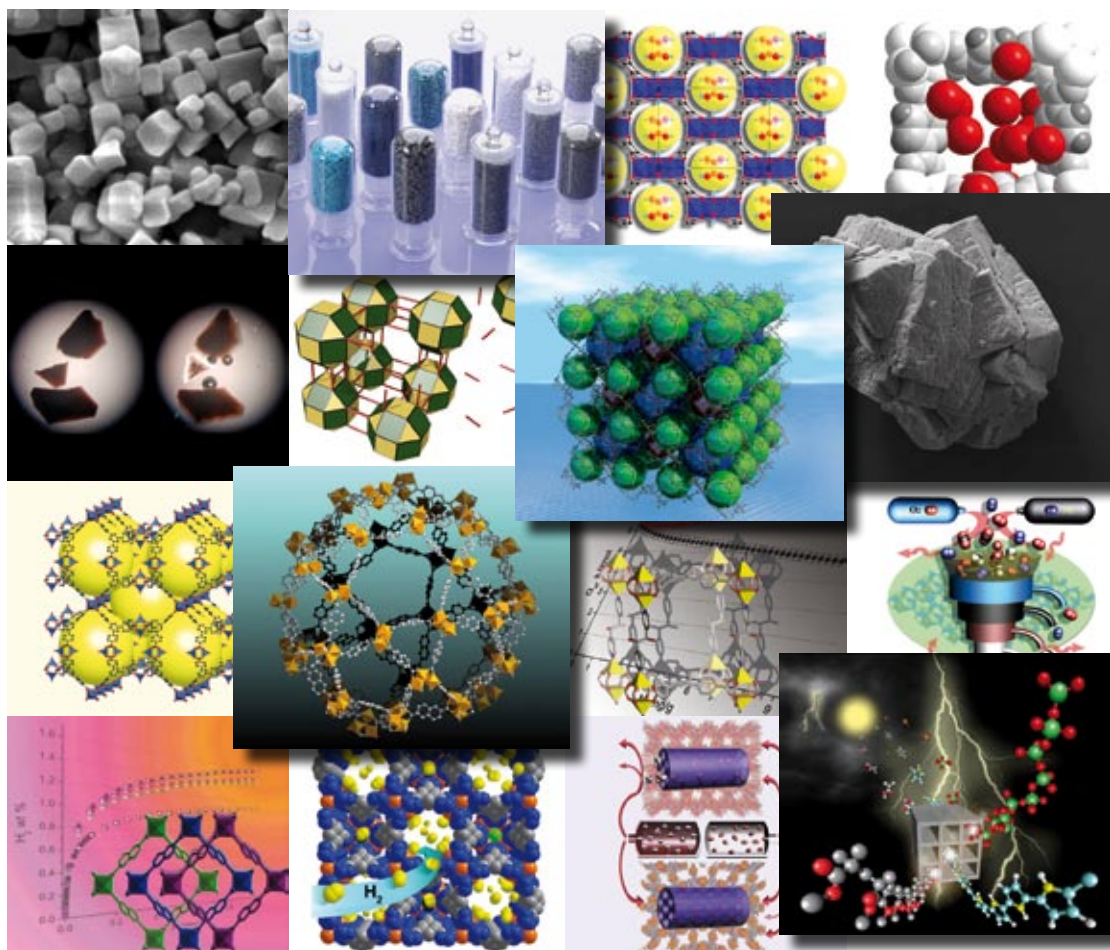# Chem Soc Rev

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Reviewing the latest developments across the interdisciplinary area of metal–organic frameworks from an academic and industrial perspective

Guest Editors Jeffrey Long and Omar Yaghi

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Metal–organic framework materials as catalysts†

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A *critical review* of the emerging field of MOF-based catalysis is presented. Discussed are examples of: (a) opportunistic catalysis with metal nodes, (b) designed catalysis with framework nodes, (c) catalysis by homogeneous catalysts incorporated as framework struts, (d) catalysis by MOF-encapsulated molecular species, (e) catalysis by metal-free organic struts or cavity modifiers, and (f) catalysis by MOF-encapsulated clusters (66 references).
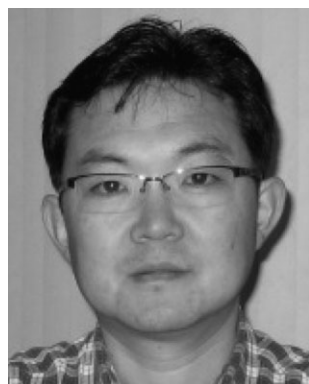
1. Introduction

Heterogeneous catalysis was one of the earliest proposed applications for crystalline metal–organic frameworks (MOF) materials,[1] as well as one of the earliest demonstrated applications.[2] A defining characteristic of functional MOF materials is porosity, and early-on the analogy between MOFs and another class of catalytic porous materials, aluminosilicate zeolites, was noted. Zeolites, of course, are among the most commercially important classes of catalyst.[3] As purely inorganic materials, they are extraordinarily robust and, therefore well suited to catalysis under extreme conditions. Their porosity yields internal surface areas that are relatively large, thereby facilitating their catalytic reactivity. The uniformity of their pore and channel sizes accounts for much of their catalytic selectivity.

Although crystalline MOFs share some of the catalytically relevant features of zeolites (large internal surface areas and uniform pore and cavity sizes), they also differ in important

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ways. First, because they also contain organic components, MOFs can be synthesized in much greater chemical variety than zeolites. Second, while many MOFs show good thermal stability—a few even showing stability to substantially above 500 °C[4,5]—none approach the stability of zeolites. This suggests that MOFs will likely not be competitive with zeolites as catalysts for reactions requiring forcing conditions. Instead, their catalytic niche may be high-value-added reactions (production of fine chemicals, delicate molecules, individual enantiomers, *etc.*) that can be accomplished under milder conditions. Third, while many MOFs exhibit zeolite-like permanent microporosity, others collapse when solvent is removed. The persistence of microporosity after solvent evacuation is essential for gas-phase catalysis, as well as for applications such as gas separations and gas storage. For catalysis of condensed-phase reactions, however, it may not be essential. Indeed, one of the earliest reported examples of MOF catalytic behavior (*i.e.*, cyanosilylation of various aldehydes) was based on a material (a 2D polymer of 4,4′-bipyridine and cadmium nitrate) that likely would not have survived solvent removal.[2]

Although MOF-based catalysis was proposed nearly 20 years ago and experimentally demonstrated 15 years ago,

