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Outlook

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Grand Challenges and Future Opportunities for Metal−Organic Frameworks

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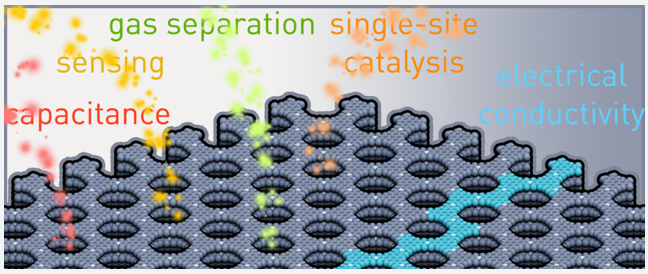
ABSTRACT: Metal−organic frameworks (MOFs) allow compositional and structural diversity beyond conventional solid-state materials. Continued interest in the field is justified by potential applications of exceptional breadth, ranging from gas storage and separation, which takes advantage of the inherent pores and their volume, to electronic applications, which requires precise control of electronic structure. In this Outlook we present some of the pertinent challenges that MOFs face in their conventional implementations, as well as opportunities in less traditional areas. Here the aim is to discuss select design concepts and future research goals that emphasize nuances relevant to this class of materials as a whole. Particular emphasis is placed on synthetic aspects, as they influence the potential for MOFs in gas separation, electrical conductivity, and catalytic applications.



■ INTRODUCTION

Historical interest in the formation of inorganic/organic hybrid compounds dates back to 1830 with Zeise's report of the first organometallic platinum species.[1] In his report Zeise detailed challenges with both synthesis and characterization of the later-named "Zeise's Salt" ($K[PtCl_3(C_2H_4)]H_2O$). Indeed, this Pt complex marked more than a triumph in experimental characterization; it initiated the entire field of organometallic chemistry and more generally the interest in reactivity occurring at the metal−organic interface.

Over the next two centuries numerous advances in chemical physics, optics, and quantum mechanics enabled the development of sophisticated analytical techniques that progressed synthetic curiosities beyond structural and compositional elucidation to targeted function and application. However, like Zeise's salt, many of the 1900s state-of-the-art chemistries were molecular, or zero-dimensional, homogeneous compounds. With industrial motivations for heterogeneous materials, and academic interests in the development of multidimensional, more complex compounds, scientists began to explore physical properties that could only arise from expanding chemical connectivity into higher dimensions (one-, two-, and three-dimensional (1D, 2D, and 3D) materials)[2] in both crystalline and amorphous structures.

Intrinsic porosity came as both a target and a consequence of higher dimensionality. Although purely inorganic, silicious zeolites were a milestone that demonstrated how novel chemical properties could be obtained by harnessing both the porosity[3] and the ability to anchor heterogeneous catalytic sites into the scaffold.[4] Yet within the zeolitic structure types, the chemical compositions were largely limited to aluminosilicates, which are able to accommodate only marginal amounts of transition metals, primarily as defects.[5,6] Expansion to heavier chalcogenides,[7] larger organic anions, and metal substitutions beyond group IV elements yielded both isostructural and novel topologies with unprecedented chemical connectivity. With the subsequent introduction of organic bridging ligands, multidimensional porous coordination complexes formed their own family: metal−organic frameworks (MOFs).[8]

Unlike bridging oxide ligands found in zeolites, the chemical diversity of organic ligands in MOFs added an extra level of electronic complexity arising from the orbital mixing at the metal−organic interface.[9−11] The local chemistry of the metal environment could be readily described with conventional molecular principles,[12] while the periodic nature of the material required concepts borrowed from condensed matter physics,[13] thereby placing MOFs at the crossroads between molecular and solid-state chemistries. For instance, in catalytic applications MOFs can be thought of as three-dimensional spatially separated single-site catalysts where electronic states are localized. For electrical conductivity applications orbital and energy overlap, as well as charge delocalization, are key for charge and energy transport. For gas storage and separation applications, where stability and pore size/topology are more important, the electronic structure is less decisive, yet the stability itself is still dictated by the nature of the metal−ligand bond, the weakest link in typical MOFs.

