

Metal-Organic Frameworks as selective or chiral oxidation catalysts

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Abstract: Since the discovery of Metal Organic Frameworks (MOFs) in the early 1990, the amount of new structures has grown exponentially. A MOF typically consists of inorganic nodes that are connected by organic linkers to form crystalline, highly porous structures. MOFs have attracted a lot of attention lately, as the versatile design of such materials holds promises of interesting applications in various fields. In this review, we will focus on the use of MOFs as heterogeneous oxidation catalysts. MOFs are very promising candidates to replace homogeneous catalysts by sustainable and stable heterogeneous catalysts.

The catalytic active function can be either the active metal sites of the MOF itself or can be introduced as an extra functionality in the linker, a dopant or a “ship-in-a-bottle” complex. As the pore size, pore shape and functionality of MOFs can be designed in numerous ways, shape selectivity and even chiral selectivity can be created. In this review, we will present an overview on the state of the art of the use of MOFs as a heterogeneous catalyst in liquid phase oxidation reactions.

Keywords: Chiral, enantioselective, encapsulation, heterogeneous catalysis, Metal-Organic Frameworks, oxidation

1. Introduction

Selective catalytic oxidation and asymmetric catalytic oxidations are of industrial importance for fine chemical syntheses. A lot of homogeneous catalysts, which generally consist of metal centers surrounded by a variety of ligands, are still employed in many industrial processes. By varying the metal center and the surrounding ligands of these homogeneous catalysts, the chemo-, regio- and stereo-selectivity can be tuned. Although homogeneous catalysts have the advantage that the reagents can easily approach the catalytically active sites, the separation of the catalyst and products can be cumbersome and expensive. Furthermore, volatile solvents need to be used to recover the catalyst from the reaction mixture. For the design of a heterogeneous variant, several factors need to be taken into consideration. Obviously, the big advantage of a solid catalyst originates in the ease of separation and its recyclability. Nevertheless, for the design of a competitive heterogeneous catalyst, high diffusion dynamics, well-isolated active sites, no-leaching and the possibility of a versatile modification of the catalyst should also be taken into consideration.

So far the most often utilized solid catalysts for oxidation reactions are metals, metal oxides or metal complexes immobilized on zeolites, silica, alumina or polymeric resins¹. Based on the interaction between the catalyst and the solid support, four common methods for the immobilization of homogeneous catalysts can be identified: covalent binding, electrostatic interaction, adsorption and encapsulation. These heterogeneous systems have some well documented disadvantages: (1) the poor dispersion of the (transition) metal oxides on the support, often coalescing to form crystals on the surface and (2) the weak metal-to-support bonding, which result in a significant leaching of the active metal species into the solution².

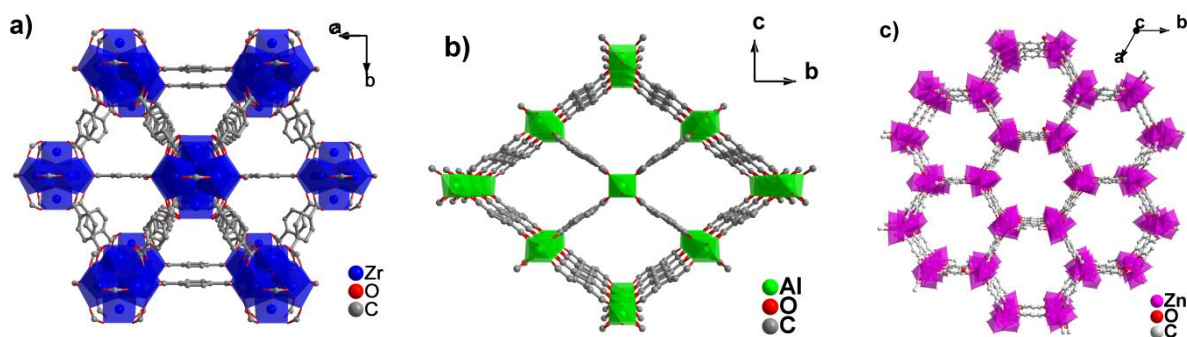


Figure 1 . Examples of MOFs with different shapes of pores and channels a) UiO-66³, b) MIL-53⁴, c) MOF-74⁵.

Metal Organic Frameworks (MOFs) are 3D crystalline atomically ordered materials, with an almost unlimited choice of building bricks, allowing a very precise control over morphology, pore size and functionalities in the walls^{6,7}. In Figure 1, some MOFs structures with different shapes of pores and channels are illustrated. The crystalline nature of MOFs and high geometric regularity allows a full characterization and therefore a thorough understanding of their behavior is possible. MOFs have typically large surface areas with almost no limitations to the surface areas and pore size (so far the maximum pore aperture is 98Å, surface area extending beyond 7000 m²/g)⁸. Moreover, MOFs are highly designable due to the chemical versatility and the secondary building blocks that helps to build up the framework⁹. Due to their attractive properties, many research groups started to explore these materials for several applications. Especially gas storage, gas separation and heterogeneous catalysis are research themes that are quickly emerging¹⁰.

Research groups are now starting to fully realize the potential of MOFs as heterogeneous catalysts. They have been successfully used as catalysts in hydrogenation and oxidation reactions¹¹ enantioselective reactions,¹² photo catalysis,¹³ and hydrosulfurization¹⁴. The highly tunable structure allows the MOF to act both as heterogeneous catalyst and as solid support. MOFs with unsaturated metal centers can be directly used as heterogeneous catalyst. For example, MIL-101¹⁵(Fe, Cr, Al) (MIL stands for Matériaux de l'Institut Lavoisier) and HKUST-1(Cu)¹⁶ (HKUST stands for The Hong Kong University of Science & Technology), which both contain unsaturated metal centers at the nodes of the framework have shown good catalytic activity in a wide range of reactions¹⁷ (see Figure 2). For non-catalytic active MOFs, catalytic sites can be introