Reduction of Nitroarenes to Amines Employing Recyclable Heterogeneous Green Catalysts. *ChemNanoMat* **2022**, *8* (6), No. e202200081.
- (200) Hu, P.; Morabito, J. V.; Tsung, C.-K. Core–Shell Catalysts of Metal Nanoparticle Core and Metal–Organic Framework Shell. *ACS Catal.* **2014**, *4* (12), 4409–4419.
- (201) Yang, Q.; Xu, Q.; Jiang, H.-L. Metal–Organic Frameworks Meet Metal Nanoparticles: Synergistic Effect for Enhanced Catalysis. *Chem. Soc. Rev.* **2017**, *46* (15), 4774–4808.
- (202) Moon, H. R.; Lim, D.-W.; Suh, M. P. Fabrication of Metal Nanoparticles in Metal–Organic Frameworks. *Chem. Soc. Rev.* **2013**, *42* (4), 1807–1824.
- (203) Rösler, C.; Fischer, R. A. Metal–Organic Frameworks as Hosts for Nanoparticles. *CrystEngComm* **2015**, *17* (2), 199–217.
- (204) Sun, J.-L.; Chen, Y.-Z.; Ge, B.-D.; Li, J.-H.; Wang, G.-M. Three-Shell Cu@Co@Ni Nanoparticles Stabilized with a Metal–Organic Framework for Enhanced Tandem Catalysis. *ACS Appl. Mater. Interfaces* **2019**, *11* (1), 940–947.
- (205) Jana, A. K.; Hota, R.; Natarajan, S. Palladium Nanoparticles Encapsulated in [M(C<sub>19</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O] (M = Co and Mn) as a Potential Catalyst for the Homocoupling of Aryl Halides. *Cryst. Growth Des.* **2016**, *16* (12), 6992–6999.
- (206) Parmeggiani, C.; Matassini, C.; Cardona, F. A Step Forward towards Sustainable Aerobic Alcohol Oxidation: New and Revised Catalysts Based on Transition Metals on Solid Supports. *Green Chem.* **2017**, *19* (9), 2030–2050.
- (207) Dhakshinamoorthy, A.; Garcia, H. Catalysis by Metal Nanoparticles Embedded on Metal–Organic Frameworks. *Chem. Soc. Rev.* **2012**, *41* (15), 5262–5284.
- (208) Ndolomingo, M. J.; Bingwa, N.; Meijboom, R. Review of Supported Metal Nanoparticles: Synthesis Methodologies, Advantages and Application as Catalysts. *J. Mater. Sci.* **2020**, *55* (15), 6195–6241.
- (209) Cai, J.; Zhuang, Y.; Chen, Y.; Xiao, L.; Zhao, Y.; Jiang, X.; Hou, L.; Li, Z. Co–MOF-74@Cu–MOF-74 Derived Bifunctional Co–C@Cu–C for One-Pot Production of 1, 4-Diphenyl-1, 3-Butadiene from Phenylacetylene. *ChemCatChem.* **2020**, *12* (24), 6241–6247.
- (210) Hao, M.; Qiu, M.; Yang, H.; Hu, B.; Wang, X. Recent Advances on Preparation and Environmental Applications of MOF-Derived Carbons in Catalysis. *Sci. Total Environ.* **2021**, *760*, No. 143333.
- (211) Wen, M.; Cui, Y.; Kuwahara, Y.; Mori, K.; Yamashita, H. Non-Noble-Metal Nanoparticle Supported on Metal–Organic Framework as an Efficient and Durable Catalyst for Promoting H<sub>2</sub> Production from Ammonia Borane under Visible Light Irradiation. *ACS Appl. Mater. Interfaces* **2016**, *8* (33), 21278–21284.
- (212) Konnerth, H.; Matsagar, B. M.; Chen, S. S.; Precht, M. H. G.; Shieh, F.-K.; Wu, K. C.-W. Metal–Organic Framework (MOF)-Derived Catalysts for Fine Chemical Production. *Coord. Chem. Rev.* **2020**, *416*, No. 213319.
- (213) Pérez-Mayoral, E.; Godino-Ojer, M.; Matos, I.; Bernardo, M. Opportunities from Metal Organic Frameworks to Develop Porous Carbons Catalysts Involved in Fine Chemical Synthesis. *Catalysts* **2023**, *13* (3), 541.
- (214) Fu, Y.; Zhai, X.; Wang, S.; Shao, L.; Bai, X.-J.; Su, Z.-S.; Liu, Y.-L.; Zhang, L.-Y.; Chen, J.-Y. Fabrication of Metal Nanoparticle Composites by Slow Chemical Reduction of Metal–Organic Frameworks. *Inorg. Chem.* **2021**, *60* (21), 16447–16454.
- (215) Li, Y.-A.; Yang, S.; Liu, Q.-K.; Chen, G.-J.; Ma, J.-P.; Dong, Y.-B. Pd(0)@UiO-68-AP: Chelation-Directed Bifunctional Heterogeneous Catalyst for Stepwise Organic Transformations. *Chem. Commun.* **2016**, *52* (39), 6517–6520.
- (216) Hinde, C. S.; Webb, W. R.; Chew, B. K. J.; Tan, H. R.; Zhang, W.-H.; Hor, T. S. A.; Raja, R. Utilisation of Gold Nanoparticles on Amine-Functionalised UiO-66 (NH<sub>2</sub>-UiO-66) Nanocrystals for Selective Tandem Catalytic Reactions. *Chem. Commun.* **2016**, *52* (39), 6557–6560.
- (217) Chen, G.-J.; Ma, H.-C.; Xin, W.-L.; Li, X.-B.; Jin, F.-Z.; Wang, J.-S.; Liu, M.-Y.; Dong, Y.-B. Dual Heterogeneous Catalyst Pd–Au@Mn(II)-MOF for One-Pot Tandem Synthesis of Imines from Alcohols and Amines. *Inorg. Chem.* **2017**, *56* (1), 654–660.

- (218) Zhang, Y.-Y.; Li, J.-X.; Ding, L.-L.; Liu, L.; Wang, S.-M.; Han, Z.-B. Palladium Nanoparticles Encapsulated in the MIL-101-Catalyzed One-Pot Reaction of Alcohol Oxidation and Aldimine Condensation. *Inorg. Chem.* **2018**, *57* (21), 13586–13593.
- (219) Moreno, J. M.; Velty, A.; Díaz, U. MOFs Based on 1D Structural Sub-Domains with Brønsted Acid and Redox Active Sites as Effective Bi-Functional Catalysts. *Catal. Sci. Technol.* **2020**, *10* (11), 3572–3585.
- (220) Jiang, W.-L.; Fu, Q.-J.; Yao, B.-J.; Ding, L.-G.; Liu, C.-X.; Dong, Y.-B. Smart PH-Responsive Polymer-Tethered and Pd NP-Loaded NMOF as the Pickering Interfacial Catalyst for One-Pot Cascade Biphasic Reaction. *ACS Appl. Mater. Interfaces* **2017**, *9* (41), 36438–36446.