As with any class of artificial materials, the development of new synthetic methods and new compositions is key for future developments, especially for targeting specific properties (e.g., pore aperture, hydrophobicity).[14] With the synthetic methodology reaching a certain level of sophistication, however, the challenge of finding firm applications for MOFs also becomes essential for the continued growth of the field. These are just as

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likely to emerge from the traditional applications in gas storage[15−17] and separation,[18−21] as they are from more recent advances such as single site heterogeneous catalysis[22−27] or electrical conductivity. The latter provides several avenues to next-generation solar,[28−30] sensing,[31,32] and electrical energy storage devices.[33,34]

In this Outlook we explore some of the current challenges for MOFs, and several future research areas in which these hybrid materials are primed to excel. A particular focus is placed on morphologically, topologically, and compositionally enabled function, in the pursuit of global MOF design principles.

■ SYNTHETIC CHALLENGES

With a vast number of possible topologies and compositions, synthetic challenges in the field stem from understanding and controlling both structural[35−37] and compositional complexity.[38−40] There are numerous compelling areas of research that are dependent on the discovery of novel framework topologies, and emphasis should continue to be placed on the generation of new materials (Figure 1). For example, through pore aperture

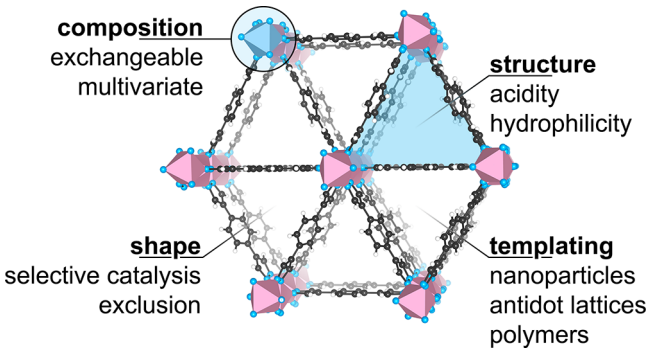

Figure 1. Complexity of metal−organic frameworks arises from both structure and composition. Control of these parameters should provide access to a range of emerging applications that depend on pore structure. Depicted is $Fe_2(BDP)_3$, with the metal nodes shown as pink polyhedra. The void space of one of the pores is emphasized in the transparent blue triangle.

and volume engineering, MOFs have the potential to be highly modular shape selective catalysts. Although shape-selective catalysis is well-developed in the zeolite community (where there are only hundreds of known topologies),[41] there are, to our knowledge, no conclusive reports of shape selective catalysis in MOFs despite the thousands of known structure types.[42]

From a physics perspective, the pore structure variability in MOFs makes them ideal templates for the formation of otherwise unattainable morphologies of encapsulated condensed phase materials. As a demonstration of this powerful design principle, MOFs have been shown to template TiO_2 antidot lattices,[43] porous carbons,[44] nanocasted single site catalysts,[45] and quantum dots with precisely controlled radii.[46] In the latter, quantum dot-in-MOF architectures were recently shown to give rise to prolonged exciton lifetimes and exciton diffusion through the crystal.[47−50] More broadly, the ability to control the distance and angle between organic chromophores with translational symmetry, as afforded by controlling MOF topology, is unmatched and should be harnessed to investigate fundamental questions related to energy transfer. Indeed, topological control has always been a fascination in the MOF community, and it should continue, as these materials are unique in affording precise control in the sub-5 nm range where typical lithography or other top-down techniques fail. Controlling matter at this scale will provide access to otherwise unattainable physical properties.

