Post-Synthetic Surface Modification of Metal–Organic Frameworks and Their Potential Applications

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Metal–organic frameworks (MOFs) are porous hybrid materials with countless potential applications. Most of these rely on their porous structure, tunable composition, and the possibility of incorporating and expanding their functions. Although functionalization of the inner surface of MOF crystals has received considerable attention in recent years, methods to functionalize selectively the outer crystal surface of MOFs are developed to a lesser extent, despite their importance. This article summarizes different types of post-synthetic modifications and possible applications of modified materials such as: catalysis, adsorption, drug delivery, mixed matrix membranes, and stabilization of porous liquids.

1. Introduction

Metal–organic frameworks (MOFs) are porous materials composed of inorganic and organic building blocks. The inorganic component usually consists of metal ions or metal (oxide) clusters with a Lewis acidic character. Organic compounds (usually Lewis bases) function as ligands, providing endless design possibilities. Under the right synthesis conditions, crystalline coordination polymers, which have a permanent porosity, are generated. **Figure 1** illustrates examples of different MOF structures (all built from the same linker and different metal clusters).

The potential of these solids in different applications, such as catalysis,[2] adsorption,[3–5] sensors,[6–9] and drug delivery,[10–14] has generated a large number of publications and scientific interest over the last few decades. Hundreds of new structures with different functionalities have been discovered.[15–17] However, many of these structures are unstable, and their functionalities cannot always be used in real applications. Consequently, modifying stable MOFs to add desired functionalities has become an area of interest.[15,18,19]

In most cases, these materials have been modified to include new functionalities within the porous structure, exploiting their high surface area and the large number of functionalities that can be attached to their structure (using either the organic ligand or the metal cluster as an anchoring point). This is relevant to applications such as catalysis, where catalytically active centers can be introduced,[2,20] and adsorption, where the affinity for different adsorbates can be induced.[21] Modifying the external surface of MOF crystals has been explored to a lesser extent. However, it is vital in drug delivery, sensing, catalysis, and MOF processing.

An example that reveals the importance of modifying the external surface of a crystal is modifying the surface of MOFs when used for drug delivery.[22,23] In this application, the crystal surface must be functionalized for MOFs to fulfill different requirements, such as inhibiting agglomeration within the bloodstream or inducing the specific recognition of the delivery location (e.g., cancer cells). The attachment of biocompatible polymeric structures or proteins is a standard method to achieve these functionalities. Other examples of applications of surface-functionalized MOFs are discussed below.

The surface of MOF crystals can be functionalized using two methods: 1) coordination modulation refers to methods where the MOF is functionalized during synthesis, and 2) post-synthetic modification (PSM) refers to when functionalization occurs after the crystalline material has been synthesized.[24]

The modulation coordination method consists of functionalizing the surface of MOFs by introducing a monodentate ligand (known as a modulator), which has a similar chemical functionality as the multidentate ligand, into the reaction mixture. This modulator causes the mono- and multidentate ligand to compete for metal coordination during MOF crystallization. The modulator has various functions, from promoting crystal growth in specific directions to inhibiting growth by acting as a capping agent. Modulators also improve the crystallinity of specific MOFs by decreasing their synthesis rate.[25] With this technique, it is possible to determine on which facet the crystal ends, the size, or the coverage of the crystals with the desired molecule. The modulation coordination method is outside the scope of this paper.[26–28]

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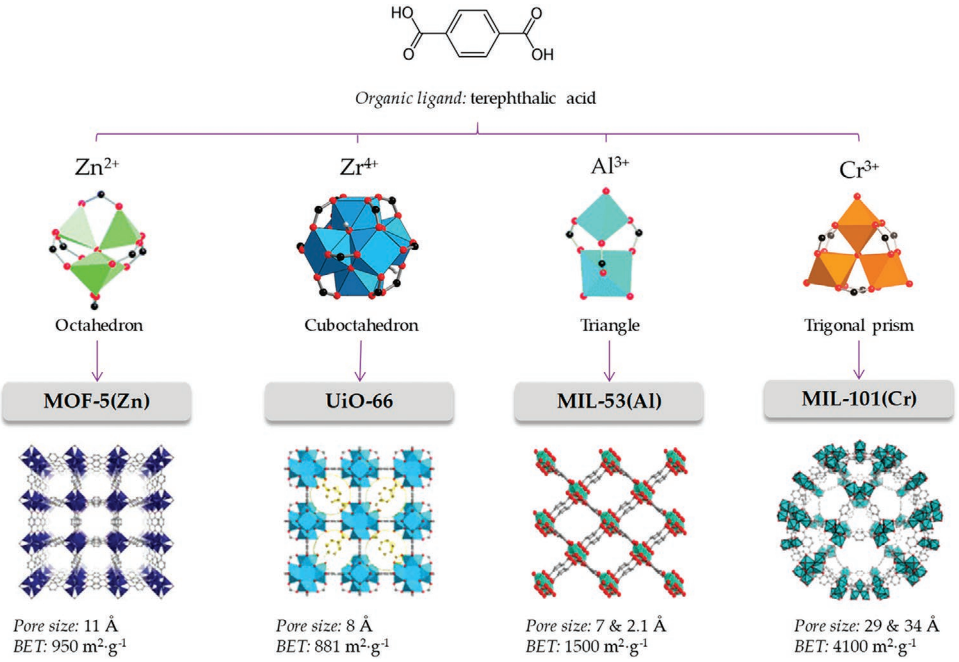

Figure 1. Different MOFs prepared by terephthalic acid and other metal clusters. Reproduced with permission under the the terms of the CC-BY license.[1] Copyright 2019, the authors. Published by MDPI.

PSM methods to functionalize the inner porosity of MOFs were first developed in 1999 by Lobkosky et al.[29] and Kim et al.[30] Nonetheless, it was not until after 2007, when Cohen and Wang[31] first used the notation "post-synthetic modification," that the field started developing.[32] Similar PSM methodologies can be used to exclusively modify the external surface of crystals, which is the focus of this paper This study reviews the latest advances in the functionalization of the outer surface of MOF crystals and their potential applications..

2. Outline

The different epigraphs of the review are based on the type of materials formed after functionalization and within each section the most important applications have been highlighted.

The first section is when the MOF surface is functionalized with discrete molecules or metals. Within this section, we have highlighted three applications: catalysis, adsorption, and drug delivery.

The second is when the surface is modified with polymers. In this section, we have chosen only one application, mixed matrix membranes, because this is the main application of polymer-coated MOFs.

The third is when the surface is decorated with another MOF (core–shell). In this section, the highlighted applications are catalysis and adsorption/separation.

The fourth is when the surface is modified by a leaching process. In this case, the surface is still composed of the same MOF but with different properties than the unmodified one. These materials still have a very limited number of applications, so this section has focused on synthesis, although it has highlighted the possible applications.

The fifth section is devoted to the stabilization of porous liquids.

3. Surface Modification with Discrete Molecules and Functional Groups

3.1. Catalytic Applications

Several requirements are desirable for preparing an active, selective, and stable catalyst. The catalyst must have active sites that catalyze one or more reactions. Furthermore, active sites catalyzing undesired reactions should be avoided. In addition to the active sites, tuning the reaction environment (i.e., active sites surroundings) is highly desired. An example is Lewis acid-catalyzed reactions, where water functions as a poison; the active centers should be surrounded by a hydrophobic environment.[33–35] Focusing heterogenous catalysts, another aspect of interest is that these catalysts have high hierarchical porosity, so reactants and products can diffuse to and from the active sites. Finally, the active sites and the catalyst body must be stable under reaction conditions.

All these requirements are, in theory, achievable with MOFs, resulting in significant interest in these materials.[34–36] However, careful design is required to achieve a breakthrough in catalytic performance. Because not every functionality can be inserted into an MOF scaffold directly during synthesis, PSM has contributed significantly to the design and tuning of catalytic sites enclosed within the MOF porosity. These approaches are beyond the scope of this paper, so we recommend referencing previous studies.[2,20,32,36–39] This article focuses entirely on exterior PSM, thus excluding the interior PSM technique. However, many of the methodologies used are the same for both.

The external surfaces of MOF crystals for catalytic applications have also been explored using different methods. For example, with the surface of crystals as active centers, the MOF crystal surface is composed of metals or ligands that are not fully coordinated, called surface defects.[40] Accordingly, only the external surface is used. Several studies have prepared crystals of different sizes and have found that the catalytic activity depends on the size of the crystal. The smallest crystals are the most active because they have the most exposed external surface area.[41,42] Because particular facets of the crystals have also exhibited higher activity,[43,44] approaches such as anisotropic etching have been developed to expose them.

3.2. Bio-Catalysis

The outer surface of the MOFs can also be functionalized with catalytically active bulky molecules, such as enzymes, that do not fit into the porosity of the MOF. Because such large molecules cannot be immobilized within micropores, other materials such as nanoparticles, mesoporous silicas,[45] and polymers[46] have been used. The use of MOFs in these biocatalytic applications has typically been restricted to a shielding role to protect biomolecules.[47–50] However, in recent years, other uses have been sought in biocatalysis beyond protecting biocatalysts. The immobilization of biocatalysts on the outer surface of MOFs creates an MOF–biocatalyst interface with unique properties.[51,52] Recent studies have developed two strategies to immobilize biocatalysts: 1) anchoring to the surface of the biocatalysts by weak interactions (Van der Waals type) and 2) covalent anchoring of the biomolecules to the external surface.

The first attempt to immobilize an enzyme on an MOFs by weak interaction was reported by Pisklak et al.[53] The authors immobilized microperoxidase-11 (MP-11) on a copper (Cu) MOF [Cu(bpdc)(dabco)] (bpdc = 4,4’-biphenyldicarboxylic acid, dabco = 1,4-diazabicyclo[2.2.2]octane). MP-11 immobilized on Cu-based mesoporous MOFs exhibited tenfold higher conversion (≈60%) than that supported on mesoporous silica (≈6%) in an oxidation reaction. The authors attributed the increase in activity when the enzyme was supported on the MOF with the same supported on mesoporous silica to the synergy between the enzyme and the MOF.

A similar approach was followed by Mao et al.,[54] who used zeolitic imidazolate frameworks (ZIFs) to immobilize methylene green and glucose dehydrogenase (GDH). ZIFs and GDH are highly hydrophobic; this chemical similarity makes them highly compatible, and the degree of interaction between the biocatalyst and the MOF is high, generating robust MOF@enzyme composites. This composite material was integrated into an electrode used as an electrocatalyst to detect glucose. **Figure 2** illustrates the reaction scheme of this catalytic system.

The same approach was followed by Ahmed et al.,[55] who immobilized cellulase on UiO-66 and the amino-functionalized version of the same. Both materials were used in the hydrolysis of carboxymethyl cellulose. The authors emphasize that the improvement in activity of the amino-functionalized sample over the nonfunctionalized one is caused by the presence of the amino groups at the interface with the enzyme. Other examples of this approach are the immobilization of Trypsin on MIL-101(Cr), MIL-88(Fe)B, and NH_2-MIL-88(Fe)B. The authors found that Trypsin is anchored to the outer surface of the MOFs by the interaction of functional groups of the Trypsin with uncoordinated carboxyl groups present on the MOF surface.[56,57]

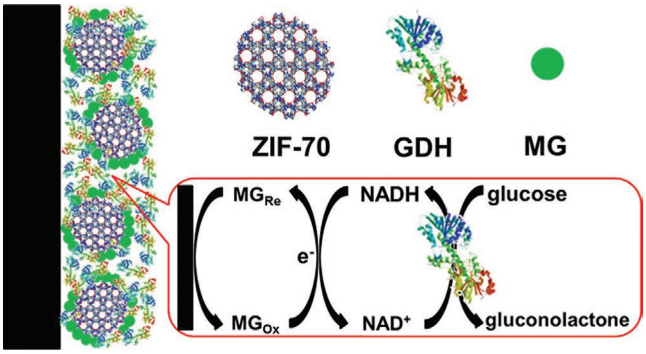

Figure 2. Catalytic cycle of the glucose oxidation using ZIF-70 as support of GDH. Reproduced with permission.[54] Copyright 2013, American Chemical Society.

Incorporating a biocatalyst on the outer surface of MOF materials can generate a composite system with catalytic properties superior to its constituents. Zhu et al.[58] modified the external surface of MIL-88(Fe) crystals with glucose oxidase (GOx) is essential for their use in cascade reactions. Thus, the GOx on the surface of the MOF crystals functions as a catalyst to transform glucose into gluconic acid and hydrogen peroxide (H_2O_2). The generated H_2O_2 triggers a chromogenic reaction in the presence of a colored reagent. This second reaction is catalyzed by MIL-88(Fe), which has peroxidase-type activity. These chain-catalyzed reactions can detect glucose—surface modification of the MOF with GOx biomimetics enzymatic systems.

In addition to weak interactions, bio-catalysts can be immobilized by strong covalent bonds, referred to as covalent conjugation by some authors, such as Wu et al.[51] and Cui et al.[59] Park et al.[60] published in 2011 the first example of immobilization of an enzyme (lipase B from *Candida Antarctica*, CAL-B) on MOFs with different dimensionalities (1D, 2D, or 3D) by covalent conjugation. Immobilization was carried out in two steps. First, the pendant carboxylate groups were activated with 1-ethyl-3-(3-dimethyl aminopropyl). Second, an enhanced green fluorescent protein (EGFP) was immobilized as a model to characterize the methodology's success. This method was then applied to immobilize the enzyme CAL-B. The enzyme was used for enantioselective catalysis in transesterifying (±)-1-phenyl ethanol.

3.3. MOFs Composites

Coating MOFs with a protective hydrophobic polymer layer can improve their stability against moisture. Thus, MOFs unstable in water or whose active centers are incompatible with water (Lewis acid sites) can be protected from water. Yu et al.[61] coated polydimethylsiloxane (PDMS), a highly hydrophobic polymer, on the surface of MOF materials (MOF-5, HKUST-1, and ZnBT) to improve their moisture resistance while maintaining their inherent porosity. In applying these composite materials in the liquid-phase cyanosilylation of benzaldehyde and trimethylsilyl cyanide, the coated HKUST-1 exhibited similar activity (48.2% yield) to that of the pristine (50.1% yield), suggesting the efficient permeability of the PDMS coating layer to the substrates. Furthermore, after treatment with saturated water vapor, the coated HKUST-1 retained its activity. In comparison, pristine HKUST-1 decreased substantially in catalytic activity (19.6% yield) after the same treatment.

Huo et al.[62] were able to coat a Pt/UiO-66 crystal with a graphene oxide (GO) layer. GO is hydrophilic to the extent that when measuring the Pt/UiO-66@GO composite material, the contact angle with water is 0°. If the material is subjected to a reduction treatment to transform GO into graphene, the contact angle becomes 106°. Thus, they found that hydrophilic catalysts functioned better on hydrophilic substrates than on hydrophobic substrates when applied in a nitroarenes reduction.

3.4. Surface Metalation

The transmetalation of the outer surface of the MOF crystal is another approach that can be followed to prepare materials with catalytic properties. Nguyen et al.[63] found that metal cations that form an intrinsic part of the linker (salen or porphyrin complexes) can be selectively removed at or near the MOF surface. MOFs composed of tetracarboxylic acid and a manganese-salen-based pillar linked by Zn^{2+} cations could be demetallized by adding H_2O_2. However, preloading the MOF pores with a water-immiscible solvent, $CHCl_3$, prevented H_2O_2 from penetrating the MOF pores, so demetallization occurred only on the surface. After the surface of the MOF is demetallized, it can be remetallized with a second metal, such as Zr, Cr, Zn, Co, and Ni causing a change in acyl transfer reaction.[64–68]

Later, the same authors published a method using the coordinative unsaturated sites (CUSs) of MOFs to functionalize the inner part of the MOF crystals with one functionality and the outer part with another.[69] CUS are generated in MOF structures when one of the MOF's metal coordination centers coordinates with species that can decoordinate when vacuum or temperature is applied, leaving a free coordination center on the metal with an acidic Lewis character. CUSs can be used as a catalyst or as an anchoring center for other molecules. The authors functionalized the CUSs on the outer surface of MIL-101-Cr with a bulky molecule (dopamine). The dopamine is bulky because it has functionalized t-butyldimethylsilyl protecting groups on the catechol moiety. After the outer surface was modified, they functionalized the CUS inside the crystal with an amine. Accordingly, they obtained a core–shell structure with catalytic properties in the oxidation of thioanisole to sulfoxide.

An approach to modifying the surface chemistry of MOF crystals is to exchange the surface ions of the MOF crystals for those with catalytic activity. Several studies found that MOFs that cannot be synthesized with the desired metal (M1) can be synthesized with another (M2) and then surface exchanged with the first (M1). One example was published by Song et al.,[70,71] where Zn^{2+} ions were substituted by Cu^{2+} in Zn-HKUST-1 and PMOF-2. Both systems contain paddlewheel secondary building units containing four carboxylate linkers and two metal ions with higher stability and porosity with Cu^{2+} than with Zn^{2+}. The authors indicate that if the solvent is well selected, the exchange kinetics can be controlled such that only the Zn^{2+} ions on the external surface are exchanged. This is an elegant method to prepare core–shell MOF with potential catalytic applications.