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only recently has there been extensive experimental exploration. The reason for the long delay is clear: it has been necessary first to develop a substantial foundation of MOF synthetic chemistry. With a significant amount of such chemistry now in place, it has proven possible for researchers in this area to envision a variety of catalysis ideas (strategies) that can be evaluated experimentally in rapid fashion. Among the now-demonstrated concepts are: heterogenization of well-defined homogeneous catalysts,[6] framework-stabilization of otherwise short-lived catalysts,[6] framework-encapsulation of molecular catalysts,[7] coupling of catalysis to chemical separations,[8] demonstration of "adventitious" catalysis by nominally coordinatively saturated nodes (metal ions or clusters[2]), post-synthesis incorporation of catalytic metal sites,[9–11] and substrate-size-selective catalysis.[2,6,9,12]

Despite the many exciting and compelling recent developments, in our view the area of MOF-based catalysis is still in an immature phase. Yet to be demonstrated, for the most part, is catalytic chemistry that fully exploits the remarkable features of MOFs to accomplish unique chemistry. Possible to envision, but yet to be demonstrated, for example, are: (a) useful multi-catalyst architectures that are very difficult to access otherwise, (b) metal coordination environments, and therefore reactivity, that can be achieved in no other way, and (c) reactivity-defining microenvironments that can be achieved in few other ways. While zeolites have offered an interesting conceptual starting point,[1,2,13] the way forward—in view of (a), (b) and (c)—may instead be to think of catalytic MOFs as analogues of enzymes.

We look forward to participating in the development of MOF catalytic chemistry along the lines of an "artificial enzyme" paradigm. For the rest of this report, however, we have limited ourselves to surveying what has already been accomplished in MOF catalysis, with an eye more towards highlighting demonstrations of concepts rather than scopes of reactivity. Our decision here again reflects the relatively early

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stage of development of the field: most reports have focused on simply documenting catalytic behavior, rather than on demonstrating catalytic chemistry that may prove useful to chemists working in areas other than porous materials. (Nevertheless, included in the section that follows is a table organized in terms of substrates and reactions.) Among the most exciting developments are those in the area of enantio-selective catalysis. Since these processes are the focus of an excellent review by Lin and co-workers elsewhere in this issue,[14] we have largely excluded them—except where they also serve to illustrate an idea not directly related to enantio-selectivity. Finally, we have limited our review to MOFs that are crystalline.[15,16]

2. Catalysis

Only a few dozen reports of chemical catalysis by crystalline, microporous metal–organic frameworks have appeared to date. Catalogued in Table 1 are the majority of the known catalytic MOFs, together with descriptions of the specific catalyzed. Following in the tradition of zeolite chemistry, many researchers have devised informal menomic names for their materials (*e.g.*, PIZA = *P*orphyrinic *I*llinois *Z*eolite *A*nalogue, POST = *P*ohang University of *S*cience and *T*echnology, HKUST = *H*ong *K*ong *U*niversity of *S*cience and *T*echnology, *etc.*). These are used in several instances below, while in other cases materials are described according to empirical formulae. Shown in Fig. 1 are the structures of several organic struts used in the synthesis of catalytically active MOFs, along with their abbreviations.

We caution the reader that catalysis ascribed to hetero-geneous entities is sometimes instead caused by dissolved material, *i.e.* homogeneous catalysts. In some of the work reviewed below, appropriate control experiments have been done, while for others the controls appear to be lacking. The simplest control is to separate the putative catalyst from the reaction mixture by filtration and then monitor the filtrate to see if catalysis persists. Also valuable are studies of substrate size selectivity. While the absence of size selectivity does not prove that the catalyst is homogeneous (catalysis could be limited to the MOF exterior, for example), the presence of size selectivity does constitute good circumstantial evidence for heterogeneous reactivity. Finally, not all heterogeneous catalysis is caused by the intended MOF catalytic site. As emphasized especially in subsection A, the nodes of most MOFs are reasonably good Lewis acids. Furthermore, these acid sites will tend to be exposed at MOF surfaces and may well function as catalysts. (Similarly, terminal ligands can present Lewis basic sites.) Useful control experiments are to examine not only putative catalytic MOFs, but also MOFs possessing similar overall structures but lacking designed catalytic sites. If residual catalytic activity is detected with a nominally non-catalytic MOF, its importance can often be corroborated and exaggerated by fragmenting the MOF (*e.g.* by stirring) and exposing additional metal sites and/or ligand termini.

A: Opportunistic catalysis with metal nodes

Among the earliest reports of MOF-based catalysis was a description in 1994 by Fujita and co-workers on the cyanosilylation of aldehydes by a 2D MOF (layered square grids) of formula Cd(4,4′-bpy)$_2$(NO$_3$)$_2$, (bpy = bipyridine).[2] This investigation centered mainly on size- and shape-selective clathration, as shown for example, in Fig. 2 for *o*-dibromo-benzene.

Also reported, however, was the catalytic cyanosilylation of aldehydes (eqn (1)). Notably, substrate-shape-selectivity was observed, indicating that aldehydes must enter the materials pores to reach catalytic sites.

$$\text{(1)}$$
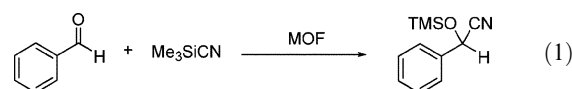
The active sites are Cd(II) ions, with Lewis-acid catalysis presumably occurring *via* substrate displacement of labile, axially coordinated water molecules rather than equatorially bound dipyridyl struts.

A second set of examples are those reported by Llabrés i Xamena *et al.* based on a two-dimensional, square-grid MOF containing single Pd(II) ions as nodes and 2-hydroxypyrimidi-nolates as struts.[34] Despite initial coordinative saturation, the palladium centers in this MOF proved capable of catalyzing alcohol oxidation, olefin hydrogenation, and Suzuki C–C coupling. At a minimum, these reactions necessarily entail redox oscillations of the metal nodes between Pd(II) and Pd(0) intermediates accompanying by drastic changes in coordina-tion number, which would certainly lead to destabilization and potential destruction of the original framework if all the Pd centers are catalytically active. The observation of substrate shape- and size-selectivity implies that the catalytic reactions are heterogeneous and are indeed occurring within the MOF. Nevertheless, at least for hydrogenation, it is difficult to rule out the possibility that catalysis is occurring at the surface of MOF-encapsulated palladium clusters/nanoparticles (*i.e.*, partial decomposition sites) or defect sites, rather than at transiently labile, but otherwise intact, single-atom MOF nodes.