Further motivation for the development of designer materials with novel pore architectures can be gleaned from their potential application in gas separation technologies. Although frequently serendipitous, there are examples of materials that have been designed to perform challenging gaseous separations based on pore geometry.[51−53] Here MOFs boast a further advantage over other porous materials; their internal surface chemistry (e.g., hydrophobicity, acidity) is tunable through both organic and inorganic functionalization. The ability to tune topology and composition, combined with advances in both synthesis and characterization of increasingly complex metal−ligand combinations, culminating perhaps with multivariate MOFs,[54,55] should see continued emphasis being placed on pore and topology engineering in the future.

■ GAS SEPARATION

The porosity of most MOFs makes them attractive for gas storage applications, where the gaseous density within the framework may be increased relative to bulk gas due to framework−guest interactions. Many reviews have examined single gas uptake;[56,57] here we will focus on the outlook of MOFs in gas separation applications. In order to achieve separation between two or more components, there must be a differentiation between how the analyte gases interact with the framework, either by size or energetically. Further, there are two primary energetic regimes of gas-framework interaction: chemisorption, where the uptake of the gas is dependent on a chemical transformation (e.g., bond formation or charge transfer) and physisorption, where the guest molecule interacts with the electric field produced by the framework.

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Size exclusion selectivity works efficiently in some MOFs, as recently exemplified by the challenging separation of acetylene from ethylene.[58] However, the size exclusion approach requires fine-tuning of pore size for separating gases with similar kinetic diameters (e.g., N_2/O_2), a degree of synthetic control that is

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often serendipitous.[59] Indeed, size exclusion is difficult to employ for separating molecules of similar size and polarizability.

An alternative approach to achieve selective gas separation for such difficult mixtures is to target the inherent reactivity of a given adsorbate through chemisorption. This approach mandates reversible bond making and breaking. In this vein, Cr-MIL-100 was shown to interact with N_2 through π-backbonding,[60] allowing for selective retention of N_2 in $N_2/CH_4/O_2$ mixtures. In another compelling report, diamines coordinated to the open metal sites in a MOF-74 analogue led to cooperative interactions that allowed high and reversible uptake of CO_2.[61] These outstanding studies are selected examples among numerous other ways in which chemisorptive interactions in MOFs address challenging problems in gas storage and separations. Cooperative chemisorptive interactions that lead to nonstandard adsorption isotherms and large stepwise adsorption of certain analytes are sure to play increasingly prominent roles in designing materials with enhanced single-gas selectivity.

The modulation of weaker physisorptive interactions to target specific gases is a more challenging, though potentially equally fruitful, endeavor. Although physisorptive interactions are inherently weaker than chemisorptive ones, the lower energy associated with the former can be an advantage when considering the efficiency of a gas separation process. A large selectivity, or difference in interaction energy between gases, is indeed desirable for favorable breakthrough curves, but maximizing the overall efficiency of a separation process requires that the energy involved in the recovery of the retained gas also be minimized.

The ability to fine-tune the physisorptive interactions in MOFs is one instance where current synthetic routes have not yet reached the necessary level of sophistication.[62−66] The strength of these interactions (E_{int}) is dependent on both the guest dipole moment (μ) and the strength of the electric field produced by the host framework ($\boldsymbol{E}_{x,y,z}$) described by the relationship $E_{int} = \mu \boldsymbol{E}_{x,y,z}$. Here, μ is the permanent dipole moment of the polar guest molecule, and the electric field is defined as the derivative of the electrostatic potential (U):

$$\boldsymbol{E}_{x,y,z} = -\frac{\mathrm{d}U}{\mathrm{d}x,\ y,\ z}$$

The magnitude of the electric field is determined by the local spatial charge density of the framework (e.g., open metal sites produce large electric fields, organic aromatics produce much smaller fields). High-field regions of the framework result in stronger interactions with guests. This has been experimentally reported on numerous occasions, for example, through the differences in gas uptake in the series of HKUST-1 derivatives[68] or through the inclusion of organic linkers with pendant functionality that installs a small electric field in the otherwise vacuous pore center.[69,70] In the latter case, the volumetric uptake decreases because the pore volume is diminished, but in both cases, the interaction strength increases proportional to field strength. From these studies, we can generalize that for a given material, the interaction energy is intimately linked to the magnitude of the dipole moment of the guest (Figure 2a).