- (221) Guo, Y.; Feng, L.; Wu, C.; Wang, X.; Zhang, X. Synthesis of 3D-Ordered Macro/Microporous Yolk–Shelled Nanoreactor with Spatially Separated Functionalities for Cascade Reaction. *ACS Appl. Mater. Interfaces* **2019**, *11* (37), 33978–33986.
- (222) Zhang, X.; Chen, L.; Li, Y.; Li, H.; Xie, Z.; Kuang, Q.; Zheng, L. Palladium NPs Supported on Sulfonic Acid Functionalized Metal–Organic Frameworks as Catalysts for Biomass Cascade Reactions. *Dalt. Trans.* **2019**, *48* (17), 5515–5519.
- (223) Kulkarni, B. B.; Kanakikodi, K. S.; Maradur, S. P. Synergistic Catalytic Activity of Core-Shell Pd@UiO-66(Hf) MOF Catalyst for the One-Pot Hydrogenation-Esterification of Furfural. *Microporous Mesoporous Mater.* **2022**, *343*, No. 112147.
- (224) Cheng, L.; Zhao, K.; Zhang, Q.; Li, Y.; Zhai, Q.; Chen, J.; Lou, Y. Chiral Proline-Decorated Bifunctional Pd@NH<sub>2</sub>-UiO-66 Catalysts for Efficient Sequential Suzuki Coupling/Asymmetric Aldol Reactions. *Inorg. Chem.* **2020**, *59* (12), 7991–8001.
- (225) Federsel, C.; Jackstell, R.; Beller, M. State-of-the-Art Catalysts for Hydrogenation of Carbon Dioxide. *Angew. Chemie Int. Ed.* **2010**, *49* (36), 6254–6257.
- (226) Dalton, D. M.; Rovis, T. C–H Carboxylation Takes Gold. *Nat. Chem.* **2010**, *2* (9), 710–711.
- (227) Tundo, P.; Selva, M. The Chemistry of Dimethyl Carbonate. *Acc. Chem. Res.* **2002**, *35* (9), 706–716.
- (228) Yoshida, S.; Fukui, K.; Kikuchi, S.; Yamada, T. Silver-Catalyzed Preparation of Oxazolidinones from Carbon Dioxide and Propargylic Amines. *Chem. Lett.* **2009**, *38* (8), 786–787.
- (229) Sakakura, T.; Kohno, K. The Synthesis of Organic Carbonates from Carbon Dioxide. *Chem. Commun.* **2009**, *11*, 1312–1330.
- (230) Federsel, C.; Jackstell, R.; Beller, M. Moderne Katalysatoren Zur Hydrierung von Kohlendioxid. *Angew. Chem.* **2010**, *122* (36), 6392–6395.
- (231) Maeda, C.; Miyazaki, Y.; Ema, T. Recent Progress in Catalytic Conversions of Carbon Dioxide. *Catal. Sci. Technol.* **2014**, *4* (6), 1482–1497.
- (232) Huang, K.; Sun, C.-L.; Shi, Z.-J. Transition-Metal-Catalyzed C–C Bond Formation through the Fixation of Carbon Dioxide. *Chem. Soc. Rev.* **2011**, *40* (5), 2435–2452.
- (233) Paddock, R. L.; Nguyen, S. T. Chemical CO<sub>2</sub> Fixation: Cr (III) Salen Complexes as Highly Efficient Catalysts for the Coupling of CO<sub>2</sub> and Epoxides. *J. Am. Chem. Soc.* **2001**, *123* (46), 11498–11499.
- (234) Yaashikaa, P. R.; Kumar, P. S.; Varjani, S. J.; Saravanan, A. A Review on Photochemical, Biochemical and Electrochemical Transformation of CO<sub>2</sub> into Value-Added Products. *J. CO<sub>2</sub> Util.* **2019**, *33*, 131–147.
- (235) Qiao, Y.; Yi, J.; Wu, S.; Liu, Y.; Yang, S.; He, P.; Zhou, H. Li-CO<sub>2</sub> Electrochemistry: A New Strategy for CO<sub>2</sub> Fixation and Energy Storage. *Joule* **2017**, *1* (2), 359–370.
- (236) Li, H.; Opgenorth, P. H.; Wernick, D. G.; Rogers, S.; Wu, T.-Y.; Higashide, W.; Malati, P.; Huo, Y.-X.; Cho, K. M.; Liao, J. C. Integrated Electromicrobial Conversion of CO<sub>2</sub> to Higher Alcohols. *Science (80-)* **2012**, *335* (6076), 1596.
- (237) Zhu, K.; Li, Y.; Li, Z.; Liu, Y.; Wu, H.; Li, H. In Situ Activation of COOH-Functionalized ZIF-90-Enabled Reductive CO<sub>2</sub>N-Formylation. *Chem. Commun.* **2022**, *58* (91), 12712–12715.
- (238) Li, Z.; Li, H.; Yang, S. Carboxylate-Functionalized Zeolitic Imidazolate Framework Enables Catalytic N-Formylation Using Ambient CO<sub>2</sub>. *Adv. Sustainable Syst.* **2022**, *6* (3), 2100380.
- (239) Gao, Z.; Liang, L.; Zhang, X.; Xu, P.; Sun, J. Facile One-Pot Synthesis of Zn/Mg-MOF-74 with Unsaturated Coordination Metal Centers for Efficient CO<sub>2</sub> Adsorption and Conversion to Cyclic Carbonates. *ACS Appl. Mater. Interfaces* **2021**, *13* (51), 61334–61345.
- (240) Chiusoli, G. P.; Costa, M.; Gabriele, B.; Salerno, G. Sequential Reaction of Carbon Dioxide and Carbon Monoxide with Acetylenic Amines in the Presence of a Palladium Catalyst. *J. Mol. Catal. A Chem.* **1999**, *143* (1), 297–310.
- (241) Shi, M.; Nicholas, K. M. Palladium-Catalyzed Carboxylation of Allyl Stannanes. *J. Am. Chem. Soc.* **1997**, *119* (21), 5057–5058.
- (242) Dutta, G.; Jana, A. K.; Singh, D. K.; Eswaramoorthy, M.; Natarajan, S. Encapsulation of Silver Nanoparticles in an Amine-Functionalized Porphyrin Metal–Organic Framework and Its Use as a Heterogeneous Catalyst for CO<sub>2</sub> Fixation under Atmospheric Pressure. *Chem. – An Asian J.* **2018**, *13* (18), 2677–2684.
- (243) Dutta, G.; Jana, A. K.; Natarajan, S. Chemical Fixation of CO<sub>2</sub> and Other Heterogeneous Catalytic Studies by Employing a Layered Cu-Porphyrin Prepared Through Single-Crystal to Single-Crystal Exchange of a Zn Analogue. *Chem. – An Asian J.* **2018**, *13* (1), 66–72.
- (244) Gao, C.-Y.; Ai, J.; Tian, H.-R.; Wu, D.; Sun, Z.-M. An Ultrastable Zirconium-Phosphonate Framework as Bifunctional Catalyst for Highly Active CO<sub>2</sub> Chemical Transformation. *Chem. Commun.* **2017**, *53* (7), 1293–1296.