Ravon *et al.* have extended studies of "opportunistic" MOF-based catalysis to the archetypal cubic compound, MOF-5.[37] This material comprises coordinatively saturated Zn$_4$O nodes and a fully complexed bdc struts (bdc = benzene-1,4-dicarboxylate); yet it apparently catalyzes the Friedel–Crafts *tert*-butylation of both toluene and biphenyl (butylating agent = *tert*-butyl chloride). Furthermore, *para* alkylation is strongly favored over *ortho* alkylation, a behavior thought to reflect the encapsulation of reactants by the MOF. In contrast, AlCl$_3$, which obviously lacks the well-defined cavities of MOF-5, is non-selective as an alkylation catalyst. The catalytic activity of "MOF-5" in Friedel–Crafts alkyl-ation is tentatively ascribed to encapsulated zinc hydroxide clusters (known contaminants in rapidly synthesized samples of MOF-5[40]) or to a hydrolytically degraded form of the parent material (presumably the MOF of formula [Zn$_3$(OH)$_2$(bdc)$_2$][41]).

B: Designed catalysis with framework nodes

Lewis acid catalysis. The porous-framework material [Cu$_3$(btc)$_2$(H$_2$O)$_3$], also known as HKUST-1[10] and as MOF-199,[42] contains large cavities having windows of

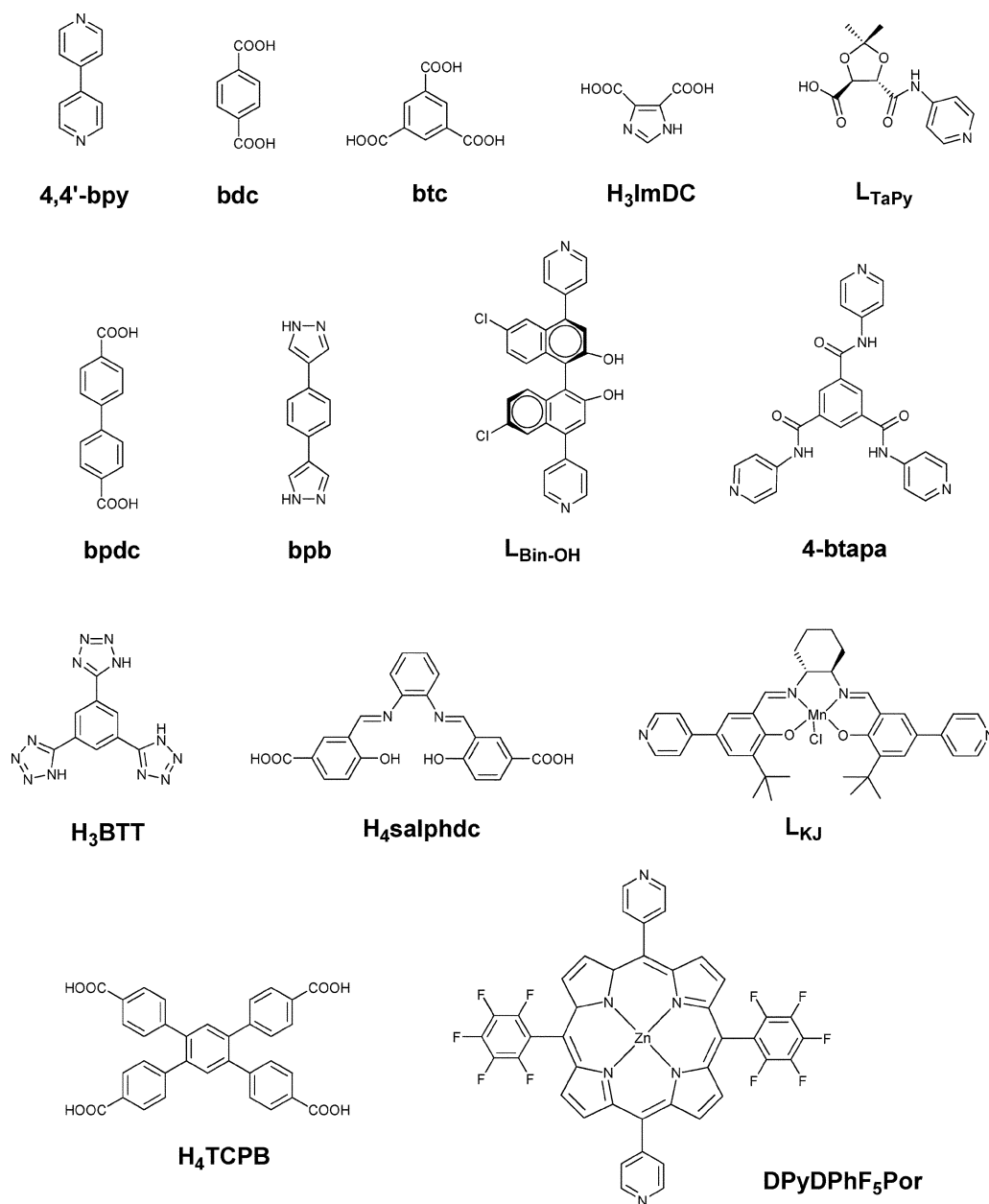**Table 1** Catalogue of known catalytic MOFs and summary of reactions catalyzed

