Metal Organic Frameworks

Subjects: Chemistry, Applied

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Metal–organic frameworks (MOFs) are a family of porous crystalline materials that serve in some cases as versatile platforms for catalysis.

heterogenous catalyst metal–organic framework (MOF)

1. Introduction

International Union of Pure and Applied Chemistry (IUPAC) defines MOFs as a coordination network with an open framework containing potential voids [1]. This emerging class of porous coordination polymers are formed by metal ion or cluster nodes and functional organic ligands, all connected through coordination bonds to form 1D, 2D o 3D networks (**Figure 1**) [2][3][4][5][6]. MOFs can be easily obtained by several different synthetic methods, such as electrochemical [7], solvothermal [8] and mechanochemical [9], slow diffusion [10], and more recently also by microwave-assisted heating [11].

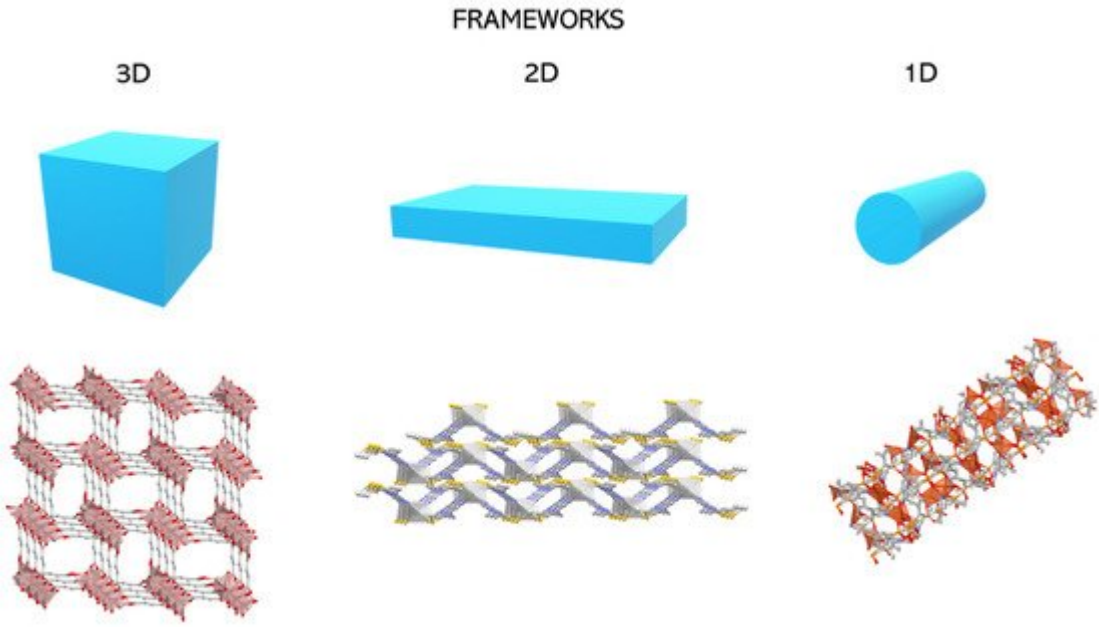

Figure 1. Schematic representation of MOFs frameworks with different dimensionalities (3D, 2D, 1D).

The crystal structures of MOFs can be customized depending on the metal and ligand choice as also on the solvents and reaction conditions employed. [12] Due to the high surface areas [13] and ultrahigh porosity they are

attractive for CH_4, CO_2, and H_2 sorption and storage. Most MOFs have higher volumetric H_2 and CH_4 storage capacities concerning traditional porous materials.

MOFs have been also investigated for their potential applications in biomedicine, for example for drug delivery [14] and biological imaging [15], mainly for the possibility to use biocompatible building blocks. MOFs were employed as electrode materials for supercapacitors using Co-based coordination polymers [16], for magnetic and electronic devices [17], for water harvesting where H_2O is extracted from the air by solar energy [18], and finally also for non-linear optics [19].

The use of MOFs as a catalyst has been widely explored and several applications have been developed, for example in the production of fine chemicals [20], or the definition of possible new green protocols replacing non-eco-friendly catalysts [21]. Differences in activity and selectivity toward specific organic reactions are significantly dependent on the MOFs structure [22]. The main MOFs advantage, when researchers consider their use in catalysis, is in the possibility to design and predict the structural properties based on of linker features, coordination number and geometry of the metal.

The presence of coordinatively unsaturated metal sites, the variety of basic linkers available, the stability to solvents and to reaction conditions, the possibility to host guest molecules within the pores makes MOFs perspective materials for heterogenous catalysis. They have also a lot of advantages concerning other inorganic systems as zeolites and aluminophosphates, i.e., they can be modified using organic synthesis, being possible to decorate their pores with catalytic sites. MOFs can be tailored by a simple change in the initial synthetic conditions or by using post-synthetic reactions. These modifications make MOFs excellent candidates for designing functional materials to allow the attachment of different catalysts [23].