These considerations are more nuanced for gases with no permanent dipole moment[57] (Figure 2b). The framework−nonpolar guest interaction energy is not null; it is determined by the guest's instantaneous (or induced) dipole (μ_i), a complementary and much weaker interaction. The instantaneous dipole is accessed by exposure of the guest compound

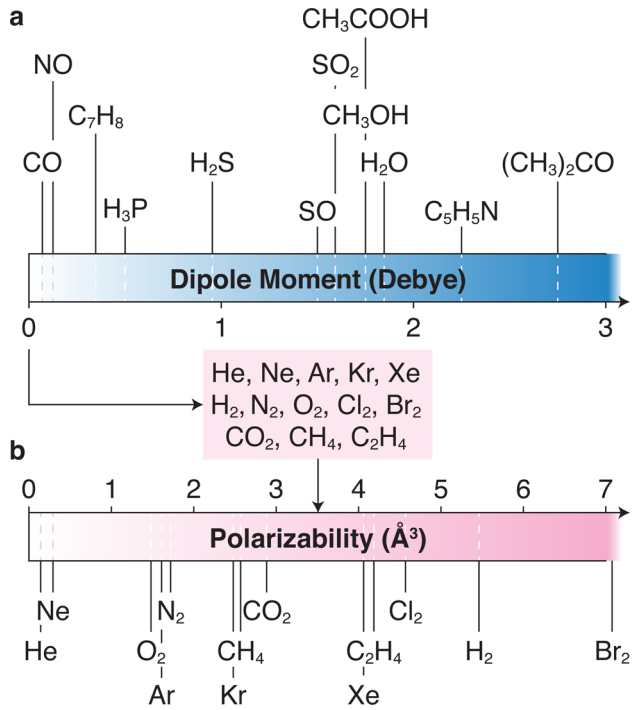

Figure 2. Permanent polarization (dipole moment, μ) of some familiar polar molecules (a) determines the interactions strength with the electric field produced by the framework. Most small gases feature no permanent dipole and their strength of interaction is determined by the magnitude of their polarizability (b).[67]

to an external electric field, inducing a polarization as a product of orbital mixing between occupied and higher quantum number unoccupied orbitals. The polarizability (α) is therefore defined as the quotient of the instantaneous dipole moment and the applied electric field in all directions, or $\mu_i = \alpha \cdot E_{x,y,z}$.

Although polar molecules are also polarizable, they are excluded from the polarizability chart shown in Figure 2b as their responses are often smaller (<2 Å^3) than most nonpolar gases (this is because their dipoles align antisymmetrically to the external electric field). Furthermore, their dipole dominates the interaction energy; the polarizability is only a minor contribution. Thus, achieving high selectivity and uptake of compounds with low and comparable polarizabilities (e.g., CH_4/Kr or N_2/O_2) poses challenges.

Modulating the internal potential of a porous material via an external applied bias would in turn change the host−guest interaction strength. In order to achieve this, the framework must be somewhat electrically conductive (insulating MOFs will instead dissipate a potential bias as heat). Indeed, electrically conductive porous materials are markedly rare. The realization of electrically conductive MOFs provides avenues to selective and tunable host−guest interaction energies, through modulation of the MOF-produced field, a concept termed potential swing adsorption.[71−73] A variable potential will allow targeting of selective gases in high-field conditions (with the caveat that the framework itself must be stable, and that the most dramatic adsorption difference would be observed in high dielectric media − differences in gas uptake may not be observable in air). This effect was demonstrated with porous conductive carbon[71] and is certainly of interest for future technologies. The limitation, however, is the discovery or design of MOFs with sufficiently high electrical conductivity.