MOF material[a]	Substrate(s)	Reaction(s) catalyzed	Ref.
$[Cd(4\text{-}btapa)_2(NO_3)_2]$	Benzaldehyde and malononitrile	Knoevenagel condensation	17
$[Cd(bpy)_2](NO_3)_2)]$	Benzaldehyde and cyanotrimethylsilane	Cyanosilylation of aldehyde	2
$[Cd_3Cl_6\mathbf{L1}_3]$	Aryl aldehyde and diethyl zinc	Alkylation of aldehyde	9
$[Co(BPB)]$	Cyclohexene	Oxidation of olefin	18
$[Cr_3F(H_2O)_2O(bdc)_3]$	Benzaldehyde and ethyl cyanoacetate; iodobenzene and acrylic acid	Knoevenagel condensation; Heck coupling	19
$[PW_{11}TiO_{40}]^{5-}@[Cr_3F(H_2O)_2O(bdc)_3]$, and $[PW_{11}CoO_{39}]^{5-}@[Cr_3F(H_2O)_2O(bdc)_3]$	α-Pinene, caryophyllene and cyclohexene	Oxidation of olefin	20
$[Cu(2\text{-}pymo)_2]$ and $[Co(PhIM)_2]$	Tetralin	Aerobic oxidation of olefin	21
$[Cu(bpy)(H_2O)_2(BF_4)_2(bpy)]$	Various epoxides	Ring-opening of epoxide	22
$[Cu(\text{D-asp})bpe_{0.5}]$ and $[Cu(\text{L-asp})bpe_{0.5}]$	cis-2,3-Epoxybutane and methanol	Methanolysis of epoxide	23
$[Cu(\mathbf{L2})_2(H_2O)_2]$, $[Cu(\mathbf{L3})_2(H_2O)(Py)_2]$, $[Cu(\mathbf{L3})_3(H_2O)Cl]$ and $[Co(sal)(H_2O)(Py)_3]$	Linear and cyclic olefins	Epoxidation of olefin	24
$[Cu(SO_4)(pbbm)]$ and $[(Cu(Ac)_2(pbbm))\cdot CH_3OH]$	2,6-Dimethylphenol	Oxidative self-coupling	25
$[Cu_3(btc)_2]$	α-Pinene oxide; citronellal; ethylene acetal of 2-bromopropiophenone	Isomerization; cyclization; rearrangement	26
	Olive oil and mill waste waters	Oxidation of polyphenol	27
	Benzaldehyde (or acetone) and cyanotrimethylsilane	Cyanosilylation of aldehyde	28
$[In(OH)(hippb)]$	Benzaldehyde and α-methylbenzeneacetaldehyde	Acetalization of aldehyde	29
$[In_2(OH)_3(bdc)_{1.5}]$	Nitrobenzene and 2-methyl-1-nitronaphthalene; methylphenyl sulfide, (2-ethylbutyl)phenyl sulfide	Reduction of nitroaromatic; oxidation of sulfide	30
$Mn(porphyrin)@[In_{48}(HImDC)_{96}]$	Cyclohexane	Oxidation of alkane	7
$[Ln(OH)(1,5\text{-}NDS)H_2O]$	Linalool	Epoxidation of olefin	31
$[(Mn(TpCPP)Mn_{1.5})(C_3H_7NO)\cdot 5C_3H_7NO]$	Cyclic alkenes; cyclic/linear alkanes	Epoxidation of olefin; oxidation of alkane	32
$[Mn_3((Mn_4Cl)_3BTT_8(CH_3OH)_{10})]_2$	Aldehydes and cyanotrimethylsilane; benzaldehyde and methyltrimethylsilyldimethylketene acetal	Cyanosilylation of aldehyde; Mukaiyama-aldol	12
$[(Na_{20}(Ni_8\mathbf{L4}_{12})(H_2O)_{28})(H_2O)_{13}(CH_3OH)_2]$	CO	Oxidation to CO_2	33
$[Pd(2\text{-}pymo)_2]$	Cinnamyl alcohol; aryl halides and arylboronic acids; 1-octene, cyclododecene	Oxidation of alcohol; Suzuki–Miyaura coupling; hydrogenation of olefin	34
$Tb[V_6O_{13}\{(OCH_2)_3C(NH_2CH_2C_6H_4\text{-}4\text{-}CO_2)\}\{(OCH_2)_3C\text{-}(NHCH_2C_6H_4\text{-}4\text{-}CO_2)\}_2]^{4-}$	Propanethiol	Oxidation of sulfide	39
$[Zn_2(bpdc)_2\mathbf{L5}]$	2,2-Dimethyl-2H-chromene	Epoxidation of olefins	6
$[Zn_2(Py_2(PhF_5)_2PorZn)(TCPB)]$	Acetyl imidazole and pyridyl carbinols	Intermolecular transfer of acyl	35
$[Zn_3(\mu_3\text{-}O)(O_2CR)_6(H_2O)_3]^{n+}$	Esters and alcohols	Transesterification	36
$[Zn_4O(bdc)_3]$ and $[Zn_4O(ndc)_3]$	tert-Butyl chloride and toluene	Friedel–Crafts alkylation	37
$[(Zn_4O)(bdc\text{-}NH_2)_3]\cdot Vsal_{0.4}$	Cyclohexene	Oxidation of olefin	38

[a] Ac = acetyl; bdc = 1,4-benzenedicarboxylate; BPB = 1,4-bis(4′-pyrazolyl)benzene; bpdc = biphenyldicarboxylate; bpe = trans-1,2-bis(4-pyridyl)ethylene); Bpy = 4,4′-bipyridine; btc = benzene-1,3,5-tricarboxylate; btapa = 1,3,5-benzene tricarboxylic acid tris[N-(4-pyridyl)amide]; BTT = 1,3,5-benzenetris(tetrazol-5-yl); D-asp = D-aspartate; HImDC = 4,5-imidazole dicarboxylic acid; hippb = 4,4′-(hexafluoroisopropylidene)bis(benzoic acid); **L1** = (R)-6,6′-dichloro-2,2′-dihydroxy-1,1′-binaphthyl-4,4′-bipyridine; **L2** = (4-formylphenoxy)acetic acid; **L3** = 2-[2-[[(2-aminoethyl)imino]methyl]phenoxy]acetic acid; **L4** = 4,5-imidazoledicarboxylic acid; **L5** = (R,R)-(−)-1,2-cyclohexanediamino-N,N-bis(3-tert-butyl-5-(4-pyridyl)salicylidene)Mn^{III}Cl; nds = naphthalenedisulfonic acid; pbbm = 1,10-(1,5-pentanediyl)bis(1H-benzimidazole); PhIM = phenyl imidazolate; pymo = 2-hydroxypyrimidinolate; Py$_2$(PhF$_5$)$_2$Por = 5,15-dipyridyl-10,20-bis(pentafluorophenyl)porphyrin; sal = salicylidene moiety; TCPB = 1,2,4,5-tetrakis(4-carboxyphenyl)benzene; TpCPP = tetra-(p-carboxyphenyl)porphyrin.

diameter $\sim$6 Å. The coordinated water molecules are easily removed, leaving open Cu(II) sites. Kaskel and co-workers showed that these Lewis acid sites could catalyze the cyanosilylation of benzaldehyde or acetone (eqn (1)).[28] Alaerts et al. investigated the behavior of the *anhydrous* version of HKUST-1 as an acid catalyst.[26] Recognizing the potential for opportunistic catalysis at defect sites (such as exposed carboxylic acids), they examined three reactions: isomerization of α-pinene oxide, cyclization of citronellal, and rearrangement of α-bromoacetals, whose product selectivity patterns differ significantly for Brønsted vs. Lewis acid-catalyzed pathways. Based on experimental data, these researchers concluded that $[Cu_3(btc)_2]$ indeed functions primarily as a Lewis acid catalyst.