While the characterization of deposited species upon conventional catalyst supports, such as metal oxides, tends to be challenging due to the non-uniform surface and pore structures of the support, the crystalline nature of MOFs enables visualization of the catalytically active species within the framework, which leads to a detailed characterization of active catalytic sites and provides insight into structure−activity relationships.

Epoxides are important species and intermediates in the production of pharmaceuticals, agrochemicals, and relevant industrial chemicals. In the global market, the production of propylene oxide achieves 8 million tons per year with an expected annual increase of 5% [24]. Due to the industrial relevance of catalytic oxidation of olefins to fine chemicals, numerous studies have been devoted to the development of efficient homogeneous [24] and heterogeneous catalysts [24]. However, high selectivity and enantioselectivity in epoxidation reactions remain a challenge. While recovery and product separation are the main drawbacks for homogenous catalysts, MOFs used as heterogeneous catalysts in the oxidation of olefins have attracted significant attention (**Figure 2**) [25].

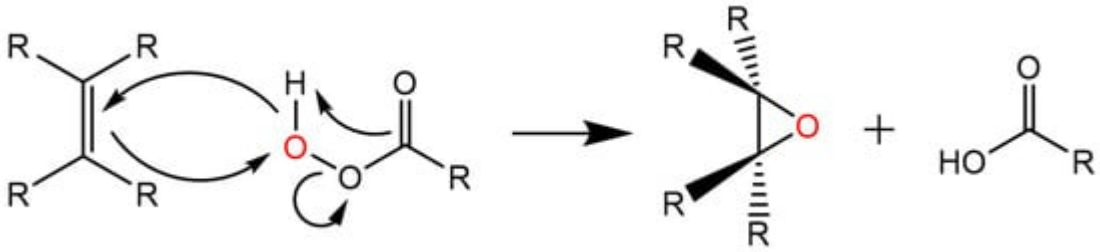

Figure 2. General mechanism of epoxidation of alkenes with peroxycarboxylic acid as co-catalyst.

CO_2 is the primary greenhouse gas in the atmosphere, and it is the cause of environmental and energy-related problems in the world. Nowadays, the development of new methods is fundamental to capture and convert CO_2 into useful chemical products to improve the environment and promote sustainable development. Several studies have been carried out on MOF's efficiency to capture CO_2. The linkers that connect the MOFs metal nodes are the major sites for CO_2 binding. The linkers that connect the MOFs metal nodes are the major sites for CO_2 binding, and they can be chemically modified with functional groups to increase their interaction with CO_2. Moreover, unsaturated metals ions can be introduced in the MOFs structure. A significantly benefit generated from the possibility to have adequate quantities of CO_2 in concentrated form within a MOF is the possible use of CO_2 as a chemical reagent (**Figure 3**).

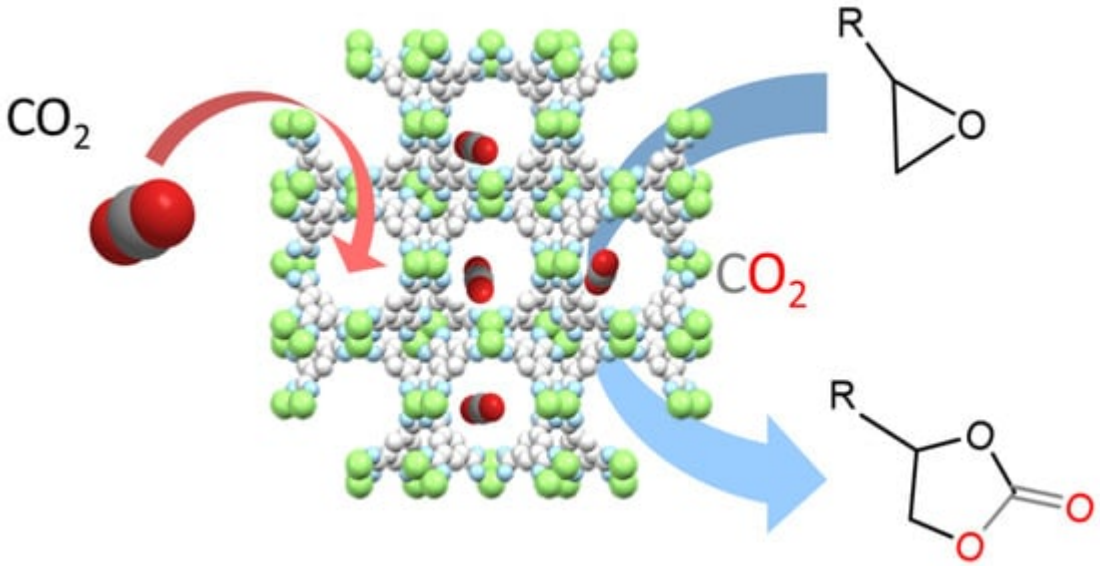

Figure 3. Representation of cycloaddition reaction of CO_2, captured by MOFs, to epoxides.