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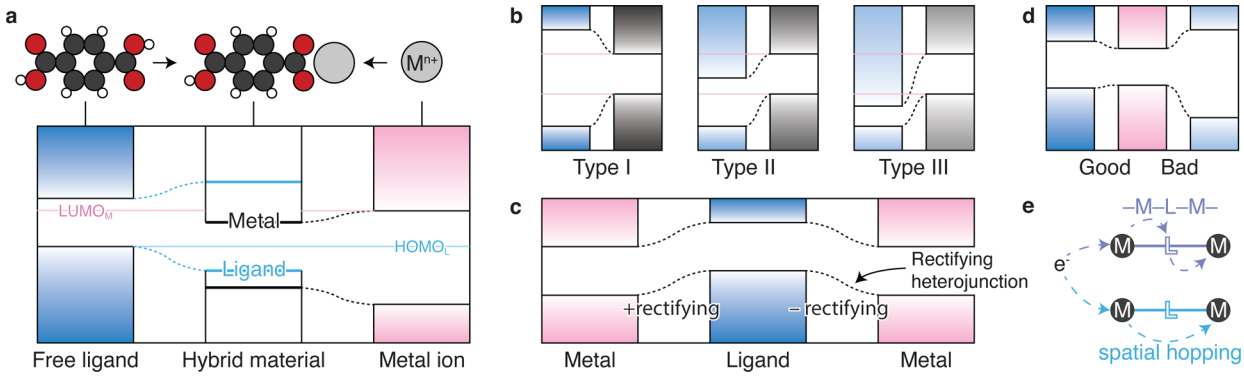

Figure 3. Metal−organic frameworks feature band edges that are augmented representatives of their daughter components (a). Borrowing from the semiconductor field, the metal/ligand energy level alignments (b) can be thought of as Type I, II, or III offsets, and the resultant material features some orbital mixing (or band bending). Energy level matching is paramount for conductive applications, because the metal−organic−metal interface occurs periodically thereby exacerbating the energy mismatch at their interface (forming a rectifying heterojunction contact, c). Depending on the charge carrier (holes or electrons), the alignment of the ligand and metal orbitals can minimize the rectifying contact in the valence and/or conduction bands can yield and electrically conductive material (d) allowing for metal−ligand−metal− or spatial hopping conductive pathways (e).

■ ELECTRICAL CONDUCTIVITY

Besides potential swing adsorption, the development of electrically conductive MOFs provides avenues to other novel technologies including sensors,[74,75] thermoelectrics,[76,77] electrical energy storage materials,[34,78,79] photovoltaics,[80] and electrocatalysts.[81,82]

The ideal electrically conductive MOF features sufficient band dispersion such that charge carriers are mobile through a band conduction mechanism.[30,83] In most cases, however, the mechanism of electrical conductivity in MOFs is best described as charge hopping,[84−86] and is dependent on the spatial separation and density of states between hopping sites. Within the handful of well-characterized electrically conductive MOFs,[87] band conductivity is extremely rare, and the identity of the charge carrier is most often unknown. We see the emergence of systematic studies of electrical transport in MOFs as both necessary and highly important for the field as a whole.

The installation of mixed redox states is one approach that has proven fruitful in the realization of electrically conductive frameworks. For example, Fe^{3+} defects in Fe^{2+}-based frameworks promote higher electrical conductivity, attributed to hole delocalization.[88] In the same vein, the deliberate formation of organic holes through oxidation in air can lead to electrically conductive MOFs. Examples include materials made from tetrathiafulvalene-tetrabenzoate[89,90] or hexa-iminotriphenylene-semiquinonate.[91] These studies merely suggest that there is ample room for redox-active ligand development.