Kaskel and co-workers[43] also evaluated the behavior of MIL-101, a large-cavity MOF having the formula $[Cr_3F(H_2O)_2O(bdc)_3]$ (Fig. 3), as a cyanosilylation catalyst. The coordinated water molecules in MIL-101 are easily removed to expose Cr(III) sites. As one might expect, given the greater Lewis acidity of Cr(III) vs. Cu(II), MIL-101 is much more active than HKUST-1 as a catalyst for the cyanosilylation of aldhydes. Additionally, the Kaskel group observed that the catalytic sites of MIL-101, in contrast to those of HKUST-1, are immune to unwanted reduction by benzaldehyde. The Lewis-acid-catalyzed cyanosilylation of aromatic aldehydes (eqn (1)) has also been carried out by Long and co-workers using a MOF of the formula $Mn_3[(Mn_4Cl)_3BTT_8(CH_3OH)_{10}]_2$ (H_3BTT = 1,3,5-benzenetris(tetrazol-5-yl)).[12] This material contains a three-dimensional pore structure, with the pore diameter equaling 10 Å. In principle, either of the two types of Mn(II) sites could function as a catalyst. Noteworthy features of this catalyst are high conversion yields (for small substrates)

4,4'-bpy **bdc** **btc** **H₃ImDC** **L_TaPy**

bpdc **bpb** **L_Bin-OH** **4-btapa**

H₃BTT **H₄salphdc** **L_KJ**

H₄TCPB **DPyDPhF₅Por**

Fig. 1 Structures of various organic struts employed in the synthesis of catalytically active MOFs.

and good substrate-size-selectivity, consistent with channel-localized catalysis.

Interestingly, $Mn_3[(Mn_4Cl)_3BTT_8(CH_3OH)_{10}]_2$ was also found to catalyze the Mukiyama aldol reaction (eqn (2)).[12]

$$ (2) $$
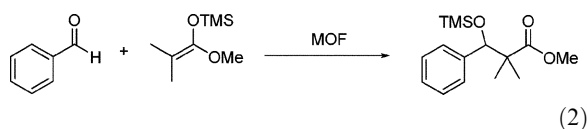
These reactions generally require stronger Lewis acids than do cyanosilylations. In another report,[29] a 2D MOF containing susbtrate-accessible higly Lewis acidic In(III) sites has been used to catalyze the acetalization of benzaldehyde with trimethyl orthoformate.

Alkene oxidation. Lu *et al*. recently examined the oxidative catalytic behavior of a porous three-dimensional MOF having the formula [Co(BPB)]·3DMF, (BPB = 1,4-bis(4'-pyrazolyl)-benzene).[18] As shown in Fig. 4, the Co(II) ions are organized as one-dimensional chains *via* tetrahedral coordination with pyrazolyl nitrogens. Exposure to *tert*-butyl hydroperoxide is believed to convert Co(II) to Co(III). Addition of cyclohexene results in the formation of *tert*-butyl-2-cyclohexenyl peroxide in 83% yield, albeit with some degradation of the MOF after a few dozen turnovers.

Oxidative coupling. Fan and co-workers have recently shown that MOFs with copper metal centers can catalyze the oxidative coupling of 2,6-dimethylphenol to form poly(1,4-phenylene ether), an industrially significant polymer.[25] These systems are capable of yielding C–O/C–C oxidative coupling
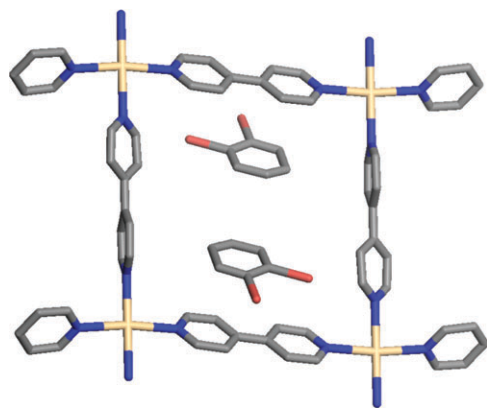
Fig. 2 A crystallographic illustration of the shape selective clathration of dibromobenzene within a square cavity of Cd(4,4′-bpy)$_2$(NO$_3$)$_2$. Cd = gold segment; N = blue segment; C = gray segment; Br = red segment. Hydrogen atoms are omitted for clarity.
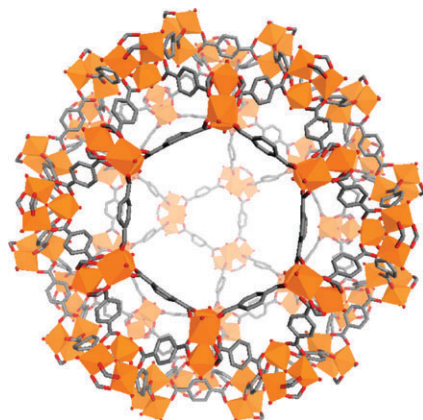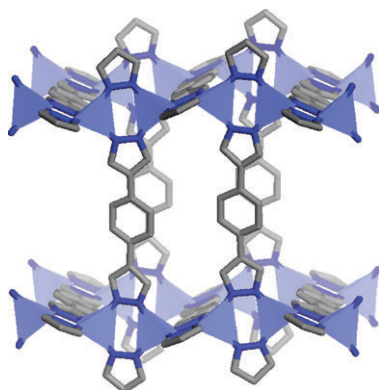

Fig. 3 A crystallographic illustration of the pore structure of MIL-101. Cr = orange polyhedron; C = gray segment; O = red segment. Hydrogen atoms are omitted for clarity.

Fig. 4 A crystallographic illustration of the framework structure of [Co(BPB)]·3DMF, shown along the crystallographic a axis. Co = blue polyhedron; N = blue segment; C = gray segment. DMF molecules and hydrogen atoms are omitted for clarity.

selectivities that are comparable to those obtained for other homo- and heterogeneous catalysts (up to ∼90% C–O/C–C coupling under optimized reaction conditions), and display

good substrate to catalyst ratios as well as short reaction times.

C: Homogeneous catalysts incorporated as MOF struts

An attractive and straightforward approach to MOF-based catalyst design is to heterogenize known homogeneous molecular catalysts by employing them as struts. Kitagawa, Noro and Nakamura have extensively discussed this strategy,[44] noting that strut-centered incorporation of coordinatively unsaturated metal centers could lead to applications in separations, chemical sensing and preferential chemisorption, in addition to catalysis.