- (245) Manna, K.; Kumar, R.; Sundaresan, A.; Natarajan, S. Fixing CO<sub>2</sub> under Atmospheric Conditions and Dual Functional Heterogeneous Catalysis Employing Cu MOFs: Polymorphism, Single-Crystal-to-Single-Crystal (SCSC) Transformation and Magnetic Studies. *Inorg. Chem.* **2023**, *62* (34), 13738–13756.
- (246) Si, X.; Pan, X.; Xue, J.; Yao, Q.; Huang, X.; Duan, W.; Qiu, Y.; Su, J.; Cao, M.; Li, J. Robust Acid–Base Ln-MOFs: Searching for Efficient Catalysts in Cycloaddition of CO<sub>2</sub> with Epoxides and Cascade Deacetalization–Knoevenagel Reactions. *RSC Adv.* **2022**, *12* (52), 33501–33509.
- (247) Lin, Y.-F.; Huang, K.-W.; Ko, B.-T.; Lin, K.-Y. A Bifunctional ZIF-78 Heterogeneous Catalyst with Dual Lewis Acidic and Basic Sites for Carbon Dioxide Fixation via Cyclic Carbonate Synthesis. *J. CO<sub>2</sub> Util.* **2017**, *22*, 178–183.
- (248) Liang, J.; Chen, R.-P.; Wang, X.-Y.; Liu, T.-T.; Wang, X.-S.; Huang, Y.-B.; Cao, R. Postsynthetic Ionization of an Imidazole-Containing Metal–Organic Framework for the Cycloaddition of Carbon Dioxide and Epoxides. *Chem. Sci.* **2017**, *8* (2), 1570–1575.
- (249) Wu, Y.-L.; Yang, G.-P.; Cheng, S.; Qian, J.; Fan, D.; Wang, Y.-Y. Facile Incorporation of Au Nanoparticles into an Unusual Twofold Entangled Zn(II)-MOF with Nanocages for Highly Efficient CO<sub>2</sub> Fixation under Mild Conditions. *ACS Appl. Mater. Interfaces* **2019**, *11* (50), 47437–47445.
- (250) Das, R.; Parihar, V.; Nagaraja, C. M. Strategic Design of a Bifunctional Ag(i)-Grafted NHC-MOF for Efficient Chemical Fixation of CO<sub>2</sub> from a Dilute Gas under Ambient Conditions. *Inorg. Chem. Front.* **2022**, *9* (11), 2583–2593.
- (251) Zhu, K.; Li, Y.; Li, Z.; Liu, Y.; Wu, H.; Li, H. In Situ Activation of COOH-Functionalized ZIF-90-Enabled Reductive CO<sub>2</sub> N-Formylation. *Chem. Commun.* **2022**, *58* (91), 12712–12715.
- (252) Flanigen, E. M.; Jansen, J. C.; van Bekkum, H. *Introduction to Zeolite Science and Practice; Studies in Surface Science and Catalysis*; Elsevier Science, 1991.
- (253) Knowles, J. R. Enzyme Catalysis: Not Different, Just Better. *Nature* **1991**, *350* (6314), 121–124.
- (254) Wright, P. A.; Thomas, J. M.; Cheetham, A. K.; Nowak, A. K. Localizing Active Sites in Zeolitic Catalysts: Neutron Powder Profile Analysis and Computer Simulation of Deuteropyridine Bound to Gallozeolite-L. *Nature* **1985**, *318* (6047), 611–614.
- (255) Yang, D.; Gates, B. C. Catalysis by Metal Organic Frameworks: Perspective and Suggestions for Future Research. *ACS Catal.* **2019**, *9* (3), 1779–1798.

- (256) Bavykina, A.; Kolobov, N.; Khan, I. S.; Bau, J. A.; Ramirez, A.; Gascon, J. Metal–Organic Frameworks in Heterogeneous Catalysis: Recent Progress, New Trends, and Future Perspectives. *Chem. Rev.* **2020**, *120* (16), 8468–8535.
- (257) Herbst, A.; Janiak, C. MOF Catalysts in Biomass Upgrading towards Value-Added Fine Chemicals. *CrystEngComm* **2017**, *19* (29), 4092–4117.
- (258) Ji, P.; Drake, T.; Murakami, A.; Oliveres, P.; Skone, J. H.; Lin, W. Tuning Lewis Acidity of Metal–Organic Frameworks via Perfluorination of Bridging Ligands: Spectroscopic, Theoretical, and Catalytic Studies. *J. Am. Chem. Soc.* **2018**, *140* (33), 10553–10561.
- (259) Feng, X.; Song, Y.; Lin, W. Dimensional Reduction of Lewis Acidic Metal–Organic Frameworks for Multicomponent Reactions. *J. Am. Chem. Soc.* **2021**, *143* (21), 8184–8192.
- (260) Agarwal, R. A.; Gupta, A. K.; De, D. Flexible Zn-MOF Exhibiting Selective CO<sub>2</sub> Adsorption and Efficient Lewis Acidic Catalytic Activity. *Cryst. Growth Des.* **2019**, *19* (3), 2010–2018.
- (261) Epp, K.; Semrau, A. L.; Cokoja, M.; Fischer, R. A. Dual Site Lewis-Acid Metal–Organic Framework Catalysts for CO<sub>2</sub> Fixation: Counteracting Effects of Node Connectivity, Defects and Linker Metalation. *ChemCatChem* **2018**, *10* (16), 3506–3512.
- (262) Lyu, J.; Zhang, X.; Li, P.; Wang, X.; Buru, C. T.; Bai, P.; Guo, X.; Farha, O. K. Exploring the Role of Hexanuclear Clusters as Lewis Acidic Sites in Isostructural Metal–Organic Frameworks. *Chem. Mater.* **2019**, *31* (11), 4166–4172.
- (263) Xiao, J.-D.; Lu, S.-M.; Jia, G.-Q.; Wang, Q.-N.; Li, C. Relation Between Coordination and Lewis-Acid Property of MOF-Derived Mononuclear Zn(II) Catalyst Toward Epoxide Hydroxylation. *ChemCatChem* **2021**, *13* (24), 5236–5242.
- (264) Karimi, M.; Hajjashrafi, T.; Heydari, A.; Azhdari Tehrani, A. Terbiun–Organic Framework as Heterogeneous Lewis Acid Catalyst for  $\beta$ -Aminoalcohol Synthesis: Efficient, Reusable and Green Catalytic Method. *Appl. Organomet. Chem.* **2017**, *31* (12), No. e3866.
- (265) Hajjashrafi, T.; Karimi, M.; Heydari, A.; Tehrani, A. A. Erbium–Organic Framework as Heterogeneous Lewis Acid Catalysis for Hantzsch Coupling and Tetrahydro-4H-Chromene Synthesis. *Catal. Lett.* **2017**, *147* (2), 453–462.
- (266) Li, X.-Y.; Ma, L.-N.; Liu, Y.; Hou, L.; Wang, Y.-Y.; Zhu, Z. Honeycomb Metal–Organic Framework with Lewis Acidic and Basic Bifunctional Sites: Selective Adsorption and CO<sub>2</sub> Catalytic Fixation. *ACS Appl. Mater. Interfaces* **2018**, *10* (13), 10965–10973.