Modulation of the organic ligands is more common and certainly synthetically more tractable toward conductive MOFs given the diversity of potential targets. Conversely, it is decidedly more rare to find electrically conductive MOFs that feature charge conduction pathways where the charge carrier moves along a metal−organic−metal path. Rather, most frameworks feature highly localized electronic structures and can be thought of as 3D arrangements of organic molecules separated by metal ions and clusters (Figure 3a).[92,93] Although charge localization is useful for applications that rely on discrete states (e.g., photonics, catalysis) and materials with low bulk conductivity can be effective even in some electronic devices (e.g., electrochromic devices),[94,95] a disperse band and mobile charge carriers with low effective mass are desirable in most electronic devices.

The charge locality manifests as flat bands (i.e., bands with <0.1 eV dispersion), sometimes referred to as crystalline molecular orbitals, which primarily arise from poor energy level matching at the metal−organic interface.[96,97] In the language of semiconductor physics, this interface acts as a rectifying heterojunction. However, energetic control of the interface should allow for the formation of "good" (i.e., non-Ohmic) contacts, Figure 3c,e, promoting electrical conductivity through the desired metal−organic−metal path. Although examples aiming for energy level matching between metals and ligands are known, especially in the context of using thiolated ligands,[53] the promotion of band-type conductivity marks a grand challenge for contemporary MOF chemistry.

There are several considerations toward ideal energy level contacts that result in disperse bands. The occupation and eigenvalues of both the organic and inorganic components are computable with electronic structure methods, and simple band alignment diagrams can be drawn to provide an estimate of the energetic contact[98] (Figure 3b). However, such computations are less common in systems with organic components due to the complexity of molecular orbitals,[99] as well as the poorly defined extent of electronic mixing at the metal−organic interface (i.e., an effect comparable to band bending). Computational advances in designing and understanding the metal−organic heterointerface will be critical for this subfield.

Borrowing further from the knowledge of transport in semiconductors is the consideration of defect chemistry. Although recent studies have shown the importance of defects in MOFs for applications in catalysis,[100] there are virtually no studies addressing the influence of defects on electrical conductivity in these materials. This relative void of information is primed to be filled, however, because MOFs should allow excellent control over the charge carrier concentration (i.e., defect concentration) through the use of conventional redox reactions. It is useful to think of controlling the redox states in MOFs as an analogy to intrinsic doping in condensed phase semiconductors, with the caveat that unlike the latter, most porous frameworks are intrinsically metastable relative to their more dense isomeric phases. Other forms of defect control (i.e., interstitials, vacancies, and Schottky defects) serve to destabilize a MOF, where the ligand and metal play both an electronic and structural role. However, certain frameworks are resilient to extremely high defect concentrations (e.g., linker vacancies in

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zirconium carboxylates[100]), and many MOFs are capable of postsynthetic exchange of both ligands and metals. The latter provides inroads to quantum energy level control and targeted electronically relevant modifications.

Given the infancy of the pursuit for electrically conductive porous materials, we expect that both redox control and compositional defect chemistry will play major roles in the development of electrically conductive MOFs in the future.

■ HETEROGENEOUS CATALYSIS

Whereas highly localized electronic states are a detriment for electrical conductivity applications, charge localization is important for catalytic applications where single-site reactivity is desired. Single-site heterogeneous catalysts are preferred by industry for reasons of recyclability and ease of product separation. Despite the advantages of heterogeneous catalysts, numerous large-scale industrially relevant processes still rely on homogeneous catalysis (e.g., Wacker oxidation, hydroformylation, ethylene oligomerization). This is due in part to the lack of compositional and electronic control of heterogeneous catalysts, which are inferior in this sense to molecular complexes. Heterogenizing molecular complexes through appendage to solid-state surfaces has provided some success in conferring molecular-level control to solids,[101,102] but more often this method leads to severe reduction in activity or selectivity for the surface-isolated complex relative to the homogeneous species. Thus, the challenge of finding heterogeneous catalysts for the industrial processes where zeolites, ceramics, metals, surface organometallic species, or indeed any other solids remain ineffective, is still largely open. It is in this space that MOFs may provide unique opportunities owing to their molecular-level electronic and steric tunability.