Metalloporphyrins. Given their enormous utility as molecular catalysts, both in artificial systems and as active sites in many metallo-enzymes, porphyrin complexes are obvious candidates for incorporation into MOFs as catalytically functional struts. Indeed, some of the earliest reports on crystalline MOFs emphasized the potential of porphyrins as building blocks.[45] However, to date there exist only two reports of catalysis by porphyrin struts in well-defined MOFs.[32,35] The near absence of catalytically active porphyrin-strut-based MOFs can be attributed to three design challenges: (1) porphyrinic MOFs featuring large open pores are unusually susceptible to collapse upon removal of solvent; (2) it is difficult to prevent porphyrin metal sites from doubling as nodes for strut coordination, thereby blocking potential catalytic sites; (3) attempts to incorporate free-base porphyrins as struts (which would then be available for post-synthesis metallation) are generally frustrated by the tendency of the porphyrin ligand to scavenge and coordinate metal ions present in the initial MOF synthesis.

The first report of porphyrin-strut-based catalysis concerns PIZA-3,[32] a MOF featuring trinuclear manganese clusters as nodes and [tetrakis(phenylcarboxylate)porphyrin]Mn(III) as struts. PIZA-3, which is stable to solvent evacuation, is capable of catalytically hydroxylating both linear and cyclic alkanes as well as epoxidizing olefins (oxidant = iodosylbenzene). Unfortunately, the absence of substrate size and shape selectivity, despite selectivity in vapor sorption studies, led the researchers to conclude that catalysis is dominated by reactivity on the MOF exterior.

In the second report, Shultz et al. successfully synthesized ZnPO-MOF, a highly porous pillared paddlewheel MOF,[46] from Zn(NO$_3$)$_2$, DPyDPhF$_5$Por (= 5,15-dipyridyl-10,20-bis-(pentafluorophenyl)porphyrin), and the tetratopic ligand H$_4$TCPB (= 1,2,4,5-tetrakis(4-carboxyphenyl)benzene) (Fig. 5) and used it for the catalysis of an intermolecular acyl-transfer reaction.[35]

ZnPO-MOF illustrates several interesting, catalysis-relevant structural and synthetic notions. First, while the free porphyrin ligand is used in the synthesis, it is spontaneously metallated (with Zn(II)) during MOF formation. Secondly, the tetratopic strut (TCPB^{4-}) provides the structural stability, and therefore permanent microporosity, lacking in many porphyrinic MOFs. The tetratopic strut also serves to inhibit framework catenation—both in ZnPO-MOF and in other frameworks.[11] Additionally, the intentional mismatch of dimensions for the two molecules used as struts, together with the comparatively
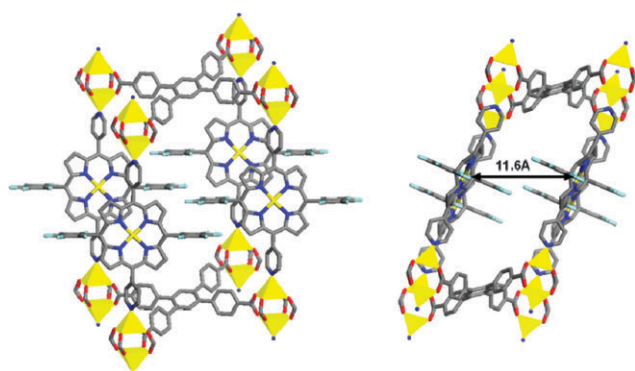
Fig. 5 Left: A crystallographic view of a single network unit for ZnPO-MOF, formed from 1,2,4,5-tetrakis(4-carboxyphenyl)benzene) and (5,15-dipyridyl-10,20-bis(pentafluorophenyl)porphyrin struts. Right: A view of the unit cell highlighting the 11.6 Å distance between cofacial porphyrins. Zn = yellow polyhedron, O = red segment, F = cyan segment, N = blue segment, C = gray segment. Solvent molecules and hydrogen atoms are omitted for clarity.

strong carboxylate–Zn(II) (paddlewheel) bonding, prevents the available porphyrinic Zn(II) sites from functioning as secondary nodes. This, in turn, leaves the sites open for subsequent catalytic chemistry. Thus, the use of H_4TCPB enabled Shultz et al. to overcome the aforementioned design challenges (1) and (2).

As illustrated in Fig. 5, the porphyrin struts in ZnPO-MOF are oriented in parallel 1D, rather than box-like 2D, fashion. As such, they present to candidate reactants large pores and cofacial Zn(II)porphyrin sites (potential binding sites) spaced by ~12 Å (Fig. 5, right), The cofacial arrangement of binding sites is reminiscent of that found in discrete Zn-based supramolecular assemblies that are catalytically active for acyl transfer between N-acetylimidazole (NAI) and various pyridylcarbinols (PCs) (eqn (3))[47,48]—suggesting that ZnPO-MOF should be similarly catalytically active.

While ZnPO-MOF is indeed catalytically competent for this transformation (~2400-fold rate enhancement compared to the uncatalyzed process), no significant rate difference was observed among the three isomers of PC. This surprising observation is in stark contrast to that observed with discrete supramolecular catalysts,[47,48] which much more effectively catalyze the transfer of an acyl group to the 3-PC and 4-PC isomers than to 2-PC. In the supramolecular systems, a key factor (eqn (3)) is proper alignment of the substrate molecules (and therefore, stabilization of the transition state) by the porphyrinic assemblies.
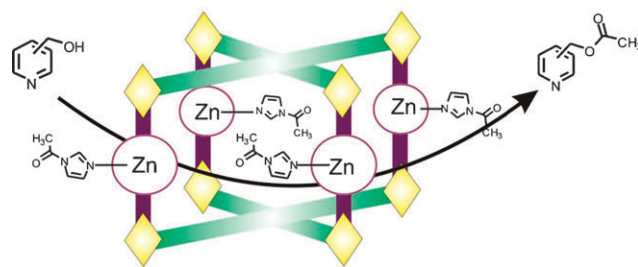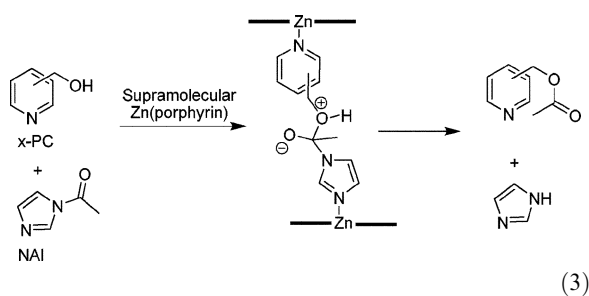
Fig. 6 A schematic view showing a unit cell of ZnPO-MOF that effectively pre-concentrates and Lewis-acid activates N-acetylimidazole for catalytic acyl transfer to pyridylcarbinol species.