A significant number of MOFs has been recently reported to catalyse the CO_2 cycloaddition reaction to epoxides to give cyclic organic carbonates (OCs) and several papers describe the potential and effectiveness of MOFs in this important process, so it is necessary to identify better strategies to build new advanced materials as MOFs or MOF-based species to grow selectivity, capacity, and conversion of this catalytic reaction.

2. Epoxidation with MOF-Based Composites

One possible way to improve the chemical and mechanical stability of MOFs as potentially heterogeneous catalysts is their immobilization onto/into supports. In this contest, solid polymer, graphene, and inorganic particles [26] or inorganic polymers [27] are largely employed as supports.

To overcome the poor hydrostability of [Cu_3-BTC_2] [28], a porous dendrimer-like porous silica nanoparticles (DPSNs) has been utilized as a carrier to support Cu-BTC Nps. The nanocomposites DPSNs@Cu-BTC were prepared by growing Cu_2O NPs in the center-radial porous channels of DPSNs. After that, Cu_2O NPs were dissolved in the presence of acid, oxidant and 1,3,5-benzenetricarboxylic acid (H_3BTC) [29]. The obtained Cu-BTC NPs have shown limited growth and a uniform distribution without agglomeration. The small size of Cu-BTC NPs (40 ± 25 nm) is useful in the aerobic epoxidation of various cyclic olefins achieving high catalytic activity without by-products. Good yield and selectivity were detected with inert terminal linear alkenes. Otherwise, epoxidation of styrene only achieved 65% of conversion due to the kinetic instability of styrene oxide [30].

The amphiphilic MIL-101-GH, a porous hierarchical material, has been explored as catalyst for the biphasic epoxidation reaction of 1-octene with H_2O_2. MIL-101-GH hydrogel was obtained by dispersing MIL-101 nanoparticles homogeneously in aqueous graphene oxide (GO) solutions. The TS-1 catalyst, commercially used in this biphasic reaction, was then introduced in MIL-101-GH. The resulting system, MIL-101-GH-TS-1, overcame the lower activity toward olefin epoxidation of TS-1, and the amphiphilic MIL-101-GH increased the contact areas of TS-1 with both H_2O_2 and 1-octene. The catalytic performance of MIL-101-GH-TS-1 has been much higher than that of single TS-1 and the 1,2-epoxyoctane was obtained without other by-products [31].

Polyoxometalate-based (POMs) heterogeneous catalysts are attractive species in the catalytic epoxidation of olefin. They have got great catalytic activity, selectivity, and easy separation but their leaching mainly due to the strong complexing capability of solvent and H_2O_2 oxidants, represents the major obstacle in the possible applications [32][33]. To overcome the stability issue of POMs, the polyoxomolybdic cobalt (CoPMA) and polyoxomolybdic acid (PMA) species were incorporated into UiO-bpy, a Zr-based MOFs, through self-assembly process under solvothermal condition [34]. CoPMA@UiO-bpy showed the highest catalytic activity for cyclooctene oxidation with H_2O_2 and also for the oxidation of styrene and 1-octene with O_2 as oxidant and *tert*-butyl hydroperoxide (t-BuOOH) as initiator. This is due to the uniform distribution and better immobilization of POM clusters within the size-matched cages of Zr-MOFs owing to the presence of bipyridine groups in the UiO-bpy framework. It is noteworthy that CoPMA@UiO-bpy shows excellent recyclability and stability against the leaching of active POM species.

Composite material has been obtained by encapsulating H_5-$PMo_{10}V_2O_{40}$ polyoxometalates (POMs) and 1-octyl-3-methylimidazolium bromide, ionic liquids (ILs), in the mesoporous cages and large surface area of MIL-100 (Fe). The synergic effect of ILs, Lewis and Brønsted acid sites in both $PMo_{10}V_2$ species and MOF created a PMo10V2-ILs@MIL-100(Fe) hybrid with significant catalytic properties in cycloolefins epoxidation. Indeed, the PMo10V2 was activated by the imidazolium cations originated from ILs and the incorporation on MIL-100(Fe) prevented the leaching of POMs [35]. This composite is easily regenerated for 12 cycles without loss catalytic performance [36].

MIL-100(Fe) combined with the polyoxometalate $(C_{16}H_{36}N)_6K_2[\gamma\text{-}SiW_{10}O_{36}]$ has been reported to catalyse epoxidation of 3Z,6Z,9Z-octadecatriene to the corresponding 6,7-epoxide with high site selectivity (82.35%). The conversion catalysed by POM/MIL-100(Fe) exhibits a greater performance when the MOF contains unsaturated Lewis acid iron ions [37]. The main product of this epoxidation is a sex pheromone of *E. obliqua* Prout and can be potentially used in pest insect control with environmental friendliness.

Two POMs-based MOFs, $[Cu_6(bip)_{12}(PMoVI_{12}O_{40})_2(PMoVMoVI_{11}O_{40}O_2)]\cdot 8H_2O$ and $[Co_3^{II}Co_2^{III}(H_2bib)_2(Hbib)_2(PW_9O_{34})_2(H_2O)_6]\cdot 6H_2O$ (H_2bip = 1,3-bis(imidazolyl)propane; bib = 1,4-bis(imidazol)butane)), have been fabricated using a flexible N-containing bidentate ligands via hydrothermal condition. They have been employed in the catalytic processes for selective alkene epoxidation and recycled four times without loss of quality (**Figure 4**) [38].