Han et al.[72] follow a similar approach to exchanging the Zn^{2+} ions, of which ZIF-8 is composed, for Ni^{2+} ions. Ni^{2+} has a d^8 electronic configuration, so it prefers a planar-square or octahedral coordination. Because the Zn^{2+} ions constituting ZIF-8 are tetrahedrally coordinated, it is difficult for Ni^{2+} to substitute Zn^{2+} within ZIF-8 crystals. However, it can replace the Zn^{2+} on the surface of the crystals because square planar coordination is allowed. The authors demonstrated the above by several experimental techniques, including EFXAS (extended X-ray absorption fine strucutre). The Ni-ZIF-8 catalysts were tested in the dimerization of ethylene to produce 1-butene. The turnover frequency of these catalysts was extremely high and, to our knowledge, never seen before in oligomerization reactions.

3.5. Gas Adsorption and Separation

High specific surface area, well-defined pore size, and affinity for adsorbates with different properties are some attributes that highlight the potential of MOFs in gas adsorption and separation. However, there are several inherent problems with MOFs that make their implementation in industrial processes limited. Many MOFs are unstable in the presence of water, as water can break the coordination bond between the metal and the ligand.[73,74] Hence, coating MOFs with a hydrophobic polymer protects them from water. Zhang et al.[61,75] demonstrated that coating water-instable MOFs (e.g., HKUST-1 and MOF-5) with a hydrophobic polymer, PDMS, prevent MOFs from moisture and maintained their adsorption properties. Thus, when the MOFs are exposed to water, they do not degrade and thus preserve their adsorptive properties (**Figure 3**).[75,76]

Martí-Gastado et al.[75,76] demonstrated by a straightforward method in which HKUST-1 can be protected from moisture by

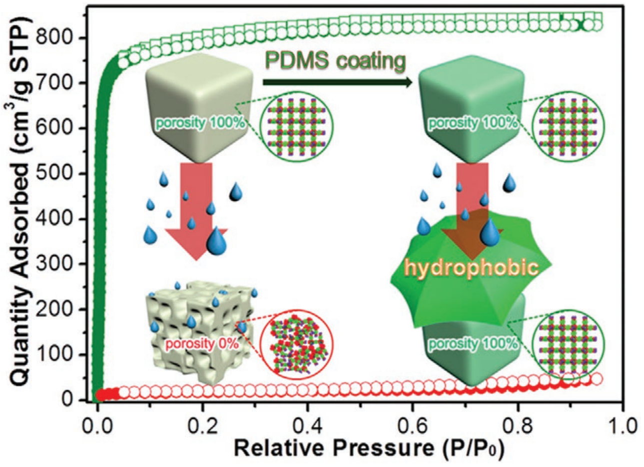

Figure 3. Schematic representation of the HKUST-1 protected for PDMS. Reproduced with permission.[61] Copyright 2014, American Chemical Society.

protecting the uncoordinated metals on the external surface of the crystal with hydrophobic ligands of the catechol type.

Ma et al.[77] developed a method to modify the MOF crystal surface with superhydrophobic motifs. Accordingly, UiO-66 and PCN-222 type MOFs were functionalized with n-octadecylphosphonic acid (OPA), resulting in the MOFs' water contact angle decreasing from 160° to 19°. This result confirms that the MOFs become highly hydrophobic. The porosity of the OPA-modified materials was equal to that of the unmodified materials. The OPA-modified materials were used in the adsorption of organic compounds. The researchers found that the hydrophobicity of these modified materials promoted the MOF–adsorbate interaction, increasing the adsorption capacity. Furthermore, they applied them in the practical separation of chloroform and water. They passed a mixture of water and chloroform through a filter in which the OPA-MOF samples were placed. Because of the hydrophobicity, chloroform preferentially passes through a filter composed of superhydrophobic MOFs, while water could not go through.

Since that pioneering study, many publications have addressed using MOFs for oil–water separation. The surface is modified with different hydrophobic molecules for this purpose. As an example of this, Gao et al.[78] modified MIL-100(Cr), UiO-66(Zr), ZIF-67, and HKUST-1 with octadecylamine. All these MOFs have in common that the outer surface is decorated with CUS and these CUSs are Lewis acids and serve as anchor sites for the Lewis base octadecylamine. Thus, the modification is simply an acid–base interaction. Fourier transform infrared spectra confirmed the presence of octadecylamine on the MOFs and this modification does not imply loss of crystallinity (powder X-ray diffraction (XRD)) or surface area (Brunauer–Emmett–Teller). Zha et al.[79] modified the surface of UiO-66-NH_2 with isostearic acid. To make this modification, isostearine chloride was reacted with the amino groups of the UiO-66 linker. They used this method for dye adsorption and separation of chloroform and water.

Another possible modification of the affinity of MOFs toward different adsorbates is coating MOF crystals with other materials—forming composite materials that have unique properties. Kwak et al.[80] demonstrated that coating MOF-5 crystals with platinum-impregnated carbon black could enhance the hydrogen adsorption capacity of the material. They ascribed this increase in adsorption to the spillover phenomenon generated by the presence of noble metal in the composite material. They also found that the material was more stable in water because of the hydrophobicity of the carbon black covering the surface.

Fischer et al.[81] used a combination of MOF@graphene with hydrophobic and oleophilic properties. This material was used to recover organic compounds present in oil spills in water. They achieved 100% separation of the oil from the water and removed 99.0% of all contaminants tested.

One way of using a post-synthetic surface modification of an MOF is to seal the porosity of the MOF, similar to a bottle cap. Thus, when an MOF adsorbs a molecule with a low affinity for the structure, it is likely to be immediately desorbed when the sample is subjected to a stimulus that promotes desorption (e.g., vacuum and heating). This can be avoided if, after adsorption, the outer surface of the crystal is functionalized with a molecule that functions as a stopper. This concept was demonstrated by Chabal et al.[82] using CPO-27(Mg), an MOF composed of linear channels. They used carbon monoxide (CO) as an adsorbate and ethylenediamine as a capping molecule. They found that when the MOF channels were not sealed, the CO desorbed within several minutes when the vacuum was applied. However, the sample sealed with ethylenediamine retained CO for several hours. The adsorption capacity is not affected by sealing with ethylenediamine. What is changed is the outward diffusion of the CO.

Concerning adsorption, MOFs may have the highest potential for use in gas separation, where MOFs have unique properties for application as molecular sieves.[83,84] The preparation of MOF membrane is of high interest. In many cases, the surface has to be modified for membrane production. There are very few cases where defect-free membranes can be prepared from MOF crystals exclusively, because generating a large surface of intergrown MOF crystals is difficult.[85] Therefore, including crystal MOFs within a polymeric matrix that permeates different gases or liquids is an elegant and cost-effective way to create MOF membranes.

3.6. Bio-Compatibles MOFs

Incorporating drugs into porous materials such as MOFs offers exciting opportunities to redefine pharmacokinetic properties, improving the therapeutic efficacy of drugs and reducing side effects. However, the primary challenge to achieving this potential is progressing methodologies that improve MOF properties, with the following prerequisites:

i) Biocompatibility
ii) High loading and protection of drug molecules
iii) Zero premature release before reaching the target
iv) Efficient cellular uptake
v) Efficient endosomal escape
vi) Controllable release rate to achieve adequate local concentration
vii) Cell targeting

Functionalization of the outer surface is crucial to satisfy these requirements. In some cases to better anchor the drug, in others to make the MOF particle biocompatible or to be able to trace its movement through the body. Wuttke et al.[86] classified the types of post-synthetic functionalizations that can improve the properties of MOFs as drug carriers into four groups (**Figure 4** illustrates the four approaches schematically).

The first approach that can be followed is the one proposed by Rowe et al.[87] which consisted of grafting the desired molecules onto the CUS. Because the CUSs can also exist on the inner surface of the crystal, the functionalization is not specific to the outer surface. The functional molecules must be larger than the pore size of the MOF (preventing them from penetrating the porosity) to functionalize only the outer surface. Rowe et al. immobilized a polymer with various functions to the external surface of $Gd(BDC)_{1.5}(H_2O)_2$ by coordinating one of the polymer's functional groups, thiolates, with the not fully saturated Gd^{3+}. The functions contained in this polymer (poly(*N*-isopropylacrylamide)-*co*-poly

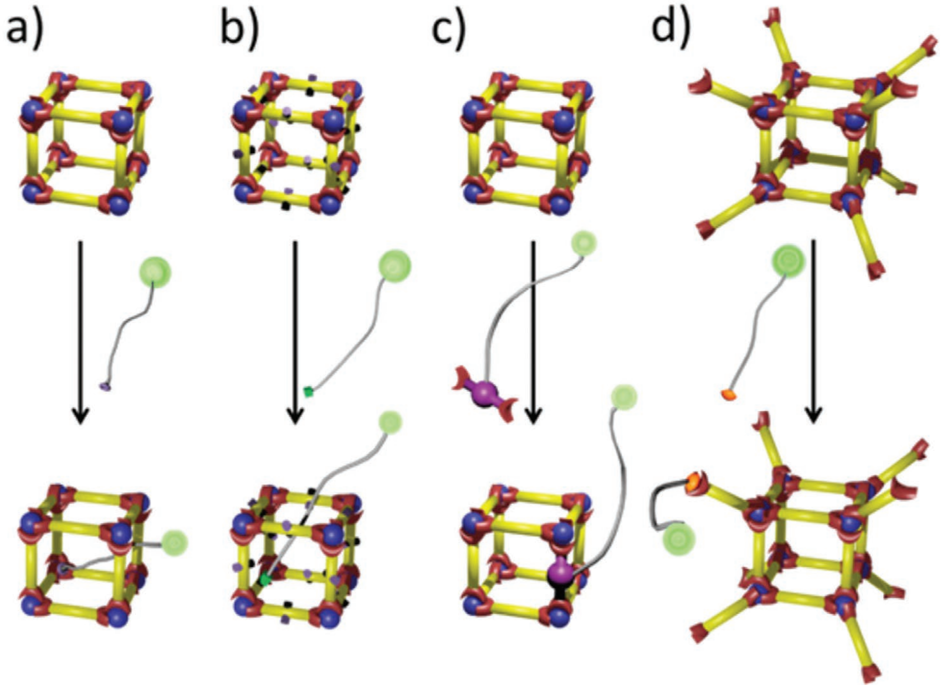

Figure 4. Schematic representation of different post-synthetic functionalization possibilities for MOFs. a) Coordinative binding on CUS, b) covalent binding of prefunctionalized linkers, c) ligand exchange, and d) covalent binding to the uncoordinated ligands. Adapted with permission.[86] Copyright 2016, American Chemical Society.

(*N*-acryloxysuccinimide)-*co*-poly(fluorescein *O*-methacrylate)) ranged from fluorescent tags to therapeutic agents. **Figure 5** illustrates these functions.

Mirkin et al.[86,88] followed a very similar method to functionalize the outer surface of UiO-66 crystals with 1,2-dioleoyl-*sn*-glycero-3-phosphate (DOPA). The phosphate group is the one that is anchored to the CUSs of the MOF. They tested this by functionalizing the surface with a molecule similar to DOPA but acting as a dye, 1-oleoyl-2-{12-[(7-nitro-2-1,3-benzoxadiazol-4-yl)amino]dodecanoyl}-*sn*-glycero-3-phosphate. They verified that only the surface was functionalized, using $^{31}P\{^1H\}$ magic angle spinning NMR spectroscopy technique. The free DOPA and the DOPA-functionalized nanoMOF have different broad resonance, which suggests that the phosphate ligands are coordinated to the zirconium oxide nodes on the external surface of the MOF nanoparticle. The hydrophobic part of the DOPA faces outward, indicating that the crystals can be suspended in different nonpolar solvents.

Horcajada et al.[89] used the outer surface of MIL-100(Fe) nanocrystals to anchor heparin, a biopolymer that prevents blood clotting. The external functionalization was performed to anchor the drug. In addition to anchoring the drug, the MOF nanoparticles had superior biological properties, such as a lack of reactive oxygen species production. In this contribution, they claim to functionalize the external surface based on the fact that the heparin size is larger than the window size of the MOF. However, they do not present experimental evidence. When this method is used, there is a risk that part of the inner surface (which also has CUS) becomes functionalized, leading to problems such as blocking the porosity and reducing the adsorption capacity.

Other methods have been developed that follow this same concept to prevent the molecules from penetrating the internal part. The molecules are not anchored to the CUS of the structure. Instead, the molecules are anchored to the metals that are not completely saturated with the ligands on the external surface of the crystal, called surface defects. The possibility of the molecule anchoring to the inner part of the crystal and blocking the porosity is eliminated. Thus, the outer surface of the crystal can be functionalized selectively, regardless of whether the crystals have CUSs or not. One example of this method was published by Brinker et al.,[90] who functionalized the MOF surface by directly coordinating a phenolic-inspired lipid molecule 1,2-dipalmitoyl-*sn*-glycero-3-galloyl with metal nodes/sites surrounding the MOF surface.

The second approach that Wuttke et al.[86] categorized is the covalent anchoring of functional molecules to the organic ligands that are part of the MOF structure. The same problem can be encountered with this method as with the first approach. The functional molecules can penetrate the internal porosity. Therefore, bulky molecules must be used to prevent them from entering the pores. Fischer et al.[91] demonstrated that if MOFs are built layer-by-layer on a surface (**Figure 6**), the last MOF layer could be a functionalized ligand. This functional group can be used to anchor a second molecule (in this case, they anchored a fluorescent molecule). They found that only the surface was functionalized using fluorescence microscopy.

Another example of this method was published by Mirkin et al. in 2014. In this work, the authors synthesized an MOF of the UiO-66 family functionalized with an azide group.

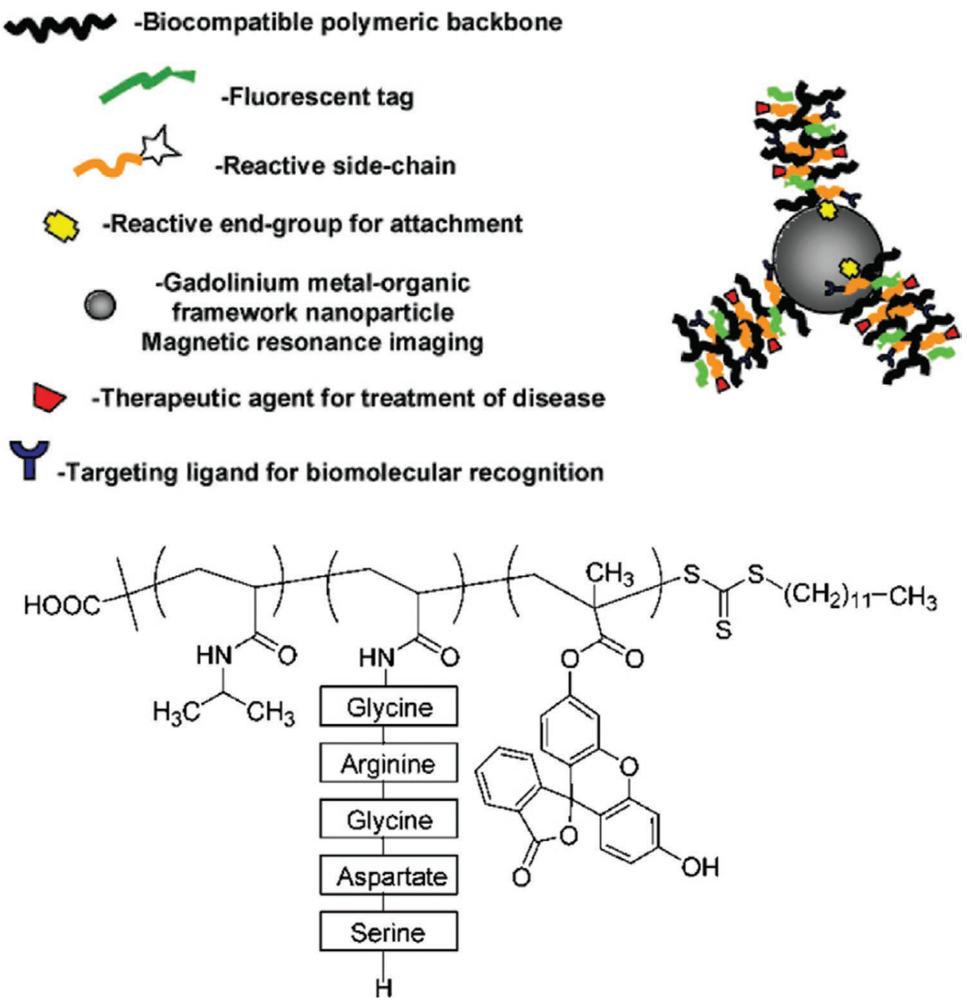

Figure 5. Top: Representation of a multifunctional polymer on the surface of a gadolinium MOF. Bottom: Functional polymer. Adapted with permission.[87] Copyright 2009, American Chemical Society.