Additional experiments reveal that preferential substrate alignment is not a major contributing factor to the catalysis seen with ZnPO-MOF. Rather, the catalysis is primarily due to pre-concentration of NAI in the MOF, effectively raising its local concentration and tremendously enhancing the catalytic rate (Fig. 6). These observations highlight a design characteristic that make MOF-heterogenized porphyrin catalysts different from homogeneous monomeric and supramolecular analogues: while the former may not possess the flexibility of their soluble counterparts, they can be engineered into well-defined, reactant-accessible MOF-based catalytically active sites comprising high local metallo-porphyrin concentrations.

Schiff-base complexes. Recognizing the importance of Schiff base complexes as homogeneous molecular catalysts, Kitagawa and co-workers reported the synthesis of a series of MOF materials comprising trinuclear zinc hydroxyl species as nodes and Cu(II), Ni(II) or Co(II) complexes of N,N′-phenylene-bis(salicylideneimine)dicarboxylate (H_4salphdc) struts.[49] To date, however, catalysis studies using these potentially interesting materials have not been reported.

Cho et al. have described a two-fold catenated, pillared-paddlewheel MOF[46] featuring pairs of zinc ions as nodes and (salen)Mn species as struts.[6] 4,4′-Biphenyldicarboxylate (bpdc) struts define robust square grids that are separated by pillars consisting of a pyridine-derivatized version of the well-known Katsuki–Jacobsen epoxidation catalysts,[50,51] (1,2-cyclohexanediamino-N,N′-bis(3-tert-butyl-5-(4-pyridyl)-salicylidene)Mn^{III}Cl[52,53] (L_{KJ} in Fig. 1). Studies of olefin epoxidation revealed that heterogenization substantially increases the activity of the catalyst. Studies of substrate size selectivity (2 : 1, small : large) that increased greatly as the catalytic reaction proceeded (18 : 1 small : large at 45% conversion). This unusual behavior was attributed to mixed "inside/outside" catalysis initially, and "mainly inside" catalysis subsequently. As the reaction proceeds, oxidant-induced damage of the outermost struts of the framework occurs, necessitating substrate permeation of the MOF to access active catalytic sites. This in turn leads to greatly increased selectivity for the small substrate.

Binaphthyl complexes. Lin and co-workers reported the synthesis of a catalytically active MOF containing pyridine-functionalized hydroxybinaphthyl units as struts (L_{Bin-OH}, Fig. 1).[9] The struts are connected to chloride-bridged chains of cadmium ions to yield a 3D structure containing sizeable

(3)

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1D channels. Once the MOF was assembled, these researchers were able to introduce Ti(IV) sites *via* coordination by secondary functional groups as shown below.
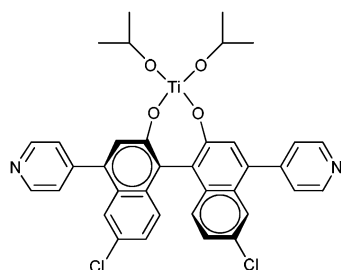
The unusual post-synthesis functionalization strategy works because of the marginal affinity of the naphthoxide site for Cd(II), present at high concentration during the initial synthesis. With the titanium-functionalized MOF in hand, Lin and co-workers were able to effect catalytic $ZnEt_2$ additions to aromatic aldehydes with high enantioselectivities.

D: MOF-encapsulated molecular catalysts

Eddaoudi and co-workers have used 4,5-imidazole dicarboxylic acid (H_3ImDC) and $In(NO_3)_3$ to create an unusually robust anionic framework (termed rho-ZMOF) that can be formulated as $[In_{48}(HImDC)_{96}]$.[7] As illustrated in Fig. 7, the cavities are large enough to encapsulate porphyrins. The pores surrounding these cavities, however, are too small to enable porphyrins to pass through. Consequently, cationic porphyrins can be electrostatically encapsulated and incarcerated during MOF synthesis.[7] Under certain conditions, loadings of >60 wt% were achieved.

Importantly, the strategy allows for the encapsulation of the porphyrin as a free base. The Eddaoudi group demonstrated that the encapsulated free-base porphyrin could be metallated subsequently with manganese, cobalt, zinc or copper ions. Additionally, they showed that the manganese version could be used to facilitate the oxidation of cyclohexane to cyclohexanol and cyclohexanone using *tert*-butyl hydroperoxide (TPHP) oxidant.

The MOF encapsulation approach invites comparison to earlier studies of oxidative catalysis by zeolite-encapsulated Fe(porphyrin)[54–56] as well as Mn(porphyrin) systems.[57,58] The zeolite studies generally employed iodosylbenzene (PhIO),
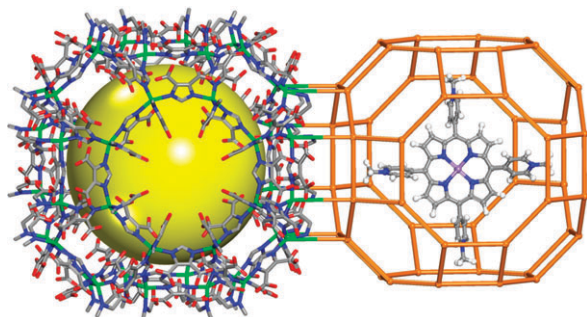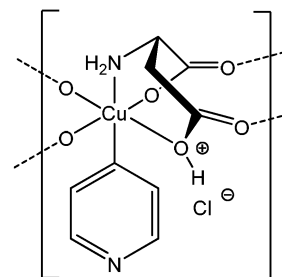
rather than TPHP as oxidant. The difference is likely mechanistically significant, thus complicating comparisons. Briefly, PhIO is a single oxygen atom donor, while TBHP is capable of more complex behavior. In addition, for the MOF-based system, it is conceivable that oxidation proceeds *via* both oxygen transfer from a manganese oxo intermediate as well as a manganese-initiated radical chain reaction pathway.[59] Regardless of mechanism, the approach is a promising one for isolating and thereby stabilizing the porphyrins against both oxo-bridged dimer formation and oxidative degradation.

E: Catalysis by metal-free organic struts or cavity modifiers

Most examples of MOF-based catalysis make use of metal ions or atoms as active sites. Among the few exceptions are two nickel- and two copper-containing MOFs synthesized by Rosseinsky and co-workers.[23] These compounds employ amino acids (L- or D-aspartate) together with dipyridyls as struts. The coordination chemistry (see Fig. 8) is such that the amine group of the aspartate cannot be protonated by added HCl, but one of the aspartate carboxylates can. Thus, the framework-incorporated amino acid can exist in a form that is not accessible for the free amino acid. While the nickel-based compounds are marginally porous, on account of tiny channel dimensions, the copper versions are clearly porous.