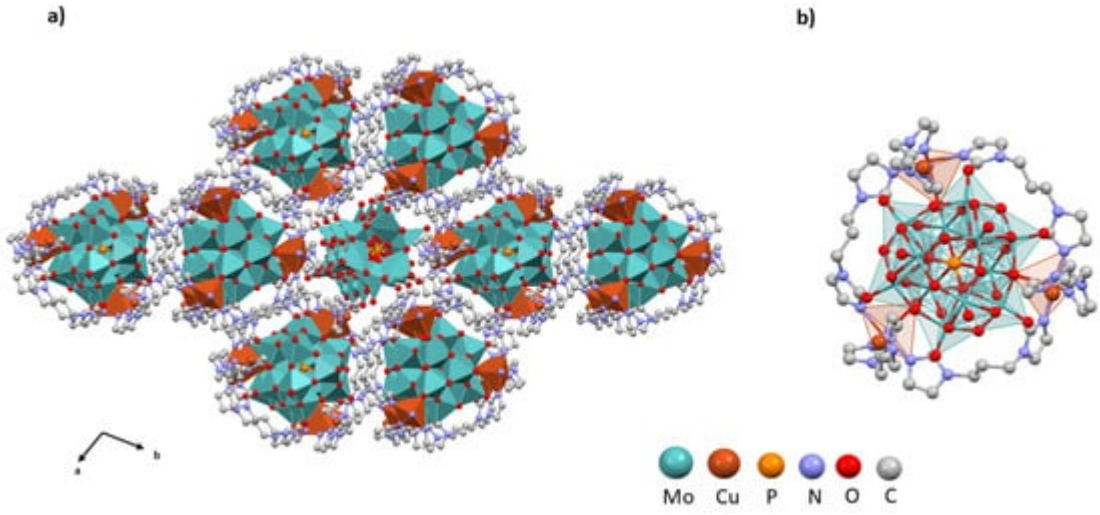

Figure 4. (**a**) The 2D structure of $[Cu_6(bip)_{12}(PMo^{VI}_{12}O_{40})_2(PMo^{V}Mo^{VI}_{11}O_{40}O_2)]\cdot 8H_2O$; (**b**) the coordination environment of the Cu(II) cations. Hydrogens and hydroxyls are omitted for clarity. Light-blue polyhedral correspond to the (PMo_{12}) polyanion.

Metal nanoparticles can grow without agglomeration in a porous matrix to produce a stable and active heterogeneous catalyst. Pd NPs have been loaded on the pre-synthesized UiO-66-NH_2 using a simple solution impregnation method and $NaBH_4$ reduction. The amino groups in the linkers allow a strong interaction with Pd (II) ions which is essential to yielding well-dispersed Pd/UiO-66-NH_2 catalyst. The experiments suggest that the best catalytic activity for styrene epoxidation has been found under Pd NPs loadings of 3.69 wt% [39].

A dually functionalized catalytic system for the tandem H_2O_2-generation/alkene-oxidation reaction has been realized. A microcrystal of UiO-66-NH_2 has been used as a platform to encapsulate Au and Pd metal NPs and later Pd/Au@UiO-66-NH_2 surfaces have been post-synthetically modified with a (sal)Mo^{VI} (sal = salicylaldimine) molecular epoxidation catalyst. The porosity of Pd@UiO-66-sal(Mo) allows H_2 and O_2 gases to come into contact with the encapsulated NPs to generate H_2O_2. The synergic effect of the generated H_2O_2 and (sal)Mo^{VI} in a MOF enhanced epoxide productivity reducing alkene hydrogenation side reaction. This study showed that (sal)Mo

moieties in Pd@UiO-66-NH_2 epoxidize cis-cyclooctene substrate faster, leading to the more effective usage of the H_2O_2 oxidant [40].

Systems composed of a magnetic uniform Fe_3O_4(PAA) microspheres core and of a copper-doped MOF shell demonstrated an easily catalyst recovery approach improving turnover number and turnover frequency. In addition, these magnetic core–shell heterogeneous catalysts improve both stability of the metal active site and dispersity of catalyst materials reducing the metal leaching. Two interesting magnetic core-shell copper-doped catalysts, Fe_3O_4@P4VP@ZIF-8 and Fe_3O_4/Cu_3(BTC)$_2$ have been prepared by combining the solvothermal method with layer-by-layer assembly. Initially, monodispersed PAA-modified Fe_3O_4 particles were synthesized by solvothermal methods [41]. In the case of Fe_3O_4/Cu_3(BTC)$_2$, Fe_3O_4 particles were alternately immersed in solutions containing $Cu(CH_3COO)_2{\cdot}H_2O$ and H_3BTC such that Cu_3(BTC)$_2$ nanocrystals grow layer-by-layer on the surface of PAA-modified Fe_3O_4 particles. This nanosized porous structure increases the contact between the Cu(II) active sites present in the Cu_3(BTC)$_2$ shell and the catalytic substrates [42]. In Fe_3O_4@P4VP@ZIF-8 catalyst, on the other hand, the Fe_3O_4(PAA) core has been coated with P4VP middle layer to adsorb a large number of Zn^{2+} for the growth of the ZIF-8 shell thickness on the surface of the core–shell Fe_3O_4(PAA)@P4VP. Then, the Zn^{2+} ions were partially substituted by Cu^{2+} ions in the ZIF-8 shell framework. The ions exchange allowed a well-dispersed copper active site in the resulting copper-doped ZIF-8 structure, avoiding their leaching [43].