- (267) Hassan, H. M. A.; Alhumaimess, M. S.; Kamel, M. M.; Alsohaimi, I. H.; Aljaddua, H. I.; Aldosari, O. F.; Algamdi, M. S.; Mohamed, R. M. K.; El-Aassar, M. R. Electrospinning NH<sub>2</sub>-MIL-101/PAN Nanofiber Mats: A Promising Catalyst with Lewis Acidic and Basic Bifunctional Sites for Organic Transformation Reactions. *Colloids Surfaces A Physicochem. Eng. Asp.* **2022**, *642*, 128659.
- (268) Gupta, A. K.; Guha, N.; Krishnan, S.; Mathur, P.; Rai, D. K. A Three-Dimensional Cu(II)-MOF with Lewis Acid–base Dual Functional Sites for Chemical Fixation of CO<sub>2</sub> via Cyclic Carbonate Synthesis. *J. CO<sub>2</sub> Util.* **2020**, *39*, 101173.
- (269) Reiner, B. R.; Mucha, N. T.; Rothstein, A.; Temme, J. S.; Duan, P.; Schmidt-Rohr, K.; Foxman, B. M.; Wade, C. R. Zirconium Metal–Organic Frameworks Assembled from Pd and Pt PNNNP Pincer Complexes: Synthesis, Postsynthetic Modification, and Lewis Acid Catalysis. *Inorg. Chem.* **2018**, *57* (5), 2663–2672.
- (270) Zhang, J.; Zou, M.; Li, Q.; Dai, W.; Wang, D.; Zhang, S.; Li, B.; Yang, L.; Luo, S.; Luo, X. Thermally Activated Construction of Open Metal Sites on a Zn–Organic Framework: An Effective Strategy to Enhance Lewis Acid Properties and Catalytic Performance for CO<sub>2</sub> Cycloaddition Reactions. *Appl. Surf. Sci.* **2022**, *572*, 151408.
- (271) Yu, D.; Wang, L.; Yang, T.; Yang, G.; Wang, D.; Ni, H.; Wu, M. Tuning Lewis Acidity of Iron-Based Metal–Organic Frameworks for Enhanced Catalytic Ozonation. *Chem. Eng. J.* **2021**, *404*, No. 127075.
- (272) Xu, Y.-P.; Wang, Z.-Q.; Tan, H.-Z.; Jing, K.-Q.; Xu, Z.-N.; Guo, G.-C. Lewis Acid Sites in MOFs Supports Promoting the Catalytic Activity and Selectivity for CO Esterification to Dimethyl Carbonate. *Catal. Sci. Technol.* **2020**, *10* (6), 1699–1707.
- (273) Ronaghi, N.; Shade, D.; Moon, H. J.; Najmi, S.; Cleveland, J. W.; Walton, K. S.; France, S.; Jones, C. W. Modulation and Tuning of UiO-66 for Lewis Acid Catalyzed Carbohydrate Conversion: Conversion of Unprotected Aldose Sugars to Polyhydroxyalkyl and C-Glycosyl Furans. *ACS Sustain. Chem. Eng.* **2021**, *9* (34), 11581–11595.
- (274) Rouhani, F.; Morsali, A. Highly Effective Brønsted Base/Lewis Acid Cooperative Catalysis: A New Cd Metal–Organic Framework for the Synthesis of Hantzsch 1,4-DHPs at Ambient Temperature. *New J. Chem.* **2017**, *41* (24), 15475–15484.
- (275) Venu, B.; Shirisha, V.; Vishali, B.; Naresh, G.; Kishore, R.; Sreedhar, I.; Venugopal, A. A Cu-BTC Metal–Organic Framework (MOF) as an Efficient Heterogeneous Catalyst for the Aerobic Oxidative Synthesis of Imines from Primary Amines under Solvent Free Conditions. *New J. Chem.* **2020**, *44* (15), 5972–5979.
- (276) Pertiwi, R.; Oozeerally, R.; Burnett, D. L.; Chamberlain, T. W.; Cherkasov, N.; Walker, M.; Kashtiban, R. J.; Krisnandi, Y. K.; Degirmenci, V.; Walton, R. I. Replacement of Chromium by Non-Toxic Metals in Lewis-Acid MOFs: Assessment of Stability as Glucose Conversion Catalysts. *Catalysts* **2019**, *9*, 437.
- (277) Moreno, J. M.; Vely, A.; Díaz, U.; Corma, A. Synthesis of 2D and 3D MOFs with Tuneable Lewis Acidity from Preformed 1D Hybrid Sub-Domains. *Chem. Sci.* **2019**, *10* (7), 2053–2066.
- (278) Shyshkanov, S.; Nguyen, T. N.; Ebrahim, F. M.; Stylianou, K. C.; Dyson, P. J. In Situ Formation of Frustrated Lewis Pairs in a Water-Tolerant Metal–Organic Framework for the Transformation of CO<sub>2</sub>. *Angew. Chemie Int. Ed.* **2019**, *58* (16), 5371–5375.
- (279) Ugale, B.; Kumar, S.; Dhilip Kumar, T. J.; Nagaraja, C. M. Environmentally Friendly, Co-Catalyst-Free Chemical Fixation of CO<sub>2</sub> at Mild Conditions Using Dual-Walled Nitrogen-Rich Three-Dimensional Porous Metal–Organic Frameworks. *Inorg. Chem.* **2019**, *58* (6), 3925–3936.
- (280) Bauer, G.; Ongari, D.; Xu, X.; Tiana, D.; Smit, B.; Ranocchiari, M. Metal–Organic Frameworks Invert Molecular Reactivity: Lewis Acidic Phosphonium Zwitterions Catalyze the Aldol-Tishchenko Reaction. *J. Am. Chem. Soc.* **2017**, *139* (50), 18166–18169.
- (281) Chai, J.; Zhang, P.; Xu, J.; Qi, H.; Sun, J.; Jing, S.; Chen, X.; Fan, Y.; Wang, L. An In-Based 3D Metal–Organic Framework as Heterogeneous Lewis Acid Catalyst for Multi-Component Strecker Reactions. *Inorg. Chim. Acta* **2018**, *479*, 165–171.
- (282) Chen, H.; Fan, L.; Hu, T.; Zhang, X. Template-Induced {Mn<sub>2</sub>}–Organic Framework with Lewis Acid–Base Canals as a Highly Efficient Heterogeneous Catalyst for Chemical Fixation of CO<sub>2</sub> and Knoevenagel Condensation. *Inorg. Chem.* **2021**, *60* (10), 7276–7283.
- (283) Gu, J.; Sun, X.; Liu, X.; Yuan, Y.; Shan, H.; Liu, Y. Highly Efficient Synergistic CO<sub>2</sub> Conversion with Epoxide Using Copper Polyhedron-Based MOFs with Lewis Acid and Base Sites. *Inorg. Chem. Front.* **2020**, *7* (22), 4517–4526.
- (284) Xu, H.; Chen, M.; Ji, M. Solid Lewis Acid–Base Pair Catalysts Constructed by Regulations on Defects of UiO-66 for the Catalytic Hydrogenation of Cinnamaldehyde. *Catal. Today* **2022**, *402*, 52–59.