These groups were reacted with a dibenzylcyclooctyne-modified DNA.[92] This method represents a new avenue to functionalization with biomolecules. This method was applied by Farruseng et al.[93] to functionalize the inner part of MOFs in 2011 but in the work of Mirkin et al. it was the first time it was used to functionalize the outer surface of MOFs with DNA (Deoxyribonuycleic acid). A very similar approach was followed by Willner et al.[94] where an amine-modified nucleic acid was reacted with dibenzocyclooctyl-sulfo-*N*-hydroxysuccinimidyl ester (DBCO-sulfo-NHS ester), and the resulting DBCO-modified nucleic acid was reacted with an MOF functionalized with an azide group. The resulting material was used to adsorb drugs and dyes, which were released with a pH change in the medium.

The third approach, described by Kitagawa et al.,[95] demonstrates that functional molecules could be anchored on the surface through post-synthetic ligand exchange because the exchange of the MOFs linkers starts at the outer surface. If the functionalized ligands used for exchange are sufficiently bulky, only those on the surface are exchanged because a steric hindrance prevents the further exchange of ligands from inside the crystal. The authors found that exchange only occurred in the first layer of the crystal. They used this technique to functionalize the surface of the crystal with a fluorescent molecule that can be used to monitor MOF particles in tissues where the MOF is present.

The fourth methodology identified by Wuttke et al.[86,96] is based on using uncoordinated linkers (surface defects) on the crystal surface as anchoring centers. For example, if the uncoordinated linkers are carboxylic acids, they can be used to covalently anchor the functional molecules needed to modify the linker surface and make them usable in drug delivery. These uncoordinated linkers on the surface are fully coordinated with the metal ions on the inner side of the crystal, so surface functionalization is performed selectively. These uncoordinated ligands on the surface of the MOF attach the functional molecules covalently. Wuttke et al.[86] used this approach to functionalize MOF crystals with fluorescent polymers to investigate the uptake of the nanoparticles in tumor cells by fluorescence microscopy. The influence of the polymer coating on the magnetic resonance imaging activity of MIL-100(Fe) was also studied.

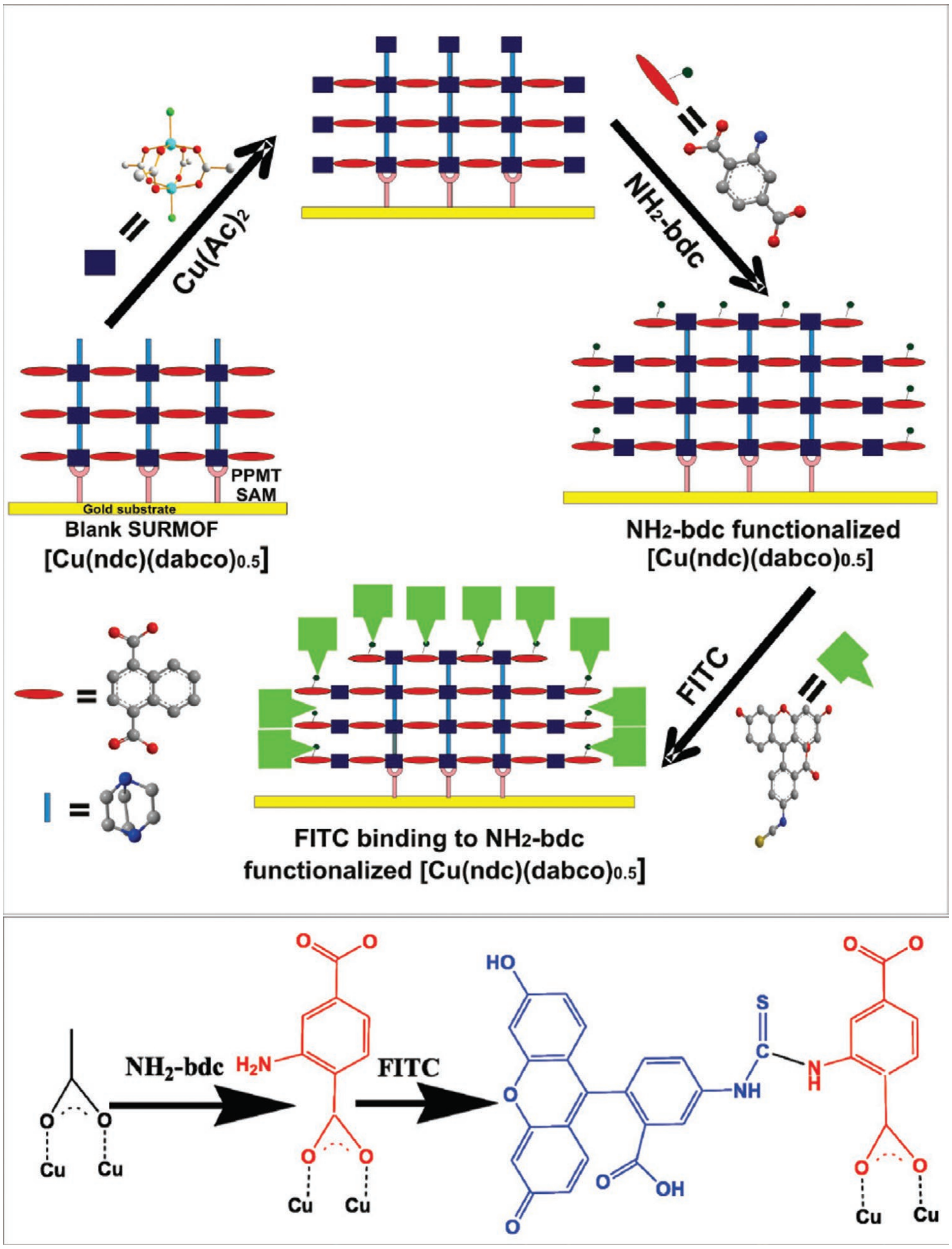

Figure 6. Scheme of the layer-by-layer growth of an MOF that ends in a fluorescent molecule. Reproduced with permission.[91] Copyright 2011, American Chemical Society.

4. MOF Modified with Polymers

The hybridization of MOF crystals with polymers has been studied over the last decades. The production of an MOF@ polymer composite material can expand the applications of MOFs to highly relevant areas of scientific and industrial interest. We refer to the production of mixed matrix membranes (MMMs). These can be used to separate molecules that have very similar kinetic diameters. This type of composite material can be synthesized in many ways; the simplest is by physically mixing the MOF with the polymer monomers (dissolved in a solvent or not). After curing, the composite material is obtained. This simple method has some limitations. The dispersion of the MOF in the reaction mixture is not always effective, leading to a low and uneven dispersion of the MOF crystals in the polymer. Moreover, this low dispersion is associated with poor properties (low permeation and poor selectivity). Therefore, post-synthetics methods have had to be developed to modify the properties of the MOF crystals to improve the compatibility between the two components.

4.1. Mixed Matrix Membranes (MMMs)

MMMs are composite materials that combine the flexibility of polymers with the properties of porous solids used as fillers. As described previously, producing membranes composed purely from MOFs is cumbersome, and their industrial scale-up is far from being implemented.[97,98] Normally, membranes that are composed only of polymers can be processed and the presence of defects is minimized. However, highly selective polymeric membranes tend to have very little permeation. In contrast, membranes that enable a high flux tend to be less selective. Therefore, a compromise between selectivity and permeability is necessary, known as the Robeson upper bound.[99]

Thus, incorporating solid materials into the polymeric matrix is an alternative. Some research has already been published whereby combining the polymer and the appropriate MOF, membranes with high flux and selectivity can be generated by breaking the Robeson upper bound. There are three ways to generate these composite materials: 1) as described previously, by physical mixing of the unmodified MOF and the polymer to induce a noncovalent interaction, 2) modifying the outer surface of the MOF crystals to enhance the noncovalent interactions at the particle–polymer interface, and 3) anchoring the polymer to the outer surface of the MOF crystal by covalent bonding. In this study, we focus on the last two approaches. For more information on this topic, we highly recommend reading several reviews dedicated to this topic.[98,100–103]

4.1.1. Modification of the MOF Crystal to Enhance Compatibility with Polymers

Compatibility between the MOF and the polymer is essential to achieve good dispersion of the MOF and no defects at the MOF–polymer interface. Simultaneously, the polymer must not block the porosity of the crystal. **Figure 7** illustrates in simplified form the different paths a molecule can follow when passing through the membrane.

One of the first approaches to improve this interaction was proposed by Gascon et al.,[104] who used MIL-53(Al) functionalized with amino groups as a filler in a commercial polymer (PSF Udel P-3500). They found that selectivity of 40 could be achieved by separating methane and carbon dioxide. They also found that there was an optimal MOF loading.[104–107] However, the authors did not compare this MOF with the nonfunctionalized version. Therefore, the impact of the amino groups is unknown. Later, Tavasoli et al.[108] compared the performance of membranes composed of MIL-53(Al) and its functionalized version with NH_2-MIL-53(Al) amino groups and found that the membrane containing the functionalized MOF had higher performance, selectivity to CO_2/CH_4 separation, and permeability. The authors ascribed this effect to the greater interaction of the polymer with the MOF crystals.

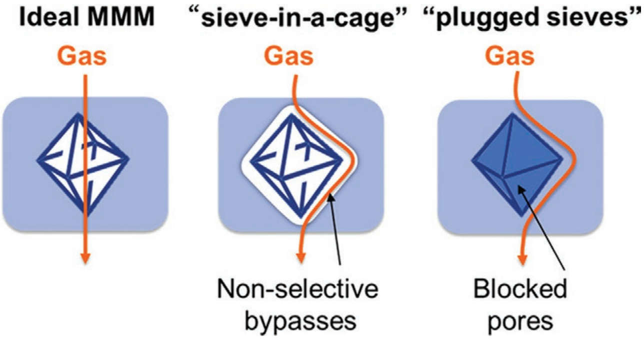

Figure 7. Examples of ideal MOF-based MMMS and nonideal MOF-based MMMs as a function of microvoids or blocked pores. Reproduced with permission.[109] Copyright 2019, American Chemical Society.

The authors used linkers containing the desired function to prepare their MOFs. The first example using post-synthetic methods to prepare MOFs as membrane fillers was published by Wu et al.,[110] who functionalized MIL-101(Cr) with sulfonic groups with a post-synthesis method developed by Goesten et al.[111,112] They hypothesized that if they used an MOF containing sulfonic groups, the compatibility with the polymer (sulfonated poly(ether ether ketone)) would be greater—with a chemical similarity between the MOF and the polymer. The authors found that the MMMs prepared with the sulfonated version of the MOF had a high selectivity to CO_2/CH_4 separation. Furthermore, the permeability was very high—they overcame Robeson's upper bound. Moreover, the membranes prepared with the sulfonated MOF outperformed the pristine MOF.

In all these cases, the functionalization of the MOF was not exclusive to the crystal surface. One of the first examples where the outer surface of the crystal was functionalized to prepare membranes was published by Wang et al.,[113] who functionalized the outer surface of NH_2-UiO-66 with a polyimide (PI) brush. They first exchanged part of the linkers on the crystal surface for 4,4′-oxidiphthalicanhydride, a more reactive molecule than the amino groups of the original linker. After this modification, they created a second modification with 2,4,6-trimethyl-m-phenylenediamine and then created the PI brushes (**Figure 8**). They then used a solution casting technique to prepare the membrane with different loading. They achieved higher CO_2/N_2 and CO_2/CH_4 ratios with these membranes than when using the unmodified material with the PI brushes. For the modified MOF, they exceeded the Robeson upper limit for CO_2/CH_4 separation set in 1991 but failed to exceed the new limit set in 2008. However, this novel approach opened the door for other researchers.

Later, Ning et al.[114] used the same method to modify crystals with PI brushes. These crystals were immobilized in GO. They found that the presence of GO resulted in a much more selective material for CO_2/N_2 separation, up to three times more than without graphene. Its CO_2 adsorption capacity was also increased by a factor of four.

Another example of these PSMs on the outer surface of MOF crystals was published by Cao et al.[115] They used a straightforward method to graft 3-aminopropyltrimethoxysilane (APTMS) on the surface of the MIL-53 crystals. The authors determined that the methoxy groups can be hydrolyzed with the -OH to form a silanol. Consequently, the amino groups of APTMS enhanced the interaction of the MOF with the polymer. Membranes prepared with the nonfunctionalized and functionalized MOF were compared: the two membranes had similar permeance. The CO_2/N_2 separation selectivity was also similar when the MOF loading was very low. However, when the MOF loading was increased, the selectivity decreased for the nonfunctionalized MOF and increased for the functionalized MOF, indicating that functionalization enabled greater dispersion

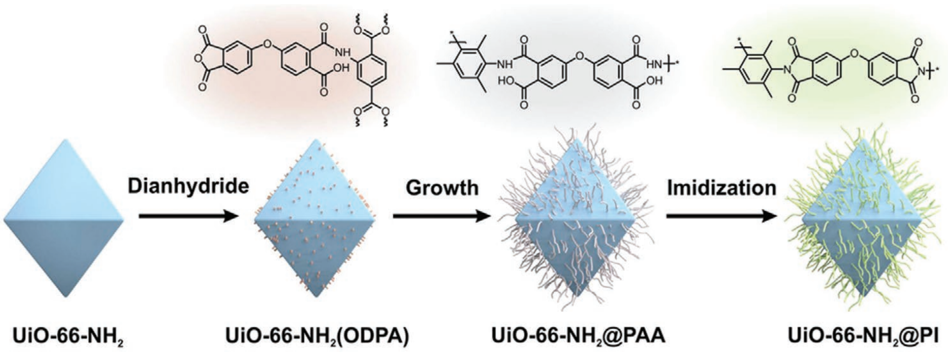

Figure 8. Scheme of the PI synthesis on top of the UiO-66 crystal. Adapted with permission.[113] Copyright 2018, American Chemical Society.

of the MOF crystals and higher MOF loadings, improving selectivity.

Another study was published by Wang et al.,[116] who functionalized ZIF-8 crystals with poly-dopamine. The poly-dopamine contains catechol groups. These groups can be anchored to the surface of the crystals using the uncoordinated metals of the crystals. Thus, only the outer surface of the crystal can be functionalized. Coating the crystal with this polymer has two functions: 1) avoiding blocking the porosity of the ZIF-8 with the matrix polymer and 2) improving the adhesion between the polymer and the ZIF-8 crystal. When the authors compared the performance of membranes prepared with poly-dopamine modified and unmodified ZIF-8, they found that for H_2/N_2 or H_2/CH_4 separation, both membranes exceeded Robeson's upper limit. However, the membrane prepared with modified ZIF-8 had higher selectivity. Another factor that improved in the membranes prepared with the modified ZIF-8 was their performance after several days. Although the membranes prepared with the original ZIF-8 membrane lost their ability to sieve gases (their permeability and selectivity decreased), this effect was much less pronounced in the modified ZIF-8 membrane.

4.1.2. Polymeric Matrices Covalently Bonded to the Outer Surface of the MOF Crystals

One approach to ensure that the MOF crystals interact well with the polymer matrix of the MMM is to covalently anchor the polymer to the outer surface of the crystal. In principle, this ensures that no defects are generated at the MOF–polymer interface and that the porosity of the MOF remains available for the target gases to pass through. This can be achieved using different methods, with the most relevant described in this section.

One of the pioneering studies in this area was by Wang et al.,[117] who described for the first time the concept of post-synthetic polymerization. They reacted the amino groups on the crystal surface with methacrylic anhydride and functionalized the crystal with methylacrylamide (**Figure 9**). These new functional groups on the surface of the crystal were used as handles. At a later stage, these methylacrylamide handles were used as butylmethacrylate polymerization sites. This polymerization was performed using a photoinitiator (phenyl-(2,4,6-trimethylbenzoyl)phosphine oxide) and UV light. The result was an MOF covalently bonded to a polymeric matrix. This type of membrane was used to remove Cr(VI) from water streams and exhibited a high retention capacity. Furthermore, the authors compared the membrane prepared with the MOF covalently bonded to the polymeric matrix with the one prepared by mixing the polymer and the MOF. The former retained almost twice as much Cr(VI) as the latter. This method encouraged the scientific community to prepare MOFs with tethers that can then be post-synthetically polymerized with a polymeric matrix. Since then, significant research has been performed to produce polymerizable MOFs in identifying different applications.[100,118,119]

Another study by the same authors[120] demonstrated that they could decorate NH_2-UiO-66(Zr) isocyanate-terminated polyurethane oligomer crystals. The first step was to prepare the isocyanate-terminated polyurethane oligomer by reacting methylene diphenyl diisocyanate and polypropylene glycol. The MOF crystals were decorated with this oligomer by reacting the isocyanate with the amino groups of the MOF. After aging, the MOF–oligomer mixture is finished in an MOF-polyurethane-based membrane. The authors used this membrane for the separation of dyes. They found that the membrane had a higher affinity for hydrophilic dyes.

Another example of modification of the external surface of MOF crystals with a urethane group was published by Dong et al.[121] In addition to improving the interaction of the MOF with the polymeric matrix, the authors aimed to include a new function (imidazolium-based ionic liquid) that would increase the affinity for CO_2. To this end, they first prepared linkers containing the imidazolium salt (Br^- as a counter anion), then synthesized the MOF and used one of the functional groups of this salt (-OH) to bind the polyurethane oligomer. They obtained membranes that had an improved affinity for CO_2 and consequently separated CO_2/CH_4 or CO_2/N_2 very efficiently.