Aerobic epoxidation of cyclic olefins (e.g., cyclohexene, norbornene) using both magnetic core–shell copper-doped Fe_3O_4@P4VP@ZIF-8 and Fe_3O_4/Cu_3(BTC)$_2$ as heterogeneous catalyst achieved high conversion and selectivity (99%) in the formation of the epoxide under mild reaction conditions. Epoxidation of styrene by using Fe_3O_4@P4VP@ZIF-8 as a catalyst has brought only 54% selectivity of the desired epoxide owing to the kinetic instability of styrene oxide and its oxidation into benzaldehyde [44].

A series of Zr-based core-shell MOF composites with mesoporous cores and microporous shells have been synthesized by solvothermal under kinetic control. PCN-222(Fe) crystals have been synthesized and used as seed crystals to grow the Zr-BPDC(UiO-67) crystals. Meso- and micro-porosity inside of PCN-222(Fe)@Zr-BPDC(UiO-67) drives the catalytic performances for olefin epoxidation reaction [45]. Indeed, the core MOF with Fe-porphyrin moieties represents the catalytic center, while the shell controls the selectivity of the substrate through tuneable pore size. This size-selective catalyst showed almost complete conversions for small olefins.

Table 1 MOF-based composites for epoxidation reaction.

MOF	Substrate	Reaction Data T (°C)	P (atm)	Time (h)	Oxidant/Cocatalyst/Solvent	[a]Conversion %	Epoxide Selectivity%	Ref.
DPSNs@Cu-BTC	Cyclooctene	40	1	4	O_2/TMA/CH_3CN	99	99	[29]
	Styrene	40	1	6	O_2/TMA/CH_3CN	62	65	[29]

MOF	Substrate	Reaction Data T (°C)	P (atm)	Time (h)	Oxidant/Cocatalyst/Solvent	[a]Conversion %	Epoxide Selectivity%	Ref.
Fe_3O_4@P4VP@ZIF-8	Cyclohexene Cyclooctene Norbornene	60	1	12	O_2/TMA/CH_3CN	99	99	[44]
$Fe_3O_4/Cu_3(BTC)_2$	Cyclohexene Cyclooctene Norbornene	40	1	6–8	O_2/IBA/CH_3CN	99	99	[42]
	Styrene	40	1	6–8	O_2/IBA/CH_3CN	99	84	[42]
PCN-222(Fe)@Zr-BPDC(UiO-67)	1-Hexene	r.t	1	12	PhIO/-/CH_3CN	99	-	[45]
	Cyclopentene	r.t	1	12	PhIO/-/CH_3CN	99	-	[45]
	Cyclohexene	r.t	1	12	PhIO/-/CH_3CN	99	-	[45]
CoPMA@UiO-bpy	Cyclooctene	70	1	6	H_2O_2/-/CH_3CN	91	99	[34]
	Styrene	80	1	6	O_2/t-BuOOH/-	80	56	[34]
PMo10V2-ILs@MIL-100(Fe)	Cyclohexene	60	1	4	H_2O_2/-/CH_3CN	92	93	[45]
$[Cu_6(bip)_{12}(PMoVI_{12}O_{40})_2(PMoVMoVI_{11}O_{40}O_2)]\cdot 8H_2O$	Cyclooctene	20	1	4	H_2O_2/tBuOH/CH_3CN	>99	74.1	[38]
	1−Hexene	20	1	4	H_2O_2/tBuOH/CH_3CN	>99	91.9	[38]
	1−Octene	20	1	4	H_2O_2/tBuOH/CH_3CN	>99	71.5	[38]
Pd/UiO-66-NH_2	Styrene	80	1	12	N_2/TBHP/CH_3CN	90.8	96.5	[39]
$[Co_3^{II}Co_2^{III}(H_2bib)_2(Hbib)_2(PW_9O_{34})_2(H_2O)_6]\cdot 6H_2O$	Cyclohexene	20	1	4	H_2O_2/tBuOH/CH_3CN	72.9	95.3	[38]
	1−Hexene	20	1	4	H_2O_2/tBuOH/CH_3CN	>99	85.9	[38]
	1−Octene	20	1	4	H_2O_2/tBuOH/CH_3CN	95.5	70.1	[38]
POM/MIL-100(Fe)	3*Z*,6*Z*,9*Z*-Octadecatriene	40	1	24	H_2O_2/-/CH_3CN	30	82	[37]
MIL-101-GH-TS-1	Octane	40	1	12	H_2O_2 (30%)/-/-	15	-	[31]
Pd@UiO-66-sal(Mo)	*cis*-Cyclooctene	r.t	1	6	H_2O_2/CH_3OH/H_2O	-	-	[40]

polymers (IUPAC Recommendations 2013). Pure Appl. Chem. 2013, 85, 1715–1724.