- (285) Niu, Z.; Bhagya Gunatilleke, W. D. C.; Sun, Q.; Lan, P. C.; Perman, J.; Ma, J.-G.; Cheng, Y.; Aguila, B.; Ma, S. Metal–Organic Framework Anchored with a Lewis Pair as a New Paradigm for Catalysis. *Chem.* **2018**, *4* (11), 2587–2599.
- (286) Guo, Q.; Ren, L.; Kumar, P.; Cybulskis, V. J.; Mkhoyan, K. A.; Davis, M. E.; Tsapatsis, M. A Chromium Hydroxide/MIL-101(Cr) MOF Composite Catalyst and Its Use for the Selective Isomerization of Glucose to Fructose. *Angew. Chemie - Int. Ed.* **2018**, *57* (18), 4926–4930.
- (287) Gao, X.; Liu, M.; Lan, J.; Liang, L.; Zhang, X.; Sun, J. Lewis Acid–Base Bifunctional Crystals with a Three-Dimensional Framework for Selective Coupling of CO<sub>2</sub> and Epoxides under Mild and Solvent-Free Conditions. *Cryst. Growth Des.* **2017**, *17* (1), 51–57.
- (288) Tian, H.; Liu, S.; Zhang, Z.; Dang, T.; Lu, Y.; Liu, S. Highly Stable Polyoxovanadate-Based Zn–MOF with Dual Active Sites as a Solvent-Free Catalyst for C–C Bond Formation. *ACS Sustain. Chem. Eng.* **2021**, *9* (12), 4660–4667.

- (289) Ansari, S. N.; Kumar, P.; Gupta, A. K.; Mathur, P.; Mobin, S. M. Catalytic CO<sub>2</sub> Fixation over a Robust Lactam-Functionalized Cu(II) Metal Organic Framework. *Inorg. Chem.* **2019**, *58* (15), 9723–9732.
- (290) Gupta, V.; Mandal, S. K. Design and Construction of a Chiral Cd(II)-MOF from Achiral Precursors: Synthesis, Crystal Structure and Catalytic Activity toward C–C and C–N Bond Forming Reactions. *Inorg. Chem.* **2019**, *58* (5), 3219–3226.
- (291) Zhang, Y.; Wang, Y.; Liu, L.; Wei, N.; Gao, M.-L.; Zhao, D.; Han, Z.-B. Robust Bifunctional Lanthanide Cluster Based Metal–Organic Frameworks (MOFs) for Tandem Deacetalization–Knoevenagel Reaction. *Inorg. Chem.* **2018**, *57* (4), 2193–2198.
- (292) Zhang, X.; Chang, L.; Yang, Z.; Shi, Y.; Long, C.; Han, J.; Zhang, B.; Qiu, X.; Li, G.; Tang, Z. Facile Synthesis of Ultrathin Metal–Organic Framework Nanosheets for Lewis Acid Catalysis. *Nano Res.* **2019**, *12* (2), 437–440.
- (293) Zheng, B.; Luo, X.; Wang, Z.; Zhang, S.; Yun, R.; Huang, L.; Zeng, W.; Liu, W. An Unprecedented Water Stable Acylamide-Functionalized Metal–Organic Framework for Highly Efficient CH<sub>4</sub>/CO<sub>2</sub> Gas Storage/Separation and Acid–Base Cooperative Catalytic Activity. *Inorg. Chem. Front.* **2018**, *5* (9), 2355–2363.
- (294) Wang, Z.; Luo, X.; Zheng, B.; Huang, L.; Hang, C.; Jiao, Y.; Cao, X.; Zeng, W.; Yun, R. Highly Selective Carbon Dioxide Capture and Cooperative Catalysis of a Water-Stable Acylamide-Functionalized Metal–Organic Framework. *Eur. J. Inorg. Chem.* **2018**, *2018* (11), 1309–1314.
- (295) Karmakar, A.; Soliman, M. M. A.; Rúbio, G. M. D. M.; Guedes Da Silva, M. F. C.; Pompeiro, A. J. L. Synthesis and Catalytic Activities of a Zn(II) Based Metallomacrocyclic and a Metal–Organic Framework towards One-Pot Deacetalization–Knoevenagel Tandem Reactions under Different Strategies: A Comparative Study. *Dalt. Trans.* **2020**, *49* (24), 8075–8085.
- (296) Li, X.; Zhang, B.; Fang, Y.; Sun, W.; Qi, Z.; Pei, Y.; Qi, S.; Yuan, P.; Luan, X.; Goh, T. W.; Huang, W. Metal–Organic-Framework-Derived Carbons: Applications as Solid-Base Catalyst and Support for Pd Nanoparticles in Tandem Catalysis. *Chem. – A Eur. J.* **2017**, *23* (18), 4266–4270.
- (297) Bao, Y.-S.; Liu, W.; Dong, Z.-L.; Xing, Z.-Q.; Yang, M.; Cui, Y.-H.; Meng, L.-X.; Li, L.-C.; Xu, X.-M.; Han, Z.-B.; Zhang, Y.-Y. Metal–Organic Frameworks as an Efficient Pickering Interfacial Catalyst for the Deacetalization–Knoevenagel Tandem Reaction. *New J. Chem.* **2023**, *47* (18), 8906–8912.
- (298) Seal, N.; Neogi, S. Lewis Acid-Base Integrated Robust Metal–Organic Framework and Reconfigurable Composite for Solvent-Free Biginelli Condensation and Tandem Catalysis with Size Selectivity. *Mater. Today Chem.* **2022**, *26*, 101064.
- (299) Wang, X.; Hou, Y.; Wang, X.; Guo, Y.; Zhang, X. Integration of Au Nanoparticles and Metal–Organic Frameworks in Hollow Double-Shelled Nanoreactor for Efficient Tandem Catalysis. *Appl. Surf. Sci.* **2023**, *608*, 155123.
- (300) Das, A.; Anbu, N.; Dhakshinamoorthy, A.; Biswas, S. A Highly Catalytically Active Hf(IV) Metal–Organic Framework for Knoevenagel Condensation. *Microporous Mesoporous Mater.* **2019**, *284*, 459–467.
- (301) Lv, H.; Zhang, Z.; Fan, L.; Gao, Y.; Zhang, X. A Nanocaged Cadmium–Organic Framework with High Catalytic Activity on the Chemical Fixation of CO<sub>2</sub> and Deacetalization–Knoevenagel Condensation. *Microporous Mesoporous Mater.* **2022**, *335*, 111791.
- (302) Chen, H.; Liu, S.; Lv, H.; Qin, Q.-P.; Zhang, X. Nanoporous {Y<sub>2</sub>}–Organic Frameworks for Excellent Catalytic Performance on the Cycloaddition Reaction of Epoxides with CO<sub>2</sub> and Deacetalization–Knoevenagel Condensation. *ACS Appl. Mater. Interfaces* **2022**, *14* (16), 18589–18599.
- (303) Das, A.; Anbu, N.; SK, M.; Dhakshinamoorthy, A.; Biswas, S. Highly Active Bisamino Functionalized Zr(IV)-UiO-67 Metal–Organic Framework for Cascade Catalysis. *Eur. J. Inorg. Chem.* **2020**, *2020* (29), 2830–2834.