■ HOMOGENEOUS-INSPIRED CATALYSIS IN A HETEROGENEOUS SCAFFOLD

There are three general approaches to installing catalytically active species in/on a MOF: (i) linker functionalization,[103−106] (ii) nanoconfinement of catalysts in the pores,[107,108] and (iii) intrinsic and extrinsic modification of the secondary building unit (SBU).[109−111] In the former, many researchers have employed linkers containing metal chelating moieties (e.g., bipyridine, porphyrins, pincer ligands) for the appendage of ligand-anchored guest metal sites. For instance, MOFs using iron-metalated porphyrin-based linkers are active in biologically relevant oxidations, mimicking heme enzymes in a heterogeneous scaffold.[112,113] This metallolinker design concept allows for near infinite permutations to achieve immobilization of homogeneous species in a MOF scaffold.

Catalytic sites can also be trapped inside MOF pores. This is most frequently achieved through encapsulation during the self-assembly process. Although this method provides similar tunability to that provided by the native catalyst, there are important limitations to this approach. First, the catalyst must be small enough to fit inside the MOF pore but large enough that it cannot fit through the pore window, lest leaching will occur. Perhaps more importantly, trapping a catalytic species within the pore decreases porosity and impedes mass transport.

An intriguing route to installing catalytic sites that sidesteps many of the challenges above is through inorganic functionalization of the SBUs. Such modifications come in two flavors; (i) metal ion appendage/grafting *onto* the surface of the inorganic SBU and (ii) cation exchange *into* the SBU.[116] In the former, atomic layer deposition has been a particularly ingenious and effective means to deposit catalytically active species at zirconium-based SBUs,[117,118] and numerous advances have been made using other synthetic routes to access grafted catalysts (Figure 4a).[119]

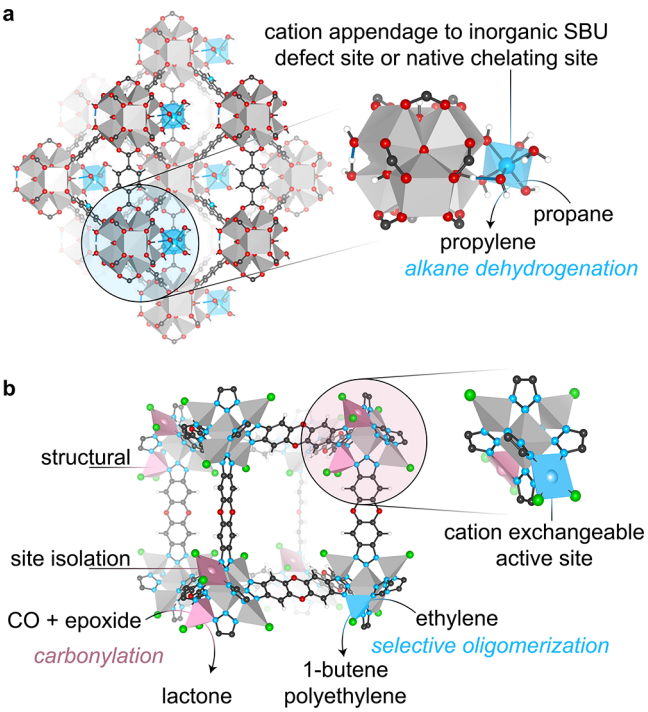

Figure 4. Catalytic centers in MOFs introduced through (a) appendage (illustrated by metal anchoring to the inorganic node of defective NH_2−UiO-66) or (b) cation exchange provide site-isolation (shown schematically is cation-exchanged MFU-4*l*). Three representative catalytic transformations of interest are shown.[25,114,115] Metal nodes are depicted in blue, gray, and pink polyhedra.