2. Furukawa, H.; Cordova, K.E.; O'Keeffe, M.; Yaghi, O.M. The Chemistry and Applications of Metal-Organic Frameworks. Science 2013, 341, 1230444.
3. Pettinari, C.; Marchetti, F.; Mosca, N.; Drozdov, A. Application of metal-organic frameworks. Polym. Int. 2017, 66, 93.
4. Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. Nat. Cell Biol. 1999, 402, 276–279.
5. Schaus, S.E.; Brandes, B.D.; Larrow, J.F.; Tokunaga, M.; Hansen, K.B.; Gould, A.E.; Furrow, M.E.; Jacobsen, E.N. Highly Selective Hydrolytic Kinetic Resolution of Terminal Epoxides Catalyzed by Chiral (salen)CoIII Complexes. Practical Synthesis of Enantioenriched Terminal Epoxides and 1,2-Diols. J. Am. Chem. Soc. 2002, 124, 1307.

[a] tBuOH = *tert*-butyl alcohol; TMA = trimethylacetaldehyde; IBA = isobutyraldehyde

3. Conclusion

MOF-based catalysts are now a very promising class of compounds as they merge relevant characteristics of both homogeneous and heterogeneous catalysts. They can be easily modified by changing linkers substituents to increase affinity for reactants, or by growing the number of active catalytic sites.

In this entry, researchers have explored the ability of MOFs, MOF nanocomposites and mixed metal species toward olefin epoxidation and carbon dioxide cycloaddition.

Researchers have observed that the olefin conversion and the epoxide selectivity are strongly dependent on the metal nodes/clusters, Co and Cu species being the most efficient, in some cases as for the epoxidation of a-pinene by Co-MOF-150-2 a conversion and an epoxide selectivity close to 100% being found.

Mixed metal MOFs can be also successfully employed in styrene and cyclohexene epoxidation, the best results being obtained with Cu/Co, Mn/Cu, and Ni/V species.

Selected functional groups introduced in organic linkers can also act as catalytically active sites. Amino, pyridyl, amide and sulfonic acid groups, but also metalloporphyrins, vanadium, and molybdenum acetylacetonate, tartaric acid, salen, and analogous molecules can be inserted or deposited to obtain also greater selectivity. UiO-66, UiO67, and PCN-224, appropriately functionalized can induce a complete conversion and selectivity as in the case of the geraniol epoxidation.

MOF-based composites are often employed to increase the hydrostability of selected MOFs or to perform epoxidation also of specific substrates as norbornene or octadecatriene. Specifically, a porous dendrimer-like DPSNs (Porous Silica Nanoparticles) used as a carrier to support Cu-BTC Nps overcame the poor hydrostability of [Cu_3-BTC_2] MOF achieving high catalytic activity without by-products under mild reaction conditions.

Finally, MOFs and MOF-based composites show a great efficiency toward CO_2 cycloaddition to epoxides, conversion being generally in the range 70-100% and selectivity close to 100%. The use of chiral ligands and amine-functionalized ligands seems to be very promising. The CO_2 binding mode can in fact open new strategies for activation of CO_2 and its transformation.

However, the low reactivity and inert nature of CO_2 make its incorporation and activation into organic substrates still a challenge. Currently, the heterogeneous MOFs-based catalysts, as well as the technical system, remain at the laboratory scale and that makes the costs of productions of these materials extremely pricey. It is desirable that the improvement of MOFs-based catalysts might lead to technically viable efficiencies to industrial production to allow their large-scale application, in the next future. This entry clearly shows that MOFs are now perspective materials and valid candidates for catalytic epoxidation and CO_2 cycloaddition reactions.