- (304) Hu, Y.; Zhang, J.; Wang, Z.; Huo, H.; Jiang, Y.; Xu, X.; Lin, K. Ion-Exchange Fabrication of Hierarchical Al-MOF-Based Resin Catalysts for the Tandem Reaction. *ACS Appl. Mater. Interfaces* **2020**, *12* (32), 36159–36167.
- (305) Nicks, J.; Zhang, J.; Foster, J. A. Tandem Catalysis by Ultrathin Metal–Organic Nanosheets Formed through Post-Synthetic Functionalisation of a Layered Framework. *Chem. Commun.* **2019**, *55* (60), 8788–8791.
- (306) Peh, S. B.; Cheng, Y.; Zhang, J.; Wang, Y.; Chan, G. H.; Wang, J.; Zhao, D. Cluster Nuclearity Control and Modulated Hydrothermal Synthesis of Functionalized Zr<sub>12</sub> Metal–Organic Frameworks. *Dalt. Trans.* **2019**, *48* (21), 7069–7073.
- (307) Zhang, Y.-Y.; Zhou, M.-L.; Cui, Y.-H.; Yang, M.; Bao, Y.-S.; Ye, Y.; Tian, D.-M.; Liu, L.-Y.; Han, Z.-B. Polymelamine Formaldehyde-Coated MIL-101 as an Efficient Dual-Functional Core–Shell Composite to Catalyze the Deacetalization–Knoevenagel Tandem Reaction. *Inorg. Chem.* **2022**, *61* (35), 13678–13684.
- (308) Lv, H.; Fan, L.; Chen, H.; Zhang, X.; Gao, Y. Nanochannel-Based {BaZn}–Organic Framework for Catalytic Activity on the Cycloaddition Reaction of Epoxides with CO<sub>2</sub> and Deacetalization–Knoevenagel Condensation. *Dalt. Trans.* **2022**, *51* (9), 3546–3556.
- (309) Chen, H.; Zhang, Z.; Hu, T.; Zhang, X. Nanochannel {InZn}–Organic Framework with a High Catalytic Performance on CO<sub>2</sub> Chemical Fixation and Deacetalization–Knoevenagel Condensation. *Inorg. Chem.* **2021**, *60* (21), 16429–16438.
- (310) Yang, M.; Bao, Y.-S.; Zhou, M.-L.; Wang, S.; Cui, Y.-H.; Liu, W.; Li, L.-C.; Meng, L.-X.; Zhang, Y.-Y.; Han, Z.-B. An Efficient Bifunctional Core–Shell MIL-101(Cr)@MOF-867 Composite to Catalyze Deacetalization–Knoevenagel Tandem Reaction. *Catal. Lett.* **2023**, *153*, 3561.
- (311) Yang, Q.; Liu, W.; Wang, B.; Zhang, W.; Zeng, X.; Zhang, C.; Qin, Y.; Sun, X.; Wu, T.; Liu, J.; Huo, F.; Lu, J. Regulating the Spatial Distribution of Metal Nanoparticles within Metal–Organic Frameworks to Enhance Catalytic Efficiency. *Nat. Commun.* **2017**, *8* (1), 14429.
- (312) Zhong, Y.; Mao, Y.; Shi, S.; Wan, M.; Ma, C.; Wang, S.; Chen, C.; Zhao, D.; Zhang, N. Fabrication of Magnetic Pd/MOF Hollow Nanospheres with Double-Shell Structure: Toward Highly Efficient and Recyclable Nanocatalysts for Hydrogenation Reaction. *ACS Appl. Mater. Interfaces* **2019**, *11* (35), 32251–32260.
- (313) Veisi, H.; Abrifam, M.; Kamangar, S. A.; Pirhayati, M.; Saremi, S. G.; Noroozi, M.; Tamoradi, T.; Karmakar, B. Pd Immobilization Biguanidine Modified Zr–UiO-66 MOF as a Reusable Heterogeneous Catalyst in Suzuki–Miyaura Coupling. *Sci. Rep.* **2021**, *11* (1), 21883.
- (314) Aparna, R. K.; Mukherjee, S.; Rose, S. S.; Mandal, S. Silver Nanoparticle-Incorporated Defect-Engineered Zr-Based Metal–Organic Framework for Efficient Multicomponent Catalytic Reactions. *Inorg. Chem.* **2022**, *61* (41), 16441–16447.
- (315) Mishra, B.; Ghosh, D.; Tripathi, B. P. Finely Dispersed AgPd Bimetallic Nanoparticles on a Polydopamine Modified Metal Organic Framework for Diverse Catalytic Applications. *J. Catal.* **2022**, *411*, 1–14.
- (316) Taher, A.; Susan, M. A. B. H.; Begum, N.; Lee, I.-M. Amine-Functionalized Metal–Organic Framework-Based Pd Nanoparticles: Highly Efficient Multifunctional Catalysts for Base-Free Aerobic Oxidation of Different Alcohols. *New J. Chem.* **2020**, *44* (44), 19113–19121.
- (317) Nabi, S.; Sofi, F. A.; Rashid, N.; Ingole, P. P.; Bhat, M. A. Au-Nanoparticle Loaded Nickel–Copper Bimetallic MOF: An Excellent Catalyst for Chemical Degradation of Rhodamine B. *Inorg. Chem. Commun.* **2020**, *117*, No. 107949.
- (318) Zhou, Y.-X.; Chen, Y.-Z.; Hu, Y.; Huang, G.; Yu, S.-H.; Jiang, H.-L. MIL-101-SO<sub>3</sub>H: A Highly Efficient Brønsted Acid Catalyst for Heterogeneous Alcoholysis of Epoxides under Ambient Conditions. *Chem. – A Eur. J.* **2014**, *20* (46), 14976–14980.
- (319) Singh, M.; Solanki, P.; Patel, P.; Mondal, A.; Neogi, S. Highly Active Ultrasmall Ni Nanoparticle Embedded Inside a Robust Metal–Organic Framework: Remarkably Improved Adsorption, Selectivity, and Solvent-Free Efficient Fixation of CO<sub>2</sub>. *Inorg. Chem.* **2019**, *58* (12), 8100–8110.

- (320) Liu, X.; Liu, Z.; Wang, R. Functionalized Metal-Organic Framework Catalysts for Sustainable Biomass Valorization. *Polym. Technol.* **2020**, *2020*, 1201923.
- (321) Kiani, A.; Alinezhad, H.; Ghasemi, S. Versatile and an Efficient Sonogashira Coupling Reaction Catalyzed with Modified Pd-Functionalized TMU-16 as a Novel and Reusable Nanocatalyst. *J. Organomet. Chem.* **2021**, *950*, 121975.
- (322) Salama, R. S.; El-Sayed, E.-S. M.; El-Bahy, S. M.; Awad, F. S. Silver Nanoparticles Supported on UiO-66 (Zr): As an Efficient and Recyclable Heterogeneous Catalyst and Efficient Adsorbent for Removal of Indigo Carmine. *Colloids Surfaces A Physicochem. Eng. Asp.* **2021**, *626*, 127089.