In a similar vein, the use of the intrinsic inorganic SBUs as active catalytic sites is attractive because the local ligand environment provided by many MOFs is electronically and sterically unusual (vide infra). However, one may imagine that the use of a metal playing a structural role as a catalytic site presents a liability for the MOF lattice. This liability is avoided if only some of the SBUs are catalytically active, with the rest providing structural support. Postsynthetic cation exchange allows access to such MOFs and enables the formation of even metastable phases that are inaccessible by direct solvothermal routes.[120]

Most importantly, cation exchange at SBUs has enabled the formation of catalytic MOFs that are not accessible by direct routes. For instance, exchange of native Zn^{2+} for Ni^{2+} in MFU-4*l*, a triazolate-based framework with scorpionate-like SBUs,[121] enabled the formation of a heterogeneous catalyst whose activity for the selective dimerization of ethylene to 1-butene surpasses that of homogeneous scorpionate catalysts.[27,122]

There is tremendous scope for the development of MOF-based catalysts that feature reactivity similar to that of the molecular complexes, and encouraging examples show that in some cases MOF catalysts perform even better than homogeneous alternatives. Future work investigating these materials as a platform for obtaining homogeneous single-site selectivity in a heterogeneous scaffold is sure to provide important solutions to problems of industrial relevance.

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MOF NODES REPLICATE KEY ENZYMATIC ATTRIBUTES

Arguably, one of the most underappreciated aspects of SBU chemistry is the electronic environment conferred by the weak ligand field of the O and N atoms comprising most MOF linkers. Metal sites supported by carboxylates, imidazoles, phenols, thiols, as seen in MOFs, are not just reminiscent, but nearly identical to those found in metalloenzymes, which perform multielectron redox catalysis requiring up to six electron transfer processes.[123] Maintaining high-spin configurations in all redox steps, as supported by the weak ligand fields, is vital to minimize reorganizational energy barriers, which in turn allows for fast kinetics. Weak ligands rarely support homogeneous catalysts because they allow for facile demetalation. In metalloenzymes, the fluxional coordination sphere around the active site is supported by the tertiary protein structure. Additionally, the overall protein structure around the metal species often stabilizes multiple open metal sites accessible for substrate binding.

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The nodes of MOFs replicate key attributes found in metalloenzymes in several important points: they are site-isolated, they are often supported by very weak ligand fields, they can have multiple open coordination sites, and they can exhibit dynamic behavior. The latter can be either local at a given SBU,[120] or cooperative throughout the lattice (e.g., breathing[124−126]). Recent examples of MOF nodes structurally mimicking enzymatic active sites involve, for instance, CO_2 fixation: the three azolate, monohydroxide coordination environment of carbonic anhydrase,[127] and the Mg^{2+} coordination environment of Rubisco.[61] Nearing closer to mimicking enzymatic *function* are examples of MOFs that perform oxidative catalysis with O_2 as the terminal oxidant, in a coordination environment similar to some trihistidine oxygenases.[128−130] Although biomimetic mimicry is itself an important target, the unique coordination environment provided by MOF nodes is exciting more broadly for heterogeneous catalysis. Borrowing concepts of efficient catalyst design from nature and applying them for unnatural transformations, such as the industrial homogeneous processes discussed above, is a very exciting prospect for future advances with MOFs.

OUTLOOK

The numerous advantages of MOFs, foremost their high surface area and modular composition, place them at a multidisciplinary crossroads. For good reason, MOFs are one of the most active research fields today, with aspects of their fundamental and applied properties permeating into disciplines as varied as electronics, chemical engineering, and optics. Whereas this Outlook does not attempt to delineate the developments and potential in all these areas, we have introduced some of the exciting prospects related to continued synthetic advances in the field. We further elaborated on three applied areas where MOFs are primed to excel: in challenging gas separations, as porous electrical conductors, and in heterogeneous catalysis. These examples are not exhaustive, but present subtleties that are applicable and relevant to many other applications of MOFs. The challenges and opportunities in these select applications, which span both the traditional and the modern aspects of the field, are illustrative of the continually expanding interest and bright future for MOF chemistry.

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Notes

The authors declare no competing financial interest.

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