6. Stock, N.; Biswas, S. Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. Chem. Rev. 2011, 112, 933.
7. Campagnol, N.; Souza, E.R.; De Vos, D.E.; Binnemans, K.; Fransaer, J. Luminescent terbium-containing metal–organic framework films: New approaches for the electrochemical synthesis and application as detectors for explosives. Chem. Commun. 2014, 50, 12545–12547.
8. Zhang, Y.; Bo, X.; Nsabimana, A.; Han, C.; Li, M.; Guo, L. Electrocatalytically active cobalt-based metal–organic framework with incorporated macroporous carbon composite for electrochemical applications. J. Mater. Chem. A 2014, 3, 732.
9. Masoomi, M.Y.; Morsali, A.; Junk, P.C. Rapid mechanochemical synthesis of two new Cd(ii)-based metal–organic frameworks with high removal efficiency of Congo red. CrystEngComm 2014, 17, 686.
10. Wu, J.-Y.; Chao, T.-C.; Zhong, M.-S. Influence of Counteranions on the Structural Modulation of Silver–Di(3-pyridylmethyl)amine Coordination Polymers. Cryst. Growth Des. 2013, 13, 2953.
11. Khan, N.A.; Jhung, S.H. Synthesis of metal-organic frameworks (MOFs) with microwave or ultrasound: Rapid reaction, phase-selectivity, and size reduction. Coord. Chem. Rev. 2015, 285, 11.
12. Maurin, G.; Serre, C.; Cooper, A.; Férey, G. The new age of MOFs and of their porous-related solids. Chem. Soc. Rev. 2017, 46, 3104–3107.
13. Murray, L.J.; Mircea, D.; Long, R.J. Hydrogen storage in metal-organic frameworks. Chem. Soc. Rev. 2009, 38, 1294–1314.
14. Sun, Y.; Zheng, L.; Yang, Y.; Qian, X.; Fu, T.; Li, X.; Yang, Z.; Yan, H.; Cui, C.; Tan, W. Metal–Organic Framework Nanocarriers for Drug Delivery in Biomedical Applications. Nano-Micro Lett. 2020, 12, 103.
15. Wang, H.-S. Metal-organic frameworks for biosensing and bioimaging applications. Coord. Chem. Rev. 2017, 349, 139–155.
16. Gao, X.; Dong, Y.; Li, S.; Zhou, J.; Wang, L.; Wang, B. MOFs and COFs for Batteries and Supercapacitors. Electrochem. Energy Rev. 2019, 3, 81–126.
17. Stavila, V.; Talin, A.A.; Allendorf, M.D. MOF-based electronic and opto-electronic devices. Chem. Soc. Rev. 2014, 43, 5994.
18. Xu, W.; Yaghi, O.M. Metal–Organic Frameworks for Water Harvesting from Air, Anywhere, Anytime. ACS Central Sci. 2020, 6, 1348–1354.
19. Zhang, L.; Li, H.; He, H.; Yang, Y.; Cui, Y.; Qian, G. Structural Variation and Switchable Nonlinear Optical Behavior of Metal–Organic Frameworks. Small 2021, 17, 2006649.

20. Dhakshinamoorthy, A.; Opanasenko, M.; Čejka, J.; Garcia, H. Metal organic frameworks as heterogeneous catalysts for the production of fine chemicals. Catal. Sci. Technol. 2013, 3, 2509–2540.
21. Vanesa, C.-C.; Rosa, M.M.-A. Advances in Metal-Organic Frameworks for Heterogeneous Catalysis. Recent Pat. Chem. Eng. 2011, 4, 1–16.
22. Farrusseng, D.; Aguado, S.; Pinel, C. Metal-Organic Frameworks: Opportunities for Catalysis. Angew. Chem. Int. Ed. 2009, 48, 7502–7513.
23. Chen, Y.; Ma, S. Biomimetic catalysis of metal–organic frameworks. Dalt. Trans. 2016, 45, 9744–9753.
24. Corma, A.; García, H. Lewis Acids as Catalysts in Oxidation Reactions: From Homogeneous to Heterogeneous Systems. Chem. Rev. 2002, 102, 3837–3892.
25. Kravchenko, D.E.; Tyablikov, I.A.; Kots, P.A.; Kolozhvari, B.A.; Fedosov, D.A.; Ivanova, I.I. Olefin Epoxidation over Metal-Organic Frameworks Modified with Transition Metals. Pet. Chem. 2019, 58, 1255–1262.
26. Martínez, H.; Cáceres, M.F.; Martínez, F.; Páez-Mozo, E.A.; Valange, S.; Castellanos, N.J.; Molina, D.; Barrault, J.; Arzoumanian, H. Photo-epoxidation of cyclohexene, cyclooctene and 1-octene with molecular oxygen catalyzed by dichloro dioxo-(4,4′-dicarboxylato-2,2′-bipyridine) molybdenum(VI) grafted on mesoporous TiO2. J. Mol. Catal. A Chem. 2016, 423, 248–255.
27. Portillo, A.S.; Navalón, S.; Cirujano, F.G.; I Xamena, F.X.L.; Alvaro, M.; Garcia, H. MIL-101 as Reusable Solid Catalyst for Autoxidation of Benzylic Hydrocarbons in the Absence of Additional Oxidizing Reagents. ACS Catal. 2015, 5, 3216–3224.
28. Kou, J.; Sun, L.-B. Fabrication of Metal–Organic Frameworks inside Silica Nanopores with Significantly Enhanced Hydrostability and Catalytic Activity. ACS Appl. Mater. Interfaces 2018, 10, 12051–12059.
29. Zhou, Z.; Li, X.; Wang, Y.; Luan, Y.; Li, X.; Du, X. Growth of Cu-BTC MOFs on dendrimer-like porous silica nanospheres for the catalytic aerobic epoxidation of olefins. New J. Chem. 2020, 44, 14350–14357.
30. Zhao, J.; Wang, W.; Tang, H.; Ramella, D.; Luan, Y. Modification of Cu2+ into Zr-based metal–organic framework (MOF) with carboxylic units as an efficient heterogeneous catalyst for aerobic epoxidation of olefins. Mol. Catal. 2018, 456, 57–64.
31. Wu, Y.; Wang, H.; Guo, S.; Zeng, Y.; Ding, M. MOFs-induced high-amphiphilicity in hierarchical 3D reduced graphene oxide-based hydrogel. Appl. Surf. Sci. 2021, 540, 148303.
32. Canioni, R.; Roch-Marchal, C.; Sécheresse, F.; Horcajada, P.; Serre, C.; Hardi-Dan, M.; Férey, G.; Grenèche, J.-M.; Lefebvre, F.; Chang, J.-S.; et al. Stable polyoxometalate insertion within the