Matzger et al.[122] used atom transfer radical polymerization to decorate the IRMOF-3 shell with poly(methyl methacrylate) while maintaining the internal porosity of the MOF (as depicted by N_2 sorption isotherms and single crystal Raman mapping).

Ring-opening metathesis polymerization is another technology used to decorate MOF crystals with covalently bonded polymers to generate an MMM. An elegant example of this was published by Zhang et al.[123] Again, using NH_2-UiO-66(Zr) as a starting MOF, they first reacted the amino groups of the MOF with cis-5-norbornene-exo-2,3-dicarboxylic anhydride. This reaction functionalizes the outer surface of the crystal with norbornene groups. This

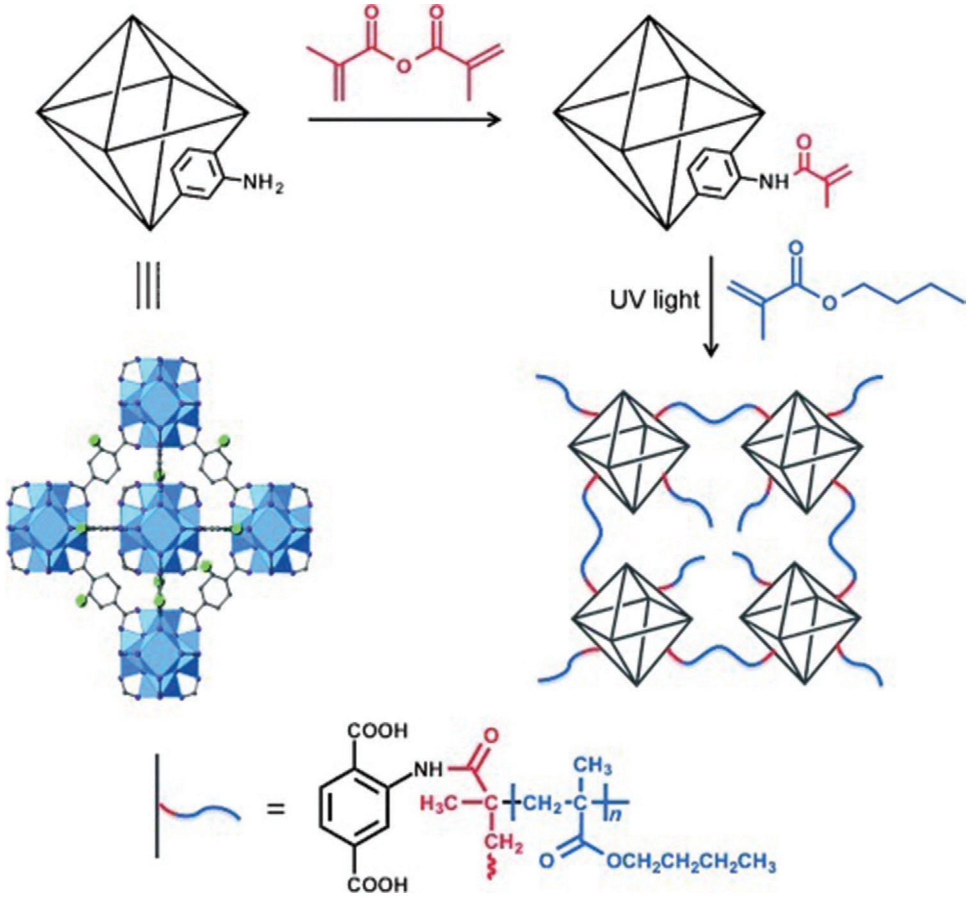

Figure 9. Representation of polyacrylate-MOF composites synthesis. Reproduced with permission.[117] Copyright 2015, Wiley-VCH.

material was then polymerized with more norbornane monomers using Grubbs' catalyst. The authors reported that up to 98% of the MOF's pending norbornene groups were transformed into polynorbornene. These MOFs also exhibited high permeability for H_2 and high selectivity for H_2/N_2 and H_2/CO_2 separations, exceeding the 2008 Robeson upper limit.

5. Core–Shell MOFs

A recent approach is to modify the outer surface of the MOF with another MOF by coating a crystal MOF with a different MOF to generate a composite material that can have distinctive properties. The strength of MOFs compared with other materials is that they can be constructed with great precision. Thus, the synthesis of MOFs on MOFs can be performed with equal precision. Combining two or more MOFs in the same crystal enriches compositional (e.g., ligands and metal cluster) and structural (e.g., pore structure, functions, and surface properties) diversity.

5.1. Synthesis Approaches

This section describes some of the most relevant approaches to form MOF on MOF structures and their possible applications.[124–126] MOF-on-MOF synthesis processes can be divided into two categories: 1) the two-step process, in which an MOF is pre-synthesized as a seed in the first step and a guest MOF is grown creating MOF-on-MOF structure, and 2) the one-pot process, where nucleation and kinetic growth of two MOF is controlled at all times.[127]

The first strategy is one-step MOF-on-MOF synthesis. This method consists of preparing a synthesis mixture where the precursors of both MOFs co-exist. One has a higher rate of nucleation (crystallization) than the other. Thus, it precipitates and serves as the nucleation center of the second MOF. By adjusting the reaction conditions appropriately, core–shell structures can be achieved. Although this approach is relatively simple, it has limitations, as only MOFs with similar chemical properties can be synthesized. Furthermore, there is a risk of mixing or segregating the target MOFs. A successful example of this approach was published by Gascon et al.,[128] who prepared core–shell and Janus particles with the MOF-5@IRMOF-2 system.

The second strategy to functionalize the outer surface of an MOF crystal with others is in two steps. First, one MOF is prepared, and a second MOF is grown on it in a post-synthetic step. This approach is more versatile, and the number of contributions using this methodology is much higher than the first approach. Post-synthetic methodologies to generate core–shell MOFs vary significantly and range from epitaxial

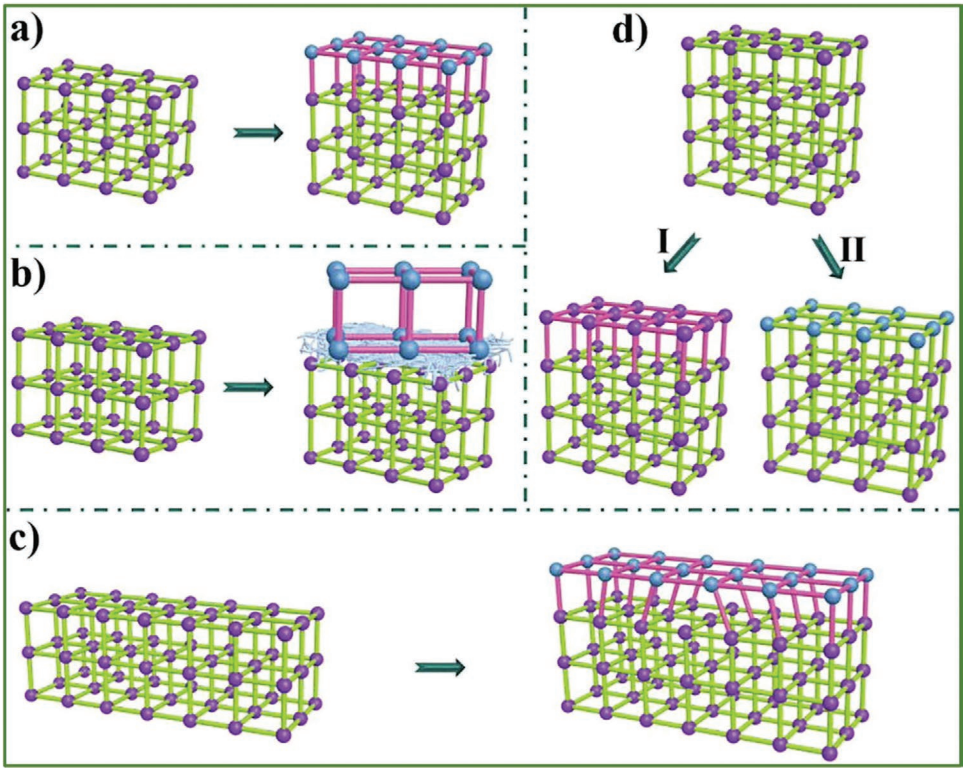

Figure 10. Schematic representation of four different approaches to prepare MOF on MOF: a) surfactant assistant growth, b) heteroepitaxial growth, c) ligand (I)/metal ion (II) exchange and d) nucleation kinetic guided growth.. Adapted with permission.[130] Copyright 2021, Wiley-VCH.

growth to surfactant-assisted synthases. An example of this synthesis strategy was published by Kitagawa et al.,[129] who succeeded in preparing an MOF with the core composed of $Zn_2(ndc)_2(dabco)]_n$ (ndc = 1,4-naphthalene dicarboxylate; dabco = diazabicyclo[2.2.2]octane) and a $[Cu_2(ndc)_2(dabco)]_n$ shell. Both the core and the shell were composed of single crystals. With XRD, they were able to determine the structure precisely.

This section describes the most significant post-synthetic methods of synthesis of one MOF on another and the possible applications of these composite materials. **Figure 10** illustrates the four critical post-synthetic methods for growing one MOF on another.[130]

The first is epitaxial growth. This method typically consists of growing the second MOF on a specific face of the first MOF. The second crystal usually has the same orientation and lattice spacing as the first. MOFs should be very similar chemically and structurally. One example is published by Li et al.,[131] who grew ZIF-67 on ZIF-8. Both MOFs have the same lattice spacing (both MOFs are identical), with the only difference being the metal with which they are produced. The primary limitation of this method is that it is impossible to synthesize core–shell structures composed of very different MOFs.

The second synthesis method is where one crystal of MOF is grown on top of another and both have very different lattice spacing (Figure 10). Although this method enables preparing core–shell structures composed of very different MOFs, it has not been matured, and only several examples have been published.[132,133]

Woll et al.[133] used a post-synthetic method based on layer-by-layer synthesis to heteroepitaxially grow an MOF on an MOF. The authors first grew an MOF composed of biphenyl-4,4′-dicarboxylic acid and copper. On this MOF, they grew another isoreticular MOF but using naphthalene-2,6-dicarboxylic acid as a ligand, which is shorter than biphenyl-4,4′-dicarboxylic acid—causing a mismatch at specific points of the MOF–MOF interface. The authors repeated the process with a shorter ligand (terephthalic acid). They also found defects caused by the size difference in the lattice spacing of the MOF (see **Figure 11**).

The third approach is the surfactant-assisted preparation of an MOF on an MOF. This is a post-synthetic method in which the surfactant functions as a glue to promote the generation of MOF-on-MOF structures. The first example of this post-synthetic method was published by Kitagawa et al.[129] They found that when NH_2-UiO-66(Zr) crystals were immersed in a solution of the NH_2-MIL-125(Ti) precursor and polyvinylpyrrolidone, the NH_2-MIL-125(Ti) grows and the NH_2-UiO-66(Zr) crystals remain on the surface of the NH_2-MIL-125(Ti). This method is counter-intuitive because it does not grow one MOF crystal on top of another. However, during the growth of the core-forming MOF, the crystals of the shell-forming MOF are trapped. The authors named this the internal extended growth method, and with it, they synthesized different MOF-on-MOF structures.

The fourth method was discussed in earlier sections. It consists of exchanging the metals of the external surface for others in a post-synthetic treatment. With this metathesis reaction, it is possible to generate an isoreticular MOF shell but constructed

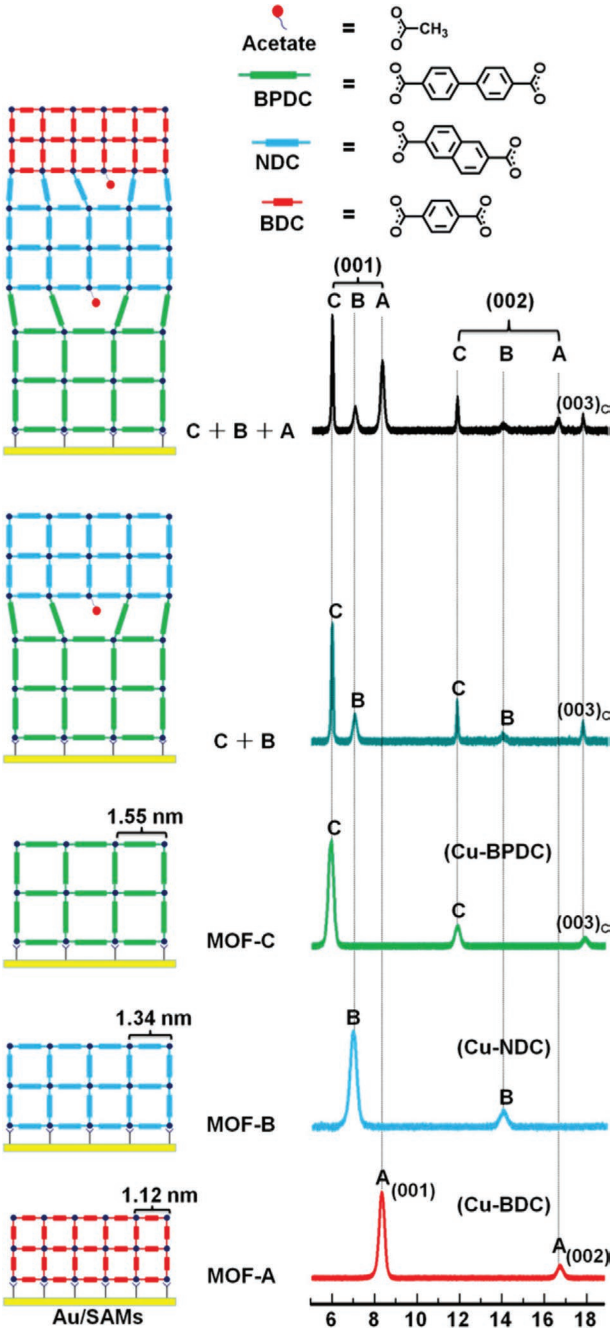

Figure 11. Illustration of layer-by-layer production of MOF on MOF. Reproduced with permission.[133] Copyright 2014, American Chemical Society.

with a different metal. Moreover, the same can be performed with the ligand, resulting in an MOF crystal with a core identical in structure to the shell but with a different composition. This method has many similarities with the first one. It is not possible to generalize MOFs with different lattice spacing or topologies.

Different MOF-on-MOF structures can be synthesized with the methods described above. **Figure 12** illustrates three examples of different structures, from a classical core–shell to asymmetric MOFs on MOFs via satellite structures.

6. Applications of Core–Shell MOFs Structures

6.1. Catalysis

The applications of core–shell structures in catalysis can vary, such as generating bi-functionals structures where the MOF in the shell catalyzes one reaction and the one in the core catalyzes another, thus being able to catalyze domino reactions that require different types of active sites. Another possible application is to use the shell as a molecular sieve so that some reactants enter the core and can be transformed while others do not.

Zhou et al.[124] succeeded in preparing a core–shell structure in which the core was composed of PCN-222(Zr) and the shell of UIO-67(Zr). PCC-222(Zr) was constructed with tetrakis(4-carboxyphenyl)porphyrin. The porphyrin of this material was complexed with Fe cation ions. These materials were applied in the olefin epoxidation. The primary finding is that the researchers could demonstrate that the shell had a sieving effect. When bulky substrates were used, the reaction rate decreased considerably, attributed to the slower diffusion rate through the shell of the bulky reagents.

The same group developed different core–shell structures (PCN-222(Fe)@ZIF-8, PCN-222@MOF-5) to be applied in size-selective catalysis. As in the previous study, the core–shell, always composed of PCN-222, the active phase, and the different MOFs used as shells, functioned as a molecular sieve. The results of PCN-222(Fe) and PCN-222(Fe)@ZIF-8 were compared in the oxidation of two different substrates: *o*-phenylenediamine (*o*-PDA) and 2,2’-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS). When using *o*-PDA, the reaction occurs in the ZI F-8-coated MOF and the uncoated MOF, although the reaction rate is lower in the coated MOF. When the same experiment is performed with ABTS, the reaction occurs in the uncoated MOF but not in the coated MOF. ABTS (0.7 × 1.6 nm) is substantially larger than *o*-PDA (0.5 × 0.5 nm) because the ABTS molecule cannot pass through the shell, given that it is larger than the pore size of ZIF-8 (0.7 nm). This example illustrates how the shell can have a very effective sieve effect.[136]

Wang et al.[137] coated ZIF-67 crystals with CPO-27 to generate a core–shell system for photocatalytic water oxidation. The core–shell MOFs exhibited higher catalytic performance in the water oxidation reaction than individual ZIF-67 or Co-MOF-74, demonstrating the synergistic effect between both MOFs.