- (323) Jiang, Y.; Zhang, X.; Dai, X.; Zhang, W.; Sheng, Q.; Zhuo, H.; Xiao, Y.; Wang, H. Microwave-Assisted Synthesis of Ultrafine Au Nanoparticles Immobilized on MOF-199 in High Loading as Efficient Catalysts for a Three-Component Coupling Reaction. *Nano Res.* **2017**, *10* (3), 876–889.
- (324) Li, J.; Xu, Z.; Wang, T.; Xie, X.; Li, D.; Wang, J.; Huang, H.; Ao, Z. A Versatile Route to Fabricate Metal/UiO-66 (Metal = Pt, Pd, Ru) with High Activity and Stability for the Catalytic Oxidation of Various Volatile Organic Compounds. *Chem. Eng. J.* **2022**, *448*, 136900.
- (325) Dai, W.; Mao, P.; Liu, Y.; Zhang, S.; Li, B.; Yang, L.; Luo, X.; Zou, J. Quaternary Phosphonium Salt-Functionalized Cr-MIL-101: A Bifunctional and Efficient Catalyst for CO<sub>2</sub> Cycloaddition with Epoxides. *J. CO<sub>2</sub> Util.* **2020**, *36*, 295–305.
- (326) Yang, D.-A.; Cho, H.-Y.; Kim, J.; Yang, S.-T.; Ahn, W.-S. CO<sub>2</sub> Capture and Conversion Using Mg-MOF-74 Prepared by a Sonochemical Method. *Energy Environ. Sci.* **2012**, *5* (4), 6465–6473.
- (327) Cho, H.-Y.; Yang, D.-A.; Kim, J.; Jeong, S.-Y.; Ahn, W.-S. CO<sub>2</sub> Adsorption and Catalytic Application of Co-MOF-74 Synthesized by Microwave Heating. *Catal. Today* **2012**, *185* (1), 35–40.
- (328) Kim, J.; Kim, S.-N.; Jang, H.-G.; Seo, G.; Ahn, W.-S. CO<sub>2</sub> Cycloaddition of Styrene Oxide over MOF Catalysts. *Appl. Catal. A Gen.* **2013**, *453*, 175–180.
- (329) Huang, X.; Chen, Y.; Lin, Z.; Ren, X.; Song, Y.; Xu, Z.; Dong, X.; Li, X.; Hu, C.; Wang, B. Zn-BTC MOFs with Active Metal Sites Synthesized via a Structure-Directing Approach for Highly Efficient Carbon Conversion. *Chem. Commun.* **2014**, *50* (20), 2624–2627.
- (330) Song, L.; Chen, C.; Chen, X.; Zhang, N. Isomorphic MOFs Functionalized by Free-Standing Acylamide and Organic Groups Serving as Self-Supported Catalysts for the CO<sub>2</sub> Cycloaddition Reaction. *New J. Chem.* **2016**, *40* (3), 2904–2909.
- (331) Babu, R.; Kathalikkattil, A. C.; Roshan, R.; Tharun, J.; Kim, D.-W.; Park, D.-W. Dual-Porous Metal Organic Framework for Room Temperature CO<sub>2</sub> Fixation via Cyclic Carbonate Synthesis. *Green Chem.* **2016**, *18* (1), 232–242.
- (332) Han, Y. H.; Zhou, Z. Y.; Tian, C. B.; Du, S. W. A Dual-Walled Cage MOF as an Efficient Heterogeneous Catalyst for the Conversion of CO<sub>2</sub> under Mild and Co-Catalyst Free Conditions. *Green Chem.* **2016**, *18* (14), 4086–4091.
- (333) Kumar, S.; Karthikeyan, S.; Lee, A. F. G-C<sub>3</sub>N<sub>4</sub>-Based Nanomaterials for Visible Light-Driven Photocatalysis. *Catalysts* **2018**, *8*, 74.
- (334) Song, X.; Wu, Y.; Pan, D.; Zhang, J.; Xu, S.; Gao, L.; Wei, R.; Zhang, J.; Xiao, G. Dual-Linker Metal-Organic Frameworks as Efficient Carbon Dioxide Conversion Catalysts. *Appl. Catal. A Gen.* **2018**, *566*, 44–51.
- (335) He, H.; Zhu, Q.; Zhao, J.; Sun, H.; Chen, J.; Li, C.; Du, M. Rational Construction of an Exceptionally Stable MOF Catalyst with Metal-Adeninate Vertices toward CO<sub>2</sub> Cycloaddition under Mild and Cocatalyst-Free Conditions. *Chem.—Eur. J.* **2019**, *25* (49), 11474–11480.
- (336) Miralda, C. M.; Macias, E. E.; Zhu, M.; Ratnasamy, P.; Carreon, M. A. Zeolitic Imidazole Framework-8 Catalysts in the Conversion of CO<sub>2</sub> to Chloropropene Carbonate. *ACS Catal.* **2012**, *2* (1), 180–183.
- (337) Tharun, J.; Mathai, G.; Kathalikkattil, A. C.; Roshan, R.; Won, Y.; Cho, S. J.; Chang, J.; Park, D. Exploring the Catalytic Potential of ZIF-90: Solventless and Co-Catalyst-Free Synthesis of Propylene Carbonate from Propylene Oxide and CO<sub>2</sub>. *ChemPlusChem.* **2015**, *80* (4), 715–721.
- (338) Kuruppatharambil, R. R.; Babu, R.; Jeong, H. M.; Hwang, G.-Y.; Jeong, G. S.; Kim, M.-I.; Kim, D.-W.; Park, D.-W. A Solid Solution Zeolitic Imidazolate Framework as a Room Temperature Efficient Catalyst for the Chemical Fixation of CO<sub>2</sub>. *Green Chem.* **2016**, *18* (23), 6349–6356.
- (339) Kuruppatharambil, R. R.; Jose, T.; Babu, R.; Hwang, G.-Y.; Kathalikkattil, A. C.; Kim, D.-W.; Park, D.-W. A Room Temperature Synthesizable and Environmental Friendly Heterogeneous ZIF-67 Catalyst for the Solvent Less and Co-Catalyst Free Synthesis of Cyclic Carbonates. *Appl. Catal. B Environ.* **2016**, *182*, 562–569.
- (340) Verma, S.; Baig, R. B. N.; Nadagouda, M. N.; Varma, R. S. Titanium-Based Zeolitic Imidazolate Framework for Chemical Fixation of Carbon Dioxide. *Green Chem.* **2016**, *18* (18), 4855–4858.
- (341) Ma, D.; Li, B.; Liu, K.; Zhang, X.; Zou, W.; Yang, Y.; Li, G.; Shi, Z.; Feng, S. Bifunctional MOF Heterogeneous Catalysts Based on the Synergy of Dual Functional Sites for Efficient Conversion of CO<sub>2</sub> under Mild and Co-Catalyst Free Conditions. *J. Mater. Chem. A* **2015**, *3* (46), 23136–23142.
- (342) Jose, T.; Hwang, Y.; Kim, D.-W.; Kim, M.-I.; Park, D.-W. Functionalized Zeolitic Imidazolate Framework F-ZIF-90 as Efficient Catalyst for the Cycloaddition of Carbon Dioxide to Allyl Glycidyl Ether. *Catal. Today* **2015**, *245*, 61–67.