mesoporous metal organic framework MIL-100(Fe). J. Mater. Chem. 2011, 21, 1226–1233.

33. Wang, S.-S.; Yang, G.-Y. Recent Advances in Polyoxometalate-Catalyzed Reactions. Chem. Rev. 2015, 115, 4893–4962.
34. Song, X.; Hu, D.; Yang, X.; Zhang, H.; Zhang, W.; Li, J.; Jia, M.; Yu, J. Polyoxomolybdic Cobalt Encapsulated within Zr-Based Metal–Organic Frameworks as Efficient Heterogeneous Catalysts for Olefins Epoxidation. ACS Sustain. Chem. Eng. 2019, 7, 3624–3631.
35. Villabrille, P.; Romanelli, G.; Gassa, L.; Vazquez, P.; Caceres, C. Synthesis and characterization of Fe- and Cu-doped molybdovanadophosphoric acids and their application in catalytic oxidation. Appl. Catal. A Gen. 2007, 324, 69–76.
36. Jin, M.; Niu, Q.; Liu, G.; Lv, Z.; Si, C.; Guo, H. Encapsulation of ionic liquids into POMs-based metal–organic frameworks: Screening of catalysts for efficient cycloolefins epoxidation. J. Mater. Sci. 2020, 55, 8199–8210.
37. Ke, F.; Guo, F.; Yu, J.; Yang, Y.; He, Y.; Chang, L.; Wan, X. Highly Site-Selective Epoxidation of Polyene Catalyzed by Metal–Organic Frameworks Assisted by Polyoxometalate. J. Inorg. Organomet. Polym. Mater. 2017, 27, 843–849.
38. Li, N.; Mu, B.; Lv, L.; Huang, R. Assembly of new polyoxometalate–templated metal–organic frameworks based on flexible ligands. J. Solid State Chem. 2015, 226, 88–93.
39. Zhang, Y.; Li, Y.-X.; Liu, L.; Han, Z.-B. Palladium nanoparticles supported on UiO-66-NH2 as heterogeneous catalyst for epoxidation of styrene. Inorg. Chem. Commun. 2019, 100, 51–55.
40. Limvorapitux, R.; Chou, L.-Y.; Young, A.P.; Tsung, C.-K.; Nguyen, S.T. Coupling Molecular and Nanoparticle Catalysts on Single Metal–Organic Framework Microcrystals for the Tandem Reaction of H2O2 Generation and Selective Alkene Oxidation. ACS Catal. 2017, 7, 6691–6698.
41. Jin, T.; Yang, Q.; Meng, C.; Xu, J.; Liu, H.; Hu, J.; Ling, H. Promoting desulfurization capacity and separation efficiency simultaneously by the novel magnetic Fe3O4@ RSC Adv. 2014, 4, 41902–41909.
42. Li, J.; Gao, H.; Tan, L.; Luan, Y.; Yang, M. Superparamagnetic Core-Shell Metal-Organic Framework Fe3O4/Cu3(btc)2Microspheres and Their Catalytic Activity in the Aerobic Oxidation of Alcohols and Olefins. Eur. J. Inorg. Chem. 2016, 2016, 4906–4912.
43. Hou, J.; Luan, Y.; Yu, J.; Qi, Y.; Wang, G.; Lu, Y. Fabrication of hierarchical composite microspheres of copper-doped Fe3O4@ and their application in aerobic oxidation. New J. Chem. 2016, 40, 10127–10135.
44. Qi, Y.; Luan, Y.; Yu, J.; Peng, X.; Wang, G. Nanoscaled Copper Metal-Organic Framework (MOF) Based on Carboxylate Ligands as an Efficient Heterogeneous Catalyst for Aerobic Epoxidation of Olefins and Oxidation of Benzylic and Allylic Alcohols. Chem. A Eur. J. 2015, 21, 1589–1597.

45. Yang, X.; Yuan, S.; Zou, L.; Drake, H.; Zhang, Y.; Qin, J.; Alsalme, A.; Zhou, H.C. One-Step Synthesis of Hybrid Core–Shell Metal–Organic Frameworks. Angew. Chem. 2018, 130, 3991–3996.