In the previous section, we described how Kitagawa et al.[129] developed an MOF-on-MOF system based on NH_2-MIL-124(Ti) as the core and MIL-100 or UiO-66 as the shell. The same authors used these systems for the photocatalytic reduction of Cr(IV) to Cr(III) (**Figure 13**). Like Wang, they found that there was a synergistic effect that caused the MOF-on-MOF systems to function better than the MOFs alone.

6.2. Adsorption and Separation

Rosi et al.[138] used a series of isoreticular bio-MOFs, the so-called 11 and 14. Although bio-MOF-11 has high porosity, bio-MOF-14 has narrower porosity and a low adsorption capacity.

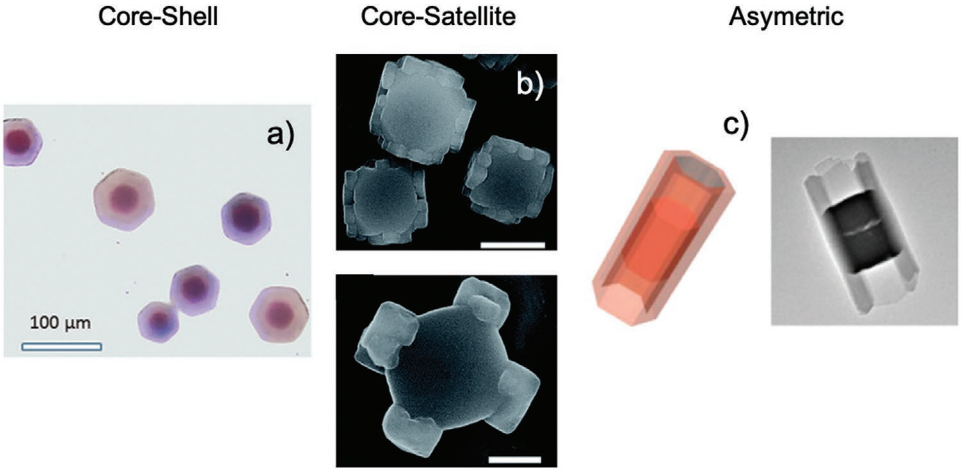

Figure 12. Different examples of core–shell MOF structures. a) Core-shell. Adapted with permission.[124] Copyright 2018, Wiley-VCH. b) Core-satellite. Adapted with permission under the terms of the CC-BY license.[134] Copyright 2020, the authors. Published by Royal Society of Chemistry. c) Asymetric. Adapted with permission.[135] Copyright 2016, American Chemical Society.

When the core–shell material is prepared using bio-MOF-11 as core and bio-MOF-14 as shell, a material with high capacity given by the bio-MOF-11 and high selectivity (CO_2:N_2 separation) provided by the bio-MOF-14 coating is obtained.

Kitagawa et al.[128,139] synthesized an MOF-on-MOF structure for isomer (n-cetane/isocetane) separation. They synthesized an MOF with a Zn2(BDC)2(DABCO) core (DABCO = 1,4-diazabicyclo[2,2,2,2] octane, BDC = benzenedicarboxylate) and a $Zn_2(ADC)_2(DABCO)$ shell (ADC = 9,10-anthracenedicarboxylate). The shell exhibited very high selectivity because it rejected isocetane.

Hecht et al.[140] mounted a thin outer layer of a photoswitchable MOF on a porous MOF. The outer layer had azobenzene pendant groups which are photoisomerizable. Thus, by irradiating with light, the azobenzene groups change from one isomer to another, so the pore size changes. The isomer can be photo-induced which generates a larger pore size. After the core is filled with the desired molecule, irradiation is stopped so that the isomer with a smaller pore size is induced, trapping the adsorbate in the core of the MOF-on-MOF structure.

7. Surface Etching

Surface etching of an MOF consists of a chemical treatment that can modify the surface properties of the crystal by the controlled removal of either or both of its components. When these surface treatments are applied, the properties of the crystal can be modified. For example, surface defects with catalytic properties or macro/mesopores can be generated in purely microporous crystals. One of the first examples of MOF surface etching was reported by Maspoch et al.[141,142] They treated different crystals of ZIF-8 and ZIF-67 with acidic solutions and found that the etching was anisotropic for ZIFs etched under acidic conditions. Some facets of the MOFs are etched faster than others. The researchers were able to generate crystals with very different shapes. For example, the final product was a cubic crystal if they etched truncated dodecahedral rhombic crystals in an acidic solution. They obtained crystals with different shapes, from pyramidal to hollow crystals, using the same approach. **Figure 14** illustrates how anisotropic etching of ZIF-8 and ZIF-67 crystals occurs.[143]

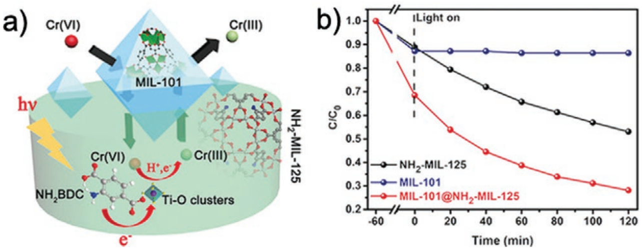

Figure 13. a) Illustration of the reaction mechanism. b) Catalytic performance of three different samples. Adapted with permission.[129] Copyright 2017, Wiley-VCH.

In this section, we outline the different strategies that have been followed to etch MOF crystals to overcome the limitations of MOF crystals and improve their applications. Chemical etching can be divided into four categories.[144,145] Yao and Feng[146] classified the improvements of MOF properties by chemical etching as follows:

i) designing materials with hierarchical porosity, which do not have mass transport problems.[147]
ii) modifying the MOF crystal polarity to facilitate functionalization or adsorptive and catalytic properties.[148]
iii) incorporating defects into the structure by partial removal of ligands or metal ions, which might have catalytic properties.[149]
iv) etch-induced conversion of MOFs into laminar double hydroxides.

Given the scope of this study, we focus on the first two points of this classification.

8. Pore Engineering

In many cases, MOF materials have a microporous structure (a pore size less than 2 nm).[150] This microporous structure

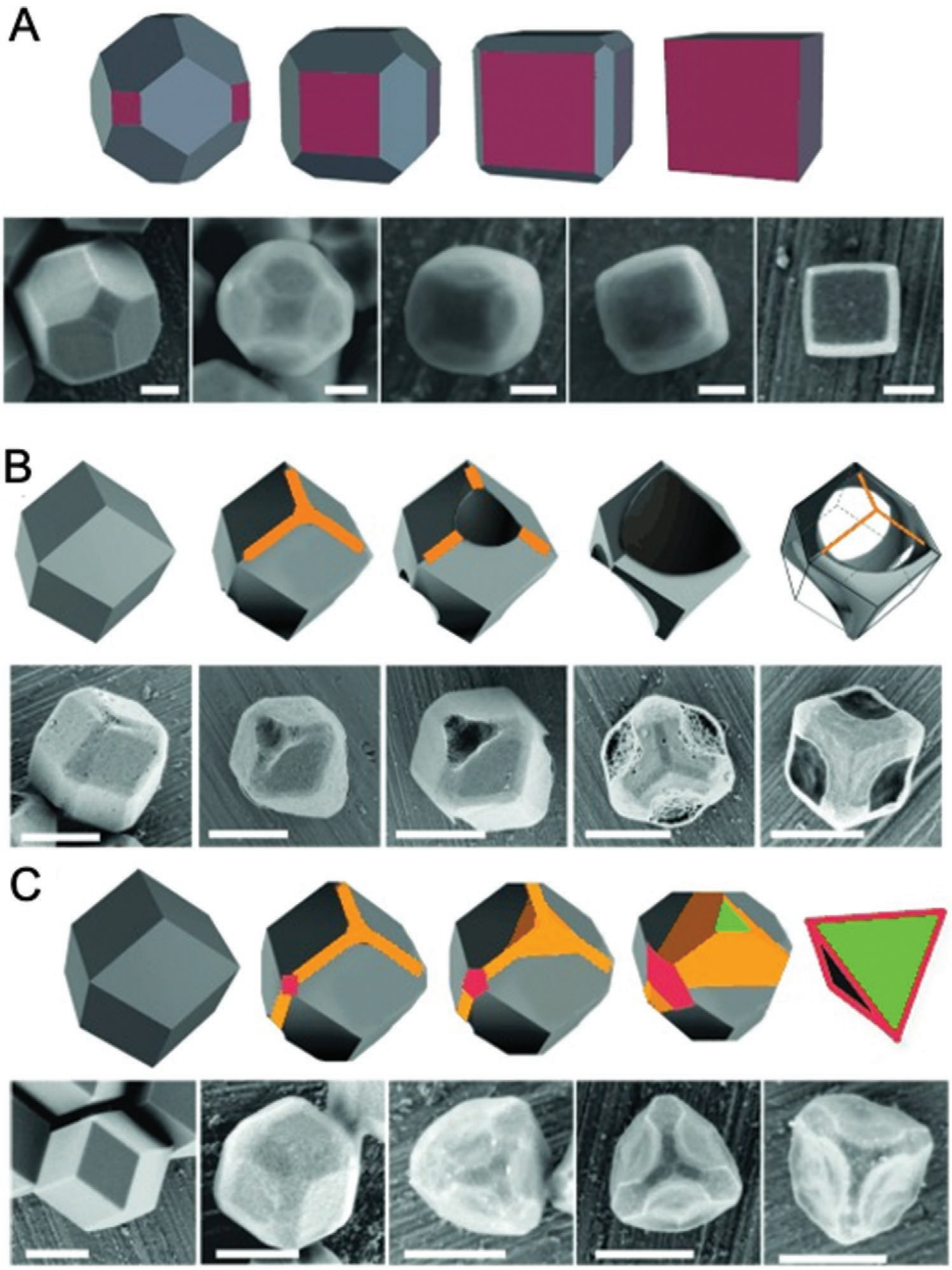

Figure 14. Anisotropic etching of different types of crystals of ZIF-67: A. Etching of truncated rhombic dodecahedral ZIF-67 crystals; B. Etching of rhombic dodecahedral ZIF-67 crystals, using an etchant solution at pH 2.5; and C. Etching of rhombic dodecahedral ZIF-67 crystals, using an etchant solution at pH 3.5. Adapted with permission.[141] Copyright 2015, Wiley-VCH.

indicates that these materials have a large specific surface area and a significant capacity to adsorb all types of adsorbates or to support all types of functional molecules that can function as active centers in catalysis or anchoring centers for drugs. However, for many applications, this narrow porosity is also a limitation. For example, in catalytic applications, when an MOF is used as a catalyst, the reactants must diffuse to the active center, and once the products are formed, they must diffuse out of the crystal. The microporosity of MOFs implies that there can be a vast number of active sites but also that the diffusion of reagents and products is slow—in many cases, slower than the rate at which the active centers can process molecules.

This phenomenon leads to the underutilization of the catalyst's active sites. Therefore, the use of microporous materials as catalysts in industry is limited to zeolites. However, this is not because zeolites do not have diffusional problems but because their acidity is so high that even if their active centers are not 100% used, they remain useful. Nonetheless, there is significant research trying to improve diffusion in zeolites. One of the methods to increase the amount of meso- and macropores in zeolites is the desilication of zeolites—a type of chemical etching. We recommend reading the study by Pérez-Ramirez et al.[151,152] in this area.

As in zeolites, MOF materials can enhance the diffusion of molecules through their porous structure by generating a hierarchical structure. MOFs are crystalline (arranged in repeating patterns that extend in all three dimensions of space), so generating hierarchical structures is complex. Most MOFs are microporous, and there are only several examples of mesoporous MOFs[111,153–161] Thus, the use of chemical etching to produce materials with hierarchical porosity is a post-synthetic method that changes the properties of MOF crystals.

Liu et al.[162] recently developed a method to prepare mesoporous HKUST-1, achieved by gas-phase chemical etching with ammonia. The facets (111) of the octahedral crystal surface are more stable than those (100) of the cubic structure that forms the inner part of the crystal. Thus, etching occurs preferentially in the interior of the crystal. The researchers found that different degrees of etching and amounts of mesopores could be generated by adjusting the temperature at which the chemical etching was performed. **Figure 15** illustrates the nitrogen adsorption isotherms of HKUST-1 treated at different temperatures, the pore size distribution, and scanning electron microscope (SEM) images. These materials were used to adsorb dyes with a molecular size larger than the pore size of the original HKUST-1.

Yu et al.[163] attempted to chemically etch HKUST-1 with ammonia in the liquid phase. However, when etching was performed under these conditions, the crystals partially decomposed into Cu_2O. Thus, different structures were generated. Only under particular conditions is mesoporous generated in the HKUST-1 crystal. These materials were used as catalysts to oxidize phenols.

Another approach to preparing mesoporous HKUST-1 is the one used by Fu and Zhai.[164] Steam was used as an etchant and ethanol as a structure stabilizer. They produced MOFs with hierarchical porosity and found that the mesoporosity

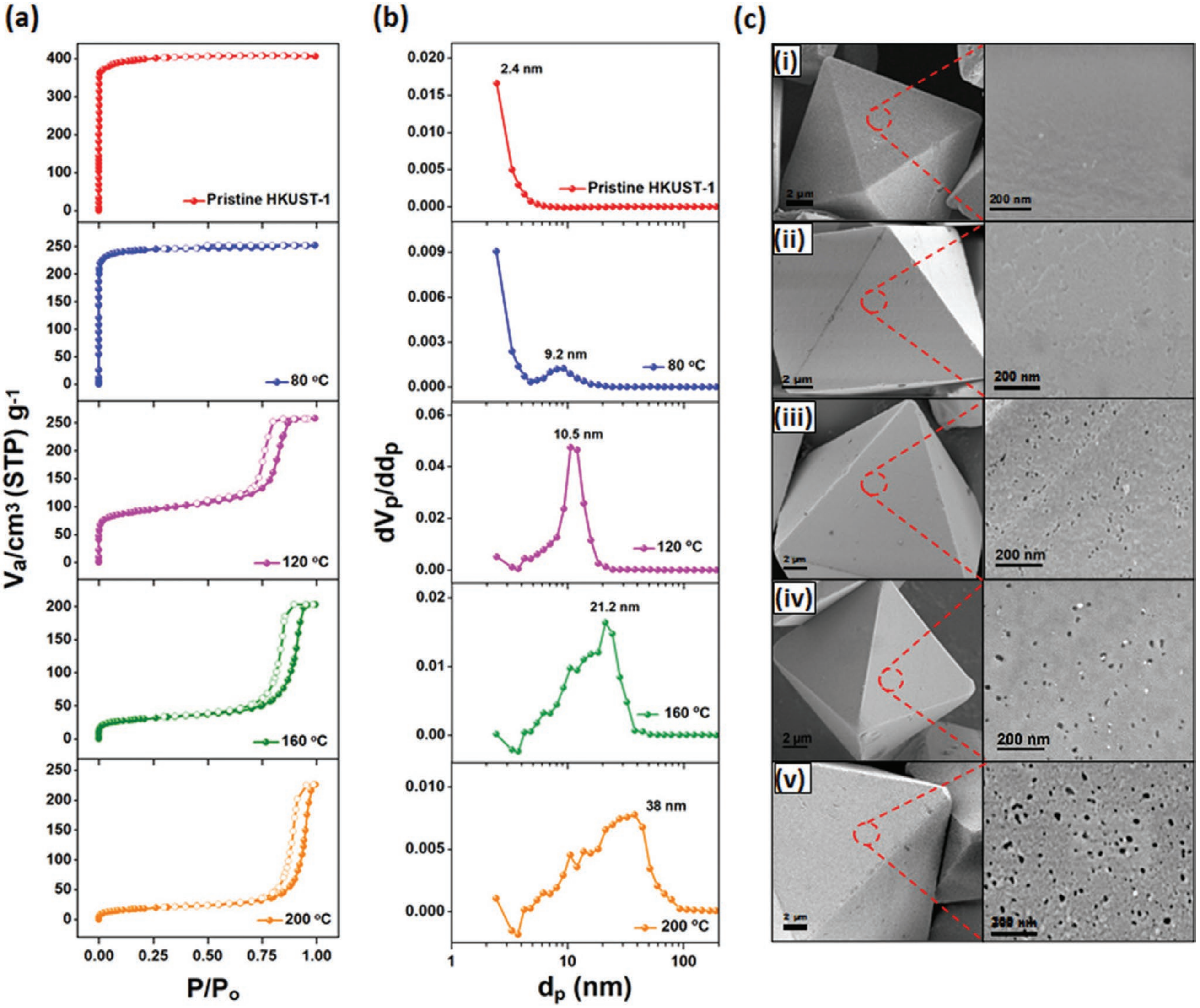

Figure 15. (a) N_2 adsorption isotherms, (b) pore size distribution and (c) SEM images of (i) pristine HKUST-1 etched with ammonia at (ii) 800C, (iii) 1200C, (iv) 1600C, and (v) 2000C for 12 hours. Reproduced with permission.[162] Copyright 2021, Wiley-VCH.

generated using steam is narrower than that generated using ammonia. Furthermore, the microporosity is not affected as much as for ammonia. When the authors used these MOFs as catalysts for CO_2 cycloaddition, they found that the reaction rate was higher in the mesoporous material because they used tetrabutylammonium bromide in the reaction as a co-catalyst, a very bulky molecule. When there are no mesopores, the diffusion is very slow.