- (343) Tharun, J.; Bhin, K.-M.; Roshan, R.; Kim, D. W.; Kathalikkattil, A. C.; Babu, R.; Ahn, H. Y.; Won, Y. S.; Park, D.-W. Ionic Liquid Tethered Post Functionalized ZIF-90 Framework for the Cycloaddition of Propylene Oxide and CO<sub>2</sub>. *Green Chem.* **2016**, *18* (8), 2479–2487.
- (344) Liang, J.; Xie, Y.-Q.; Wu, Q.; Wang, X.-Y.; Liu, T.-T.; Li, H.-F.; Huang, Y.-B.; Cao, R. Zinc Porphyrin/Imidazolium Integrated Multivariate Zirconium Metal–Organic Frameworks for Transformation of CO<sub>2</sub> into Cyclic Carbonates. *Inorg. Chem.* **2018**, *57* (5), 2584–2593.
- (345) Liu, T.-T.; Liang, J.; Xu, R.; Huang, Y.-B.; Cao, R. Salen-Co (III) Insertion in Multivariate Cationic Metal–Organic Frameworks for the Enhanced Cycloaddition Reaction of Carbon Dioxide. *Chem. Commun.* **2019**, *55* (28), 4063–4066.
- (346) Ding, L.-G.; Yao, B.-J.; Jiang, W.-L.; Li, J.-T.; Fu, Q.-J.; Li, Y.-A.; Liu, Z.-H.; Ma, J.-P.; Dong, Y.-B. Bifunctional Imidazolium-Based Ionic Liquid Decorated UiO-67 Type MOF for Selective CO<sub>2</sub> Adsorption and Catalytic Property for CO<sub>2</sub> Cycloaddition with Epoxides. *Inorg. Chem.* **2017**, *56* (4), 2337–2344.
- (347) Liang, J.; Xie, Y.-Q.; Wang, X.-S.; Wang, Q.; Liu, T.-T.; Huang, Y.-B.; Cao, R. An Imidazolium-Functionalized Mesoporous Cationic Metal–Organic Framework for Cooperative CO<sub>2</sub> Fixation into Cyclic Carbonate. *Chem. Commun.* **2018**, *54* (4), 342–345.
- (348) Sun, Y.; Huang, H.; Vardhan, H.; Aguilá, B.; Zhong, C.; Perman, J. A.; Al-Enizi, A. M.; Nafady, A.; Ma, S. Facile Approach to Graft Ionic Liquid into MOF for Improving the Efficiency of CO<sub>2</sub> Chemical Fixation. *ACS Appl. Mater. Interfaces* **2018**, *10* (32), 27124–27130.
- (349) Liu, D.; Li, G.; Liu, H. Functionalized MIL-101 with Imidazolium-Based Ionic Liquids for the Cycloaddition of CO<sub>2</sub> and Epoxides under Mild Condition. *Appl. Surf. Sci.* **2018**, *428*, 218–225.
- (350) Wang, T.; Song, X.; Luo, Q.; Yang, X.; Chong, S.; Zhang, J.; Ji, M. Acid-Base Bifunctional Catalyst: Carboxyl Ionic Liquid Immobilized on MIL-101-NH<sub>2</sub> for Rapid Synthesis of Propylene Carbonate from CO<sub>2</sub> and Propylene Oxide under Facile Solvent-Free Conditions. *Microporous Mesoporous Mater.* **2018**, *267*, 84–92.
- (351) Ding, M.; Jiang, H. L. Incorporation of Imidazolium-Based Poly(ionic liquid)s into a Metal–Organic Framework for CO<sub>2</sub> Capture and Conversion. *ACS Catal.* **2018**, *8*, 3194–3201.
- (352) Aguilá, B.; Sun, Q.; Wang, X.; O'Rourke, E.; Al-Enizi, A. M.; Nafady, A.; Ma, S. Lower Activation Energy for Catalytic Reactions through Host–Guest Cooperation within Metal–Organic Frameworks. *Angew. Chem. Int. Ed.* **2018**, *57* (32), 10107–10111.

(353) Sun, Y.; Jia, X.; Huang, H.; Guo, X.; Qiao, Z.; Zhong, C. Solvent-Free Mechanochemical Route for the Construction of Ionic Liquid and Mixed-Metal MOF Composites for Synergistic CO<sub>2</sub> Fixation. *J. Mater. Chem. A* **2020**, *8* (6), 3180–3185.

(354) Zhou, X.; Zhang, Y.; Yang, X.; Zhao, L.; Wang, G. Functionalized IRMOF-3 as Efficient Heterogeneous Catalyst for the Synthesis of Cyclic Carbonates. *J. Mol. Catal. A Chem.* **2012**, *361*, 12–16.

(355) Kim, Y.-J.; Park, D.-W. Functionalized IRMOF-3: An Efficient Heterogeneous Catalyst for the Cycloaddition of Allyl Glycidyl Ether and CO<sub>2</sub>. *J. Nanosci. Nanotechnol.* **2013**, *13* (3), 2307–2312.

(356) Zhou, L.; Sun, W.; Yang, N.; Li, P.; Gong, T.; Sun, W.; Sui, Q.; Gao, E. A Facile and Versatile “Click” Approach Toward Multifunctional Ionic Metal–Organic Frameworks for Efficient Conversion of CO<sub>2</sub>. *ChemSusChem* **2019**, *12* (10), 2202–2210.

(357) Wu, Y.; Song, X.; Xu, S.; Zhang, J.; Zhu, Y.; Gao, L.; Xiao, G. 2-Methylimidazole Modified Co-BTC MOF as an Efficient Catalyst for Chemical Fixation of Carbon Dioxide. *Catal. Lett.* **2019**, *149*, 2575–2585.

(358) Wu, Y.; Song, X.; Li, S.; Zhang, J.; Yang, X.; Shen, P.; Gao, L.; Wei, R.; Zhang, J.; Xiao, G. 3D-Monoclinic M–BTC MOF (M= Mn, Co, Ni) as Highly Efficient Catalysts for Chemical Fixation of CO<sub>2</sub> into Cyclic Carbonates. *J. Ind. Eng. Chem.* **2018**, *58*, 296–303.

(359) Bahadori, M.; Marandi, A.; Tangestaninejad, S.; Moghadam, M.; Mirkhani, V.; Mohammadpoor-Baltork, I. Ionic Liquid-Decorated MIL-101 (Cr) via Covalent and Coordination Bonds for Efficient Solvent-Free CO<sub>2</sub> Conversion and CO<sub>2</sub> Capture at Low Pressure. *J. Phys. Chem. C* **2020**, *124* (16), 8716–8725.

(360) He, H.; Zhu, Q.; Zhang, C.; Yan, Y.; Yuan, J.; Chen, J.; Li, C.; Du, M. Encapsulation of an Ionic Metalloporphyrin into a Zeolite Imidazolate Framework in Situ for CO<sub>2</sub> Chemical Transformation via Host–Guest Synergistic Catalysis. *Chem.—Asian J.* **2019**, *14* (7), 958–962.