The Rosseinsky group showed that the carboxylic acids behave as Brønsted acidic catalysts, facilitating (in the copper cases) the ring-opening methanolysis of a small, cavity-accessible epoxide at up to 65% yield. These researchers point out that superior homogeneous catalysts exist, but emphasize that the catalyst formed here is unique to the MOF environment, thus representing an interesting proof of concept.

Kitagawa and co-workers have reported the synthesis of a catalytic MOF having the formula $[Cd(4\text{-btapa})_2(NO_3)_2]$ (4-btapa = 1,3,5-benzene tricarboxylic acid tris[*N*-(4-pyridyl)-amide]; see Fig. 1).[17] The MOF is three-dimensional, consisting of an identical catenated pair of networks, yet still featuring pores of molecular dimensions. The nodes consist of single cadmium ions, octahedrally ligated by pyridyl nitrogens. From a catalysis standpoint, however, the most interesting feature of this material is the presence of guest-accessible amide functionalities. The researchers showed that the amides are capable of base-catalyzing the Knoevenagel condensation of benzaldehyde with malononitrile. Reactions with larger nitriles, however, are only marginally accelerated, implying

Fig. 7 The pore structure of rho-ZMOF (left), and encapsulated $[H_2TMPyP]^{4+}$ porphyrin in rho-ZMOF α-cage (right). Solvent molecules and hydrogen atoms are omitted for clarity. (Figure courtesy of Prof. M. Eddaoudi.)


Fig. 8 A schematic view of the coordination environment around the Cu center in a MOF with D-aspartate struts.[23]

that catalysis takes place chiefly within the material's channels rather than on its exterior. A noteworthy finding is the *lack* of catalysis by the free strut in homogeneous solution, evidently due to intermolecular H-bonding between bptda molecules.[60] Thus, the MOF architecture elicits catalytic activity not otherwise encountered.

In an interesting alternative approach, Férey and co-workers[19] were able to modify the interior of MIL-101 *via* Cr(III) coordination of one of the two available nitrogen atoms of each of several ethylenediamine molecules. (Related coordination-based, post-synthetic tailoring of MOF cavities has been described for materials featuring open Cu(II)[10] or Zn(II)[11] sites. For a general review of post-synthetic modification of MOFs see the article by Wang and Cohen in this issue of *Chem. Soc. Rev.*[61]) The free non-coordinated ends of the ethylenediamines were then used as Brønsted basic catalysts, again for Knoevenagel condensation of benzaldehyde with nitriles.

A third approach has been described by Kim and co-workers.[36] Using a pyridine-functionalized derivative of tartaric acid (L_{TaPy}; see Fig. 1) and a Zn(II) source they were able to synthesize a 2D MOF termed POST-1.

As illustrated in Fig. 9, POST-1 possesses 1D channels whose cross sections are defined by six trinuclear zinc clusters and six struts. While three of the six pyridines are coordinated by zinc ions, the remaining three are protonated and directed toward the channel interior. When neutralized, the non-coordinated pyridyl groups are found to catalyze transesterification reactions, such as eqn (4), presumably by facilitating deprotonation of the reactant alcohol. The absence of significant catalysis when large alcohols are employed strongly suggests that the catalysis occurs within the channels of the MOF.

(4)
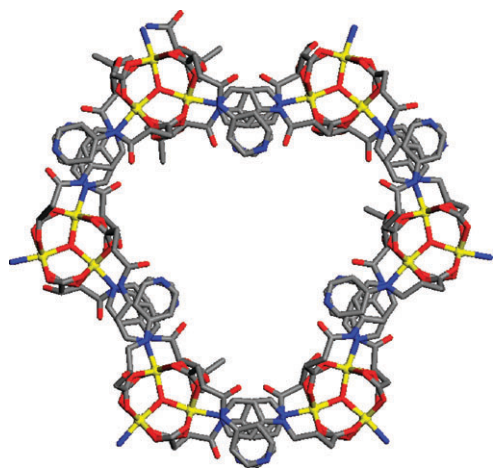
Fig. 9 A hexagonal large-pore structure of POST-1 with three pyridyl groups pointing to the pore. Zn atoms are shown in yellow, O in red, N in blue, and C in gray. Solvent molecules and hydrogen atoms have been omitted for clarity.

F: Catalysis by MOF-encapsulated clusters

Controlled growth of catalytic clusters or nanoparticles within MOF cavities is an idea that has captured the attention of several research groups;[62–65] and a number of intriguing preliminary results, based chiefly on metals or metal oxides, have been obtained. It has generally proven difficult, however, to demonstrate that clusters/nanoparticles are actually encapsulated within well-defined MOF cavities. Indeed, in some instances the opposite has been shown, with catalyst particle sizes clearly exceeding the dimensions of single MOF cavities.

The only unambiguous examples of (exclusively) single-cavity encapsulation of well-defined clusters appear to be Keggin-type polyoxometallates within the rather sizeable cavities of MIL-101 (Fig. 3).[66] The encapsulation is electro-static, entailing the displacement of initially present fluoride ions. (The clusters are small enough to enter the MIL-101 cavities through the available ports.) Kholdeeva and co-workers showed that by employing either titanium- or cobalt-substituted Keggin ions, the composite cluster@MOF materials could be rendered catalytic.[20] For example, $[PW_{11}TiO_{40}]^{5-}$@MIL-101 was found to be capable of facilitating the oxidation of α-pinene to the corresponding alcohol and ketone using hydrogen peroxide oxidant. $[PW_{11}CoO_{39}]^{5-}$@MIL-101, on the other hand, was observed to be catalytically competent for the same reaction, but with O_2 as the oxidant. Fair turnover frequencies were observed (80 h^{-1} at 50 °C for $[PW_{11}Co_{39}]^{5-}$@MIL-101, and 40 h^{-1} at 30 °C for $[PW_{11}TiO_{40}]^{5-}$@MIL-101). Hydrogen peroxide was ultimately found to degrade the MOF framework, but O_2 was not.

3. Conclusions

Over the past five years, the notion of metal–organic frameworks as catalysts has advanced from being a largely hypothetical one, to a fledgling "real" application encompassing more than two dozen experimental examples. Like other heterogeneous catalysts, MOFs allow for easier post-reaction separation and recyclability than homogeneous catalysts. In some cases, they also lend highly enhanced catalyst stability. Additionally, they typically offer substrate-size selectivity. Nevertheless, while clearly important for reactions in living systems, selectivity on the basis of substrate size is of limited value in abiotic catalysis, as reasonably pure feedstocks are generally available. The future of the field clearly lies in demonstrating advantageous catalytic behavior that is unique to MOFs. As noted above, a small number of examples of unique catalyst structures and product distributions have begun to appear. Many more remain to be discovered.

Acknowledgements

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