Given these published studies on the generation of mesoporous MOFs by chemical etching, and because of the large number of publications in this area, we describe the most important studies and classify them with respect to the etchant used. For the sake of brevity, we only refer to the most important ones and do not describe them in detail.

MOF crystals have been etched with cyanuric chloride,[165] NaCl solution,[166] hydroquinone,[167] guanidinium surfactants,[168] H_2O_2,[169] ozone,[170] and methanol.[164] Acid treatment has become one of the most widely used post-synthetic methods to induce larger pores, especially in the field of Zr-MOFs. The most used acids are hydrochloric acid,[171] phosphoric acid,[172,173] citric acid,[174] fatty acid,[175] and several others.[176]

8.1. Surface Modification and Faceting

Surface etching is helpful in forming MOFs with preferentially exposed facets. Generating crystals with preferentially oriented faces can have applications in catalysis. The catalytic activity of some MOFs is given by defects on the crystal surface. Thus, the type and number of surface defects can be designed by preparing MOFs with preferentially exposed facets. Depending on which facet the crystal of an MOF ends up on, the density of coordination bonds is different; the component on which the crystal ends up is also different: metal or linker.[42–44] One approach to generating crystals that end on a given facet is chemical etching. If the etchant is well chosen, chemical etching can be anisotropic, i.e., one facet degrades faster than others in the MOF. Thus, MOFs with exposed structures and facets that cannot be synthesized directly can be produced after etching.

An example of catalysis using the surface defects of MOFs is when ZIFs are used as catalysts. These materials have no unsaturated sites, yet they catalyze reactions in a remarkable way. All authors ascribe unexpected catalytic activity to the presence of surface defects.[44]

Chen et al.[177] modified ZIF-8 crystals with a truncated rhombic dodecahedra shape using a xylenol orange (XO) etching solution to create hexapod ZIF-8 colloids. The solution is acidic (pH = 3), and the acid protonates the 2-methylimidazole, breaking the bond between the linker and the Zn^{2+} metal ion. The XO binds to the free Zn^{2+} ion creating water-soluble complexes and preventing recrystallization. Consequently, the hexagonal facets of the truncated rhombic dodecahedron (100) are more unstable under etching than the square facets (110). This results in concavities that form the hexapod shape of ZIF-8. Knoevenagel reaction between benzaldehyde and malononitrile, the conversion was 76% for the hexapods and 8.6% for the truncated rhombic dodecahedron after 1.5 h at room temperature.

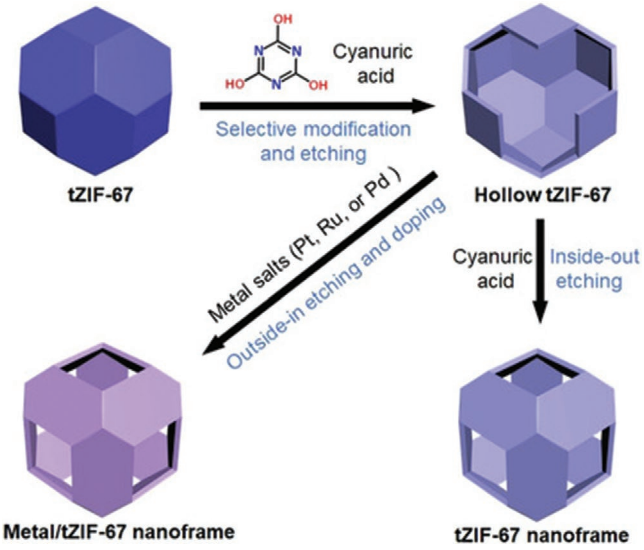

Figure 16. Etching of ZIF-67 with cyanuric acid. Reproduced with permission.[144] Copyright 2021, Wiley-VCH.

Cai et al.[144] found that anisotropic etching of ZIF-67 could be performed (similar to Maspoch et al.[141]) in this case using cyanidric acid as an etchant. They found that the (100) facet was more susceptible to etching than other MOF faces and thus obtained a hollow structure, as depicted in **Figure 16**. Several groups used hollow structures as precursors for electrocatalysts. Thereupon, they calcined these hollow structures in a controlled manner to obtain cobalt supported on nitrogen-containing carbons that were applied in the hydrogen evolution reaction. They found that these catalysts' functions and other catalysts based on cobalt are supported on carbon.

Wang et al.[178] investigated the three-coordinated Cu prepared by selectively etching the classical HKUST-1 along the (111) facets. The as-prepared CASFZU-1 (the etched MOF) exhibited high-strength Lewis acid Cu sites and a high affinity for CO_2. The conversions of cyclic carbonates from 2-octyloxirane or 1,2-epoxydodecane were 87% and 72% for CASFZU-1, 2% and 4% for HKUST-1, and 39% and 34% for random-etching MOF (**Figure 17**). This improvement the authors associate with the increase in pore size and the enhancement of the strength of the Lewis acid sites.

For reactions confined to the crystal's outer surface, it is necessary to increase the surface roughness to promote reaction kinetics. Furthermore, the roughened surface endows MOFs with a high surface-to-volume ratio to expose active surface sites for adsorption, catalysis, and sensing. For example, HCl was applied to roughen the (111) facet of the Zn-MOF to expose more Zn atoms on the outer surface, resulting in a catalytic copolymerization reaction of CO_2 with the epoxide.[173]

9. Porous Liquids

Until recently, the concept of porosity has been associated exclusively with solids. The usefulness of a porous material is enormous and ranges from adsorption to catalysis. Accordingly, developing porous materials such as activated carbons,

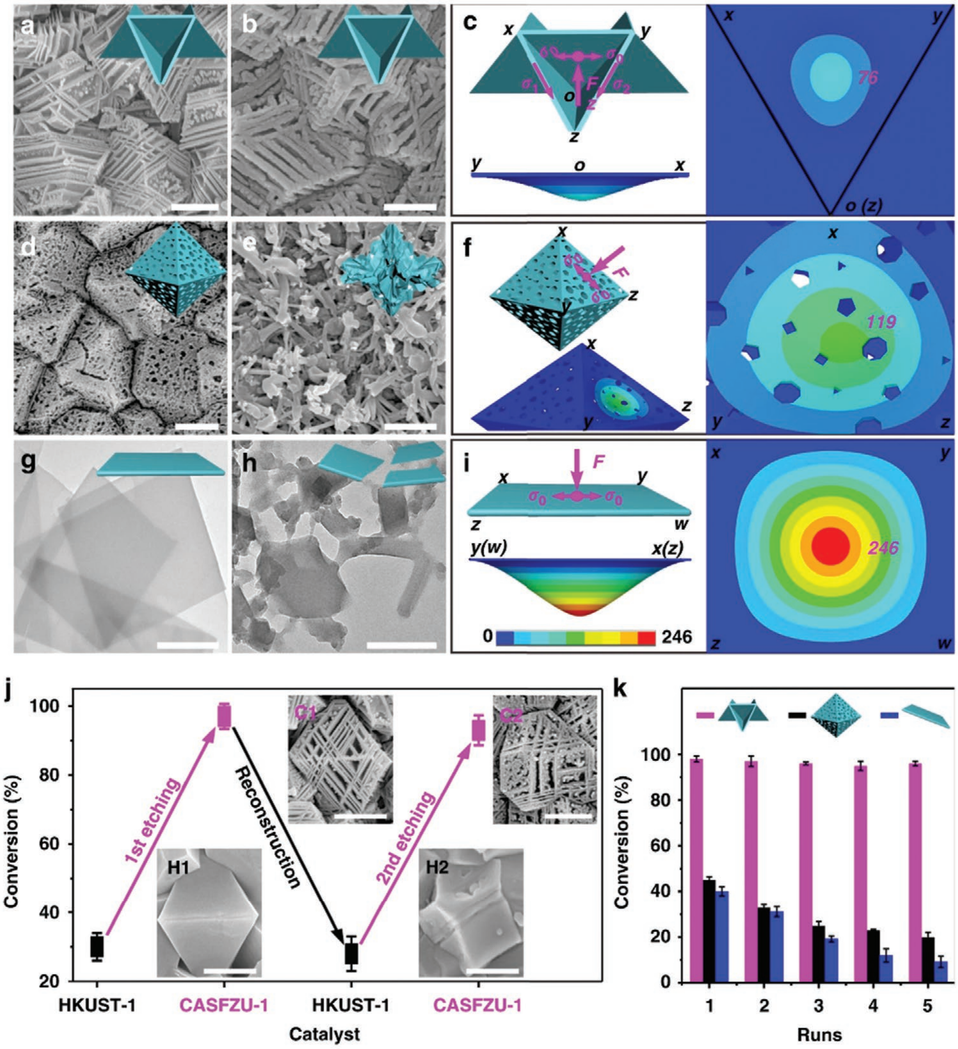

Figure 17. Mechanical stability and reconstruction of CASFZU-1 in cycloaddition of CO_2 with 2-ethyloxirane. a,b) SEM images of CASFZU-1 before and after 5 reuses in reaction. c) Simulated model of CASFZU-1 subjected to external stress, F. d,e) SEM images of random-etching MOFs before and after 5 reuses in reaction. f) Simulated model of random MOFs subjected to external stress, F. g,h) TEM images of HKUST-1 nanosheets before and after 5 reuses in reaction. i) Simulated model of HKUST-1 nanosheets subjected to external stress, F. j) Transformation of CASFZU-1 into HKUST-1 and its catalytic activity. k) Recyclability of CASFZU-1 (red), random-etching MOFs (black) and HKUST-1 nanosheets (blue). Reproduced with permission under the terms of the CC-BY license.[178] Copyright 2019, the authors. Published by Springer Nature.

zeolites, and MOFs has significantly impacted the industry and scientific community. Using porous solids has several technological advantages but some limitations. One of the limitations of solids is the low thermal conductivity of porous solids, which causes large temperature gradients to be generated in chemical reactors when used as catalysts in adsorption columns (as adsorbents). The same occurs for mass transport because the porous nature of these materials indicates that diffusion of reactants and products is not always efficient.

A solution to these problems may be the development of porous liquids.[179] They combine the high adsorption capacity of porous solids with the suitable fluid dynamic properties of liquids. Until Cooper et al.[180] published ground-breaking research in this field, this topic had not aroused much interest in the scientific community. One of the ways to make porous liquids is by using metal organic polyhedral or nanometric crystals of MOFs. If MOFs are suspended in liquids that cannot penetrate the MOF's porosity (mesitylene or ionic liquids), porous systems with fluidity can be generated. There are few published examples of this approach because preparing stable suspensions of MOFs is challenging. The crystal surface must be modified to increase the compatibility between the liquid and the nanometric MOF crystals, requiring post-functionalization methods for the external surface.

Li et al.[181] developed a breakthrough method to develop porous liquids by post-functionalizing the outer surface of the crystal. They functionalized the UiO-66(Zr) crystals with a polymer that had a low melting point (PMPP = poly(monomethacryloxypropyl-terminated polydimethylsiloxane)). They used an atom transfer radical polymerization method. All crystals were coated with the PMPP shell. When the composite material was brought to the melting temperature of PMPP, it behaved as a liquid. This coating did not affect the adsorption capacity of the unmodified material.

Gascon et al.[182,183] confirmed that modifying the surface of the ZIF-67 crystals with two different types of carbenes could generate very stable suspensions. They coordinated the carbenes to the cobalt cations on the outer surface of the crystal. They measured the rheological properties of the pore liquids and found that the viscosity of the pore liquid increased with MOF loading and behaved like a non-Newtonian fluid. Furthermore, they found that the adsorbent properties were not affected by functionalization with carbenes. The authors extended this approach to other ZIF materials and found similar results.

10. Summary and Perspectives

MOF research has developed over the recent years into a subdiscipline of chemistry and materials science. Thousands of new structures have been invented using organic ligands (e.g., carboxylates, imidazolates, and phosphates) and practically all the metals of the periodic table. All these new structures and post-functionalization methods have led to a wide range of applications being investigated. The primary research effort has focused on the synthesis of new structures that are stable under the conditions of application (e.g., stability in reaction media when used as catalysts). Therefore, in many cases, research has focused on synthesizing MOFs with high intrinsic chemical and thermal resistance.

Metals with a high oxidation state (Zr^{+4}, Hf^{+4}, Ti^{+4}, Cr^{3+}), which have a high Lewis acidity, are often used for this purpose. They are coordinated with carboxylates, which are Lewis bases that have a high affinity for these early transition metals. Concerning late-transition metals, the most stable MOFs are obtained when imidazoles or pyrazoles are used as ligands. Hence, a wide variety of stable ZIFs has been identified. Nonetheless, only a handful of stable MOFs have valuable properties in applications such as catalysis or adsorption. The scientific community has placed much effort into modifying these stable MOFs to make them useful for specific applications. Most approaches have focused on modifying the intrinsic properties of MOFs by introducing functions into the structure.

However, for most of the possible applications of MOFs, especially adsorption and catalysis, the molecules must pass through the outer surfaces of the MOF crystals. The outer surface is the first barrier of the MOF crystal. The tuning of this first barrier is fundamental to improving the properties of the MOFs being used.

The main problem with using MOFs as catalysts is their low stability, both thermally and chemically.[184] Much work has been done to prepare stable structures (which are not always intrinsically active). For this reason, the literature has described many post-synthetic methods to functionalize MOFs with different active centers. From nanoparticles to organometallic catalysts. These advances have not yet succeeded in moving MOFs from being a laboratory curiosity to being exploited industrially. In this sense, we believe that modifications of the external surface to improve the compatibility of MOFs with the reaction medium, their water resistance or to increase the mesoporosity of the material will bring the goal of exploiting MOFs as catalysts closer.

The commercial application of MOFs as adsorbents has been achieved. Several companies commercialize MOFs to adsorb hazardous gases or for the dosing of compounds that prevent fruit ripening.[185–189] They are limited to small-scale applications because large-scale applications such as CO_2 adsorption or natural gas storage are limited by a number of constraints. Perhaps the most important is the low thermal conductivity of MOFs. This causes a large increase in temperature during adsorption along with a capacity drop. On a laboratory level this is relatively simple to solve, but becomes cumbersome at industrial scale. Despite great efforts in the engineering of adsorption columns, storage tanks, and adsorbent structuring, this remains a problem that prevents MOFs from being used as adsorbent materials on a large scale. At this point, we believe that this is not only an engineering problem but a material problem. Materials need to be developed that have a higher thermal conductivity while maintaining their adsorption capacity. Post-functionalization of the outer surface may be one avenue to explore to solve this problem.

The use of MOFs as drug carriers. It is a very complex process, as the drug-carrying crystals must meet a very high number of requirements. They have to have a high capacity to adsorb the drug, they have to release it at a controlled rate, be biocompatible, be traceable, and have a specific interaction with the target. For each of these requirements, a specific function is needed. For example, to trace that the MOF has reached a target organ, fluorescent molecules anchored to the surface are needed. The complexity of this is that many of these functionalities must be located on the outer surface of the crystal. This implies that the outer surface must be composed of several functionalities, thus generating a multivariate surface. There are very few articles in the literature where multivariate external surfaces are reported. This is because the functionalities to be immobilized may be antagonistic or very difficult to anchor to the surface. In this sense, there is still a lot to be developed in spite of the great and important advances that have been made recently.

There are very few examples of porous liquids based on MOF nanocrystals. This is because MOF crystals in suspension tend to aggregate and decant. There are only two publications in which the external surface of the MOF crystals is modified with functional molecules that prevent aggregation and stabilize the suspension. This shows that there is much room for improvement in this area. There are still many MOFs and surface modifiers that have not been explored for preparing porous liquids.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

catalysis, drug delivery, membrane, metal organic frameworks, porous liquids, post-synthetic functionalizations

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[1] P. Rocío-Bautista, I. Taima-Mancera, J. Pasán, V. Pino, *Separations* **2019**, *6*, 33.
[2] S. M. J. Rogge, A. Bavykina, J. Hajek, H. Garcia, A. I. Olivos-Suarez, A. Sepúlveda-Escribano, A. Vimont, G. Clet, P. Bazin, F. Kapteijn, M. Daturi, E. v. Ramos-Fernandez, F. X. I. Llabrés Xamena, V. van Speybroeck, J. Gascon, *Chem. Soc. Rev.* **2017**, *46*, 3134.
[3] M. Mon, X. Qu, J. Ferrando-Soria, I. Pellicer-Carreño, A. Sepúlveda-Escribano, E. v. Ramos-Fernandez, J. C. Jansen, D. Armentano, E. Pardo, *J. Mater. Chem. A* **2017**, *5*, 20120.
[4] G. Sneddon, A. Greenaway, H. H. P. Yiu, *Adv. Energy Mater.* **2014**, *4*, 1301873.
[5] C. Petit, *Curr. Opin. Chem. Eng.* **2018**, *20*, 132.
[6] X. Fang, B. Zong, S. Mao, *Nano-Micro Lett.* **2018**, *10*, 64.
[7] M. S. Hosseini, S. Zeinali, M. H. Sheikhi, *Sens. Actuators, B* **2016**, *230*, 9.
[8] F. Zhao, T. Sun, F. Geng, P. Chen, Y. Gao, *Int. J. Electrochem. Sci.* **2016**, *14*, 5287.
[9] I. Stassen, N. Burtch, A. Talin, P. Falcaro, M. Allendorf, R. Ameloot, *Chem. Soc. Rev.* **2017**, *46*, 3185.
[10] M. Mon, R. Bruno, J. Ferrando-Soria, L. Bartella, L. di Donna, M. Talia, R. Lappano, M. Maggiolini, D. Armentano, E. Pardo, *Mater. Horiz.* **2018**, *5*, 683.
[11] D. Cunha, M. ben Yahia, S. Hall, S. R. Miller, H. Chevreau, E. Elkaïm, G. Maurin, P. Horcajada, C. Serre, *Chem. Mater.* **2013**, *25*, 2767.
[12] P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.-S. Chang, Y. K. Hwang, V. Marsaud, P.-N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur, R. Gref, *Nat. Mater.* **2010**, *9*, 172.
[13] B. Liu, Y. He, L. Han, V. Singh, X. Xu, T. Guo, F. Meng, X. Xu, P. York, Z. Liu, J. Zhang, *Cryst. Growth Des.* **2017**, *17*, 1654.
[14] V. Duplan, M. Hoshino, W. Li, T. Honda, M. Fujita, *Angew. Chem., Int. Ed.* **2016**, *55*, 4919.
[15] M. C. Wasson, C. T. Buru, Z. Chen, T. Islamoglu, O. K. Farha, *Appl. Catal., A* **2019**, *586*, 117214.
[16] F. J. Uribe-romo, C. B. Knobler, M. O. Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2010**, *43*, 58.
[17] J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450.
[18] J. L. C. Rowsell, O. M. Yaghi, *Microporous Mesoporous Mater.* **2004**, *73*, 3.
[19] H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444.
[20] E. v. Ramos-Fernández, J. C. Serrano-Ruiz, A. Sepúlveda-Escribano, J. Narciso, J. Ferrando-Soria, E. Pardo, in *Heterogeneous Catalysis for Energy Applications* (Eds: T. R. Reina, J. A. Odriozola), The Royal Society Of Chemistry, London **2020**, pp. 235–303.
[21] T. Grancha, M. Mon, J. Ferrando-Soria, J. Gascon, B. Seoane, E. v. Ramos-Fernandez, D. Armentano, E. Pardo, T. Grancha, M. Mon, J. Ferrando-Soria, D. Armentano, B. Seoane, E. Pardo, J. Gascon, *J. Mater. Chem. A* **2017**, *5*, 11032.
[22] S. W. Choi, W. S. Kim, J. H. Kim, *J. Dispersion Sci. Technol.* **2003**, *24*, 475.
[23] R. J. Marshall, R. S. Forgan, *Eur. J. Inorg. Chem.* **2016**, *2016*, 4310.
[24] S. Mandal, S. Natarajan, P. Mani, A. Pankajakshan, *Adv. Funct. Mater.* **2021**, *31*, 2006291.
[25] G. Zahn, P. Zerner, J. Lippke, F. L. Kempf, S. Lilienthal, C. A. Schröder, A. M. Schneider, P. Behrens, *CrystEngComm* **2014**, *16*, 9198.
[26] R. S. Forgan, *Chem. Sci.* **2020**, *11*, 4546.
[27] C. v McGuire, R. S. Forgan, *Chem. Commun.* **2015**, *51*, 5199.
[28] R. S. Forgan, *Dalton Trans.* **2019**, *48*, 9037.
[29] Y.-H. Kiang, G. B. Gardner, S. Lee, Z. Xu, E. B. Lobkovsky, *J. Am. Chem. Soc.* **1999**, *121*, 8204.
[30] J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982.
[31] Z. Wang, S. M. Cohen, *J. Am. Chem. Soc.* **2007**, *129*, 12368.
[32] S. M. Cohen, *J. Am. Chem. Soc.* **2017**, *139*, 2855.
[33] L. Liu, A. Corma, *Chem* **2021**, *7*, 2347.
[34] J. Cure, E. Mattson, K. Cocq, H. Assi, S. Jensen, K. Tan, M. Catalano, S. Yuan, H. Wang, L. Feng, P. Zhang, S. Kwon, J.-F. Veyan, Y. Cabrera, G. Zhang, J. Li, M. Kim, H.-C. Zhou, Y. J. Chabal, T. Thonhauser, *J. Mater. Chem. A* **2019**, *7*, 17536.
[35] M. Tejeda-Serrano, M. Mon, B. Ross, F. Gonell, J. Ferrando-Soria, A. Corma, A. Leyva-Pérez, D. Armentano, E. Pardo, *J. Am. Chem. Soc.* **2018**, *140*, 8827.
[36] J. Gascon, A. Corma, F. Kapteijn, F. X. Llabrés I Xamena, *ACS Catal.* **2014**, *4*, 361.
[37] K. K. Tanabe, S. M. Cohen, *Chem. Soc. Rev.* **2011**, *40*, 498.
[38] S. M. Cohen, *Chem. Rev.* **2012**, *112*, 970.
[39] Z. Wang, S. M. Cohen, *Chem. Soc. Rev.* **2009**, *38*, 1315.
[40] M. Xiang, D. Li, H. Xiao, J. Zhang, H. Qi, W. Li, B. Zhong, Y. Sun, *Fuel* **2008**, *87*, 599.
[41] A. Schejn, L. Balan, V. Falk, L. Aranda, G. Medjahdi, R. Schneider, *CrystEngComm* **2014**, *16*, 4493.
[42] C. Huang, S. Zhang, Y. Quan, K. Ren, Y. Tian, S. Zhu, R. Liu, *Solid State Sci.* **2022**, *123*, 106798.
[43] F. Guo, J.-H. Guo, P. Wang, Y.-S. Kang, Y. Liu, J. Zhao, W.-Y. Sun, *Chem. Sci.* **2019**, *10*, 4834.
[44] L. Chen, B. Duan, Q. Luo, Z. Gu, J. Liu, C. Duan, *Catal. Sci. Technol.* **2016**, *6*, 1616.
[45] Q. Min, R. Wu, L. Zhao, H. Qin, M. Ye, J.-J. Zhu, H. Zou, *Chem. Commun.* **2010**, *46*, 6144.
[46] B. C. Kim, D. Lopez-Ferrer, S.-M. Lee, H.-K. Ahn, S. Nair, S. H. Kim, B. S. Kim, K. Petritis, D. G. Camp, J. W. Grate, R. D. Smith, Y.-M. Koo, M. B. Gu, J. Kim, *Proteomics* **2009**, *9*, 1893.
[47] X. Wu, J. Ge, C. Yang, M. Hou, Z. Liu, *Chem. Commun.* **2015**, *51*, 13408.
[48] X. Lian, Y. Fang, E. Joseph, Q. Wang, J. Li, S. Banerjee, C. Lollar, X. Wang, H.-C. Zhou, *Chem. Soc. Rev.* **2017**, *46*, 3386.
[49] W. Liang, H. Xu, F. Carraro, N. K. Maddigan, Q. Li, S. G. Bell, D. M. Huang, A. Tarzia, M. B. Solomon, H. Amenitsch, L. Vaccari, C. J. Sumby, P. Falcaro, C. J. Doonan, *J. Am. Chem. Soc.* **2019**, *141*, 2348.
[50] F.-S. Liao, W.-S. Lo, Y.-S. Hsu, C.-C. Wu, S.-C. Wang, F.-K. Shieh, J. v. Morabito, L.-Y. Chou, K. C. W. Wu, C.-K. Tsung, *J. Am. Chem. Soc.* **2017**, *139*, 6530.
[51] X. Wu, S. Liu, W.-Y. Lou, J. Xiong, M.-H. Zong, M. Bilal, in *Nanomaterials for Biocatalysis* (Eds: G. R. Castro, A. K. Nadda, T. A. Nguyen, X. Qi, G. Yasin), Elsevier, New York **2022**, pp. 267–300.
[52] W.-H. Chen, M. Vázquez-González, A. Zoabi, R. Abu-Reziq, I. Willner, *Nat. Catal.* **2018**, *1*, 689.
[53] T. J. Pisklak, M. Macías, D. H. Coutinho, R. S. Huang, K. J. Balkus, *Top. Catal.* **2006**, *38*, 269.
[54] W. Ma, Q. Jiang, P. Yu, L. Yang, L. Mao, *Anal. Chem.* **2013**, *85*, 7550.

[55] I. N. Ahmed, X.-L. Yang, A. A. Dubale, R.-F. Li, Y.-M. Ma, L.-M. Wang, G.-H. Hou, R.-F. Guan, M.-H. Xie, *Bioresour. Technol.* **2018**, *270*, 377.
[56] Y.-H. Shih, S.-H. Lo, N.-S. Yang, B. Singco, Y.-J. Cheng, C.-Y. Wu, I.-H. Chang, H.-Y. Huang, C.-H. Lin, *ChemPlusChem* **2012**, *77*, 982.
[57] W.-L. Liu, S.-H. Lo, B. Singco, C.-C. Yang, H.-Y. Huang, C.-H. Lin, *J. Mater. Chem. B* **2013**, *1*, 928.
[58] W. Xu, L. Jiao, H. Yan, Y. Wu, L. Chen, W. Gu, D. Du, Y. Lin, C. Zhu, *ACS Appl. Mater. Interfaces* **2019**, *11*, 22096.
[59] J. Cui, S. Ren, B. Sun, S. Jia, *Coord. Chem. Rev.* **2018**, *370*, 22.
[60] S. Jung, Y. Kim, S.-J. Kim, T.-H. Kwon, S. Huh, S. Park, *Chem. Commun.* **2011**, *47*, 2904.
[61] W. Zhang, Y. Hu, J. Ge, H.-L. Jiang, S.-H. Yu, *J. Am. Chem. Soc.* **2014**, *136*, 16978.
[62] X. Chen, P. Qian, T. Zhang, Z. Xu, C. Fang, X. Xu, W. Chen, P. Wu, Y. Shen, S. Li, J. Wu, B. Zheng, W. Zhang, F. Huo, *Chem. Commun.* **2018**, *54*, 3936.
[63] A. M. Shultz, A. A. Sarjeant, O. K. Farha, J. T. Hupp, S. T. Nguyen, *J. Am. Chem. Soc.* **2011**, *133*, 13252.
[64] M. H. Alkordi, Y. Liu, R. W. Larsen, J. F. Eubank, M. Eddaoudi, *J. Am. Chem. Soc.* **2008**, *130*, 12639.
[65] A. M. Shultz, O. K. Farha, J. T. Hupp, S. T. Nguyen, *J. Am. Chem. Soc.* **2009**, *131*, 4204.
[66] F. Bonino, S. Chavan, J. G. Vitillo, E. Groppo, G. Agostini, C. Lamberti, P. D. C. Dietzel, C. Prestipino, S. Bordiga, *Chem. Mater.* **2008**, *20*, 4957.
[67] D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei, H.-C. Zhou, *Angew. Chem., Int. Ed.* **2012**, *51*, 10307.
[68] K. Wang, D. Feng, T.-F. Liu, J. Su, S. Yuan, Y.-P. Chen, M. Bosch, X. Zou, H.-C. Zhou, *J. Am. Chem. Soc.* **2014**, *136*, 13983.
[69] H. G. T. Nguyen, M. H. Weston, O. K. Farha, J. T. Hupp, S. T. Nguyen, *CrystEngComm* **2012**, *14*, 4115.
[70] X. Song, T. K. Kim, H. Kim, D. Kim, S. Jeong, H. R. Moon, M. S. Lah, *Chem. Mater.* **2012**, *24*, 3065.
[71] X. Song, S. Jeong, D. Kim, M. S. Lah, *CrystEngComm* **2012**, *14*, 5753.
[72] C. Chen, M. R. Alalouni, X. Dong, Z. Cao, Q. Cheng, L. Zheng, L. Meng, C. Guan, L. Liu, E. Abou-Hamad, J. Wang, Z. Shi, K.-W. Huang, L. Cavallo, Y. Han, *J. Am. Chem. Soc.* **2021**, *143*, 7144.
[73] S. Zuluaga, E. M. A. Fuentes-Fernandez, K. Tan, F. Xu, J. Li, Y. J. Chabal, T. Thonhauser, *J. Mater. Chem. A* **2016**, *4*, 5176.
[74] J. A. Greathouse, M. D. Allendorf, *J. Am. Chem. Soc.* **2006**, *128*, 10678.
[75] J. Castells-Gil, F. Novio, N. M. Padial, S. Tatay, D. Ruíz-Molina, C. Martí-Gastaldo, *J. Visualized Exp.* **2018**, *139*, e58052.
[76] J. Castells-Gil, F. Novio, N. M. Padial, S. Tatay, D. Ruíz-Molina, C. Martí-Gastaldo, *ACS Appl. Mater. Interfaces* **2017**, *9*, 44641.
[77] Y. Sun, Q. Sun, H. Huang, B. Aguila, Z. Niu, J. A. Perman, S. Ma, *J. Mater. Chem. A* **2017**, *5*, 18770.
[78] M.-L. Gao, S.-Y. Zhao, Z.-Y. Chen, L. Liu, Z.-B. Han, *Inorg. Chem.* **2019**, *58*, 2261.
[79] Q. Zha, X. Sang, D. Liu, D. Wang, G. Shi, C. Ni, *J. Solid State Chem.* **2019**, *275*, 23.
[80] J. Kim, S. Yeo, J.-D. Jeon, S.-Y. Kwak, *Microporous Mesoporous Mater.* **2015**, *202*, 8.
[81] K. Jayaramulu, K. K. R. Datta, C. Rösler, M. Petr, M. Otyepka, R. Zboril, R. A. Fischer, *Angew. Chem., Int. Ed.* **2016**, *55*, 1178.
[82] K. Tan, S. Zuluaga, E. Fuentes, E. C. Mattson, J.-F. Veyan, H. Wang, J. Li, T. Thonhauser, Y. J. Chabal, *Nat. Commun.* **2016**, *7*, 13871.
[83] T.-H. Bae, J. S. Lee, W. Qiu, W. J. Koros, C. W. Jones, S. Nair, *Angew. Chem.* **2010**, *122*, 10059.
[84] C. Zhang, Y. Dai, J. R. Johnson, O. Karvan, W. J. Koros, *J. Membr. Sci.* **2012**, *389*, 34.
[85] Y. Zhang, X. Feng, S. Yuan, J. Zhou, B. Wang, *Inorg. Chem. Front.* **2016**, *3*, 896.
[86] A. Zimpel, T. Preiß, R. Röder, H. Engelke, M. Ingrisch, M. Peller, J. O. Rädler, E. Wagner, T. Bein, U. Lächelt, S. Wuttke, *Chem. Mater.* **2016**, *28*, 3318.
[87] M. D. Rowe, D. H. Tham, S. L. Kraft, S. G. Boyes, *Biomacromolecules* **2009**, *10*, 983.
[88] S. Wang, W. Morris, Y. Liu, C. M. McGuirk, Y. Zhou, J. T. Hupp, O. K. Farha, C. A. Mirkin, *Angew. Chem., Int. Ed.* **2015**, *54*, 14738.
[89] E. Bellido, T. Hidalgo, M. V. Lozano, M. Guillevic, R. Simón-Vázquez, M. J. Santander-Ortega, Á. González-Fernández, C. Serre, M. J. Alonso, P. Horcajada, *Adv. Healthcare Mater.* **2015**, *4*, 1246.
[90] W. Zhu, G. Xiang, J. Shang, J. Guo, B. Motevalli, P. Durfee, J. O. Agola, E. N. Coker, C. J. Brinker, *Adv. Funct. Mater.* **2018**, *28*, 1705274.
[91] B. Liu, M. Ma, D. Zacher, A. Bétard, K. Yusenko, N. Metzler-Nolte, C. Wöll, R. A. Fischer, *J. Am. Chem. Soc.* **2011**, *133*, 1734.
[92] W. Morris, W. E. Briley, E. Auyeung, M. D. Cabezas, C. A. Mirkin, *J. Am. Chem. Soc.* **2014**, *136*, 7261.
[93] M. Savonnet, E. Kockrick, A. Camarata, D. Bazer-Bachi, N. Bats, V. Lecocq, C. Pinel, D. Farrusseng, *New J. Chem.* **2011**, *35*, 1892.
[94] W.-H. Chen, X. Yu, A. Cecconello, Y. S. Sohn, R. Nechushtai, I. Willner, *Chem. Sci.* **2017**, *8*, 5769.
[95] M. Kondo, S. Furukawa, K. Hirai, S. Kitagawa, *Angew. Chem., Int. Ed.* **2010**, *49*, 5327.
[96] M. Köppen, O. Beyer, S. Wuttke, U. Lüning, N. Stock, *Dalton Trans.* **2017**, *46*, 8658.
[97] A. Huang, L. Wan, J. Caro, *Mater. Res. Bull.* **2018**, *98*, 308.
[98] B. Seoane, J. Coronas, I. Gascon, M. E. Benavides, O. Karvan, J. Caro, F. Kapteijn, J. Gascon, *Chem. Soc. Rev.* **2015**, *44*, 2421.
[99] L. M. Robeson, Q. Liu, B. D. Freeman, D. R. Paul, *J. Membr. Sci.* **2015**, *476*, 421.
[100] M. Kalaj, K. C. Bentz, S. Ayala, J. M. Palomba, K. S. Barcus, Y. Katayama, S. M. Cohen, *Chem. Rev.* **2020**, *120*, 8267.
[101] M. S. Denny, J. C. Moreton, L. Benz, S. M. Cohen, *Nat. Rev. Mater.* **2016**, *1*, 16078.
[102] J. Gascon, F. Kapteijn, *Angew. Chem., Int. Ed.* **2010**, *49*, 1530.
[103] J. Dechnik, J. Gascon, C. J. Doonan, C. Janiak, C. J. Sumby, *Angew. Chem., Int. Ed.* **2017**, *56*, 9292.
[104] T. Rodenas, M. van Dalen, P. Serra-Crespo, F. Kapteijn, J. Gascon, *Microporous Mesoporous Mater.* **2014**, *192*, 35.
[105] B. Zornoza, A. Martinez-Joaristi, P. Serra-Crespo, C. Tellez, J. Coronas, J. Gascon, F. Kapteijn, *Chem. Commun.* **2011**, *47*, 9522.
[106] T. Rodenas, M. van Dalen, E. García-Pérez, P. Serra-Crespo, B. Zornoza, F. Kapteijn, J. Gascon, *Adv. Funct. Mater.* **2014**, *24*, 249.
[107] J. Benito, M. Fenero, S. Sorribas, B. Zornoza, K. J. Msayib, N. B. McKeown, C. Téllez, J. Coronas, I. Gascón, *Colloids Surf., A* **2015**, *470*, 161.
[108] E. A. Feijani, H. Mahdavi, A. Tavasoli, *Chem. Eng. Res. Des.* **2015**, *96*, 87.
[109] Y. Katayama, K. C. Bentz, S. M. Cohen, *ACS Appl. Mater. Interfaces* **2019**, *11*, 13029.
[110] Q. Xin, T. Liu, Z. Li, S. Wang, Y. Li, Z. Li, J. Ouyang, Z. Jiang, H. Wu, *J. Membr. Sci.* **2015**, *488*, 67.
[111] M. G. Goesten, J. Juan-Alcañiz, E. v. Ramos-Fernandez, K. B. Sai Sankar Gupta, E. Stavitski, H. van Bekkum, J. Gascon, F. Kapteijn, *J. Catal.* **2011**, *281*, 177.
[112] A. L. W. Demuynck, M. G. Goesten, E. v. Ramos-Fernandez, M. Dusselier, J. Vanderleyden, F. Kapteijn, J. Gascon, B. F. Sels, *ChemCatChem* **2014**, *6*, 2211.
[113] H. Wang, S. He, X. Qin, C. Li, T. Li, *J. Am. Chem. Soc.* **2018**, *140*, 17203.
[114] H. Ning, Z. Yang, Z. Yin, D. Wang, Z. Meng, C. Wang, Y. Zhang, Z. Chen, *ACS Appl. Mater. Interfaces* **2021**, *13*, 17781.

[115] H. Zhu, L. Wang, X. Jie, D. Liu, Y. Cao, *ACS Appl. Mater. Interfaces* **2016**, *8*, 22696.
[116] Z. Wang, D. Wang, S. Zhang, L. Hu, J. Jin, *Adv. Mater.* **2016**, *28*, 3399.
[117] Y. Zhang, X. Feng, H. Li, Y. Chen, J. Zhao, S. Wang, L. Wang, B. Wang, *Angew. Chem., Int. Ed.* **2015**, *54*, 4259.
[118] W.-L. Jiang, L.-G. Ding, B.-J. Yao, J.-C. Wang, G.-J. Chen, Y.-A. Li, J.-P. Ma, J. Ji, Y. Dong, Y.-B. Dong, *Chem. Commun.* **2016**, *52*, 13564.
[119] M. Kalaj, M. S. Denny Jr., K. C. Bentz, J. M. Palomba, S. M. Cohen, *Angew. Chem., Int. Ed.* **2019**, *58*, 2336.
[120] B.-J. Yao, W.-L. Jiang, Y. Dong, Z.-X. Liu, Y.-B. Dong, *Chemistry* **2016**, *22*, 10565.
[121] B.-J. Yao, L.-G. Ding, F. Li, J.-T. Li, Q.-J. Fu, Y. Ban, A. Guo, Y.-B. Dong, *ACS Appl. Mater. Interfaces* **2017**, *9*, 38919.
[122] K. Koh, A. G. Wong-Foy, A. J. Matzger, *Chem. Commun.* **2009**, 6162.
[123] X. Gao, J. Zhang, K. Huang, J. Zhang, *ACS Appl. Mater. Interfaces* **2018**, *10*, 34640.
[124] X. Yang, S. Yuan, L. Zou, H. Drake, Y. Zhang, J. Qin, A. Alsalme, H.-C. Zhou, *Angew. Chem., Int. Ed.* **2018**, *57*, 3927.
[125] L. Feng, K.-Y. Wang, X.-L. Lv, T.-H. Yan, H.-C. Zhou, *Natl. Sci. Rev.* **2020**, *7*, 1743.
[126] L. Chai, J. Pan, Y. Hu, J. Qian, M. Hong, *Small* **2021**, *17*, 2100607.
[127] D. H. Hong, H. S. Shim, J. Ha, H. R. Moon, *Bull. Korean Chem. Soc.* **2021**, *42*, 956.
[128] P. Á. Szilágyi, M. Lutz, J. Gascon, J. Juan-Alcañiz, J. van Esch, F. Kapteijn, H. Geerlings, B. Dam, R. van de Krol, *CrystEngComm* **2013**, *15*, 6003.
[129] Y. Gu, Y. Wu, L. Li, W. Chen, F. Li, S. Kitagawa, *Angew. Chem., Int. Ed.* **2017**, *56*, 15658.
[130] C. Liu, J. Wang, J. Wan, C. Yu, *Coord. Chem. Rev.* **2021**, *432*, 213743.
[131] Y. Pan, K. Sun, S. Liu, X. Cao, K. Wu, W.-C. Cheong, Z. Chen, Y. Wang, Y. Li, Y. Liu, D. Wang, Q. Peng, C. Chen, Y. Li, *J. Am. Chem. Soc.* **2018**, *140*, 2610.
[132] M. Tu, R. A. Fischer, *J. Mater. Chem. A* **2014**, *2*, 2018.
[133] Z. Wang, J. Liu, B. Lukose, Z. Gu, P. G. Weidler, H. Gliemann, T. Heine, C. Wöll, *Nano Lett.* **2014**, *14*, 1526.
[134] C. Liu, L. Lin, Q. Sun, J. Wang, R. Huang, W. Chen, S. Li, J. Wan, J. Zou, C. Yu, *Chem. Sci.* **2020**, *11*, 3680.
[135] S. Choi, T. Kim, H. Ji, H. J. Lee, M. Oh, *J. Am. Chem. Soc.* **2016**, *138*, 14434.
[136] L. Feng, S. Yuan, J. L. Li, K. Y. Wang, G. S. Day, P. Zhang, Y. Wang, H. C. Zhou, *ACS Cent. Sci.* **2018**, *4*, 1719.
[137] C. Guo, J. Guo, Y. Zhang, D. Wang, L. Zhang, Y. Guo, W. Ma, J. Wang, *CrystEngComm* **2018**, *20*, 7659.
[138] T. Li, J. E. Sullivan, N. L. Rosi, *J. Am. Chem. Soc.* **2013**, *135*, 9984.
[139] K. Hirai, S. Furukawa, M. Kondo, H. Uehara, O. Sakata, S. Kitagawa, *Angew. Chem., Int. Ed.* **2011**, *50*, 8057.
[140] D. Mutruc, A. Goulet-Hanssens, S. Fairman, S. Wahl, A. Zimathies, C. Knie, S. Hecht, *Angew. Chem., Int. Ed.* **2019**, *58*, 12862.
[141] C. Avci, J. Ariñez-Soriano, A. Carné-Sánchez, V. Guillerm, C. Carbonell, I. Imaz, D. Maspoch, *Angew. Chem., Int. Ed.* **2015**, *54*, 14417.
[142] M. Rubio-Martinez, C. Avci-Camur, A. W. Thornton, I. Imaz, D. Maspoch, M. R. Hill, *Chem. Soc. Rev.* **2017**, *46*, 3453.
[143] X. Ge, C. Li, Z. Li, L. Yin, *Electrochim. Acta* **2018**, *281*, 700.
[144] Z. Cai, Z. Wang, Y. Xia, H. Lim, W. Zhou, A. Taniguchi, M. Ohtani, K. Kobiro, T. Fujita, Y. Yamauchi, *Angew. Chem.* **2021**, *133*, 4797.
[145] F. Tang, X. Gao, Z. Jin, *Electrochim. Acta* **2020**, *337*, 135807.
[146] Y. Feng, J. Yao, *Coord. Chem. Rev.* **2022**, *470*, 214699.
[147] I. Ibrahim, S. Zheng, C. Y. Foo, N. M. Huang, H. N. Lim, *J. Energy Storage* **2021**, *43*, 103304.
[148] W. Zhu, X. Li, Y. Sun, R. Guo, S. Ding, *RSC Adv.* **2019**, *9*, 23390.
[149] X. Feng, H. S. Jena, C. Krishnaraj, K. Leus, G. Wang, H. Chen, C. Jia, P. Van Der Voort, *ACS Appl. Mater. Interfaces* **2021**, *13*, 60715.
[150] M. Thommes, K. Kaneko, A. v Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K. S. W. Sing, *Pure Appl. Chem.* **2015**, *87*, 1051.
[151] S. Mitchell, R. Qin, N. Zheng, J. Pérez-Ramírez, *Nat. Nanotechnol.* **2021**, *16*, 129.
[152] S. Mitchell, A. B. Pinar, J. Kenvin, P. Crivelli, J. Kärger, J. Pérez-Ramírez, *Nat. Commun.* **2015**, *6*, 8633.
[153] G. Férey, *Science* **2001**, *291*, 994.
[154] G. Férey, *J. Solid State Chem.* **2000**, *152*, 37.
[155] G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191.
[156] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040LP.
[157] P. Serra-Crespo, E. v. Ramos-Fernandez, J. Gascon, F. Kapteijn, *Chem. Mater.* **2011**, *23*, 2565.
[158] F. Kapteijn, J. Gascon, E. v. Ramos-Fernandez, J. Juan-Alcañiz, U. Lafont, *J. Catal.* **2009**, *269*, 229.
[159] J. Juan-Alcañiz, M. G. Goesten, E. v. Ramos-Fernandez, J. Gascon, F. Kapteijn, *New J. Chem.* **2012**, *36*, 977.
[160] E. v. Ramos-Fernandez, M. Garcia-Domingos, J. Juan-Alcañiz, J. Gascon, F. Kapteijn, *Appl. Catal., A* **2011**, *391*, 261.
[161] M. Ronda-Lloret, S. Rico-Francés, A. Sepúlveda-Escribano, E. v. Ramos-Fernandez, *Appl. Catal., A* **2018**, *562*, 28.
[162] M. K. Albolkany, C. Liu, Y. Wang, C.-H. Chen, C. Zhu, X. Chen, B. Liu, *Angew. Chem., Int. Ed.* **2021**, *60*, 14601.
[163] K. Jia, J. Ye, G. Zhuang, Z. Zhuang, Y. Yu, *Small* **2019**, *15*, 1805478.
[164] X. Zhai, Y. Fu, *Inorg. Chem.* **2022**, *61*, 6881.
[165] Y. Yoo, H.-K. Jeong, *Chem. Eng. J.* **2012**, *181–182*, 740.
[166] G. Wang, Z. Xu, Z. Chen, W. Niu, Y. Zhou, J. Guo, L. Tan, *Chem. Commun.* **2013**, *49*, 6641.
[167] A. Ahmed, N. Hodgson, M. Barrow, R. Clowes, C. M. Robertson, A. Steiner, P. McKeown, D. Bradshaw, P. Myers, H. Zhang, *J. Mater. Chem. A* **2014**, *2*, 9085.
[168] S. El-Hankari, J. Huo, A. Ahmed, H. Zhang, D. Bradshaw, *J. Mater. Chem. A* **2014**, *2*, 13479.
[169] Y. Kim, T. Yang, G. Yun, M. B. Ghasemian, J. Koo, E. Lee, S. J. Cho, K. Kim, *Angew. Chem., Int. Ed.* **2015**, *54*, 13273.
[170] V. Guillerm, H. Xu, J. Albalad, I. Imaz, D. Maspoch, *J. Am. Chem. Soc.* **2018**, *140*, 15022.
[171] F. Vermoortele, R. Ameloot, L. Alaerts, R. Matthessen, B. Carlier, E. V. R. Fernandez, J. Gascon, F. Kapteijn, D. E. de Vos, *J. Mater. Chem.* **2012**, *22*, 10313.
[172] J. Koo, I.-C. Hwang, X. Yu, S. Saha, Y. Kim, K. Kim, *Chem. Sci.* **2017**, *8*, 6799.
[173] H. v Doan, A. Sartbaeva, J.-C. Eloi, S. A. Davis, V. P. Ting, *Sci. Rep.* **2019**, *9*, 10887.
[174] T. Liu, Y. Liu, L. Yao, W. Yang, L. Tian, H. Liu, D. Liu, C. Wang, *Nanoscale* **2018**, *10*, 13194.
[175] L. H. Wee, T. Lescouet, J. Ethiraj, F. Bonino, R. Vidruk, E. Garrier, D. Packet, S. Bordiga, D. Farrusseng, M. Herskowitz, J. A. Martens, *ChemCatChem* **2013**, *5*, 3562.
[176] Y. Mao, D. Chen, P. Hu, Y. Guo, Y. Ying, W. Ying, X. Peng, *Chemistry* **2015**, *21*, 15127.
[177] Z. Ou, X. Song, W. Huang, X. Jiang, S. Qu, Q. Wang, P. V. Braun, J. S. Moore, X. Li, Q. Chen, *ACS Appl. Mater. Interfaces* **2018**, *10*, 40990.
[178] C. Huang, J. Dong, W. Sun, Z. Xue, J. Ma, L. Zheng, C. Liu, X. Li, K. Zhou, X. Qiao, Q. Song, W. Ma, L. Zhang, Z. Lin, T. Wang, *Nat. Commun.* **2019**, *10*, 2779.
[179] A. Bavykina, A. Cadiau, J. Gascon, *Coord. Chem. Rev.* **2019**, *386*, 85.
[180] N. Giri, M. G. del Pópolo, G. Melaugh, R. L. Greenaway, K. Rätzke, T. Koschine, L. Pison, M. F. C. Gomes, A. I. Cooper, S. L. James, *Nature* **2015**, *527*, 216.

[181] S. He, L. Chen, J. Cui, B. Yuan, H. Wang, F. Wang, Y. Yu, Y. Lee, T. Li, *J. Am. Chem. Soc.* **2019**, *141*, 19708.
[182] A. Knebel, A. Bavykina, S. J. Datta, L. Sundermann, L. Garzon-Tovar, Y. Lebedev, S. Durini, R. Ahmad, S. M. Kozlov, G. Shterk, M. Karunakaran, I. D. Carja, D. Simic, I. Weilert, M. Klüppel, U. Giese, L. Cavallo, M. Rueping, M. Eddaoudi, J. Caro, J. Gascon, *Nat. Mater.* **2020**, *19*, 1346.
[183] D. Poloneeva, S. J. Datta, L. Garzon-Tovar, S. Durini, M. Rueping, M. Eddaoudi, A. Bavykina, J. Gascon, *Acc. Mater. Res.* **2021**, *2*, 1133.
[184] M. Ding, X. Cai, H. L. Jiang, *Chem. Sci.* **2019**, *10*, 10209.
[185] A. Dailly, in *Metal-Organic Frameworks: Applications from Catalysis to Gas Storage* (Ed: D. Farrusseng), Wiley-VCH, Weinheim, Germany **2011**, pp. 151–169.
[186] S. Aguado, D. Farrusseng, in *Metal-Organic Frameworks: Applications from Catalysis to Gas Storage* (Ed: D. Farrusseng), Wiley-VCH, Weinheim, Germany **2011**, pp. 121–149.
[187] G. D. Pirngruber, P. L. Llewellyn, in *Metal-Organic Frameworks: Applications from Catalysis to Gas Storage* (Ed: D. Farrusseng), Wiley-VCH, Weinheim, Germany **2011**, pp. 99–119.
[188] E. Barea, F. Turra, J. A. Rodriguez Navarro, in *Metal-Organic Frameworks: Applications from Catalysis to Gas Storage* (Ed: D. Farrusseng), Wiley-VCH, Weinheim, Germany **2011**, pp. 69–97.
[189] F.-X. Coudert, in *Metal-Organic Frameworks: Applications from Catalysis to Gas Storage* (Ed: D. Farrusseng), Wiley-VCH, Weinheim, Germany **2011**, pp. 49–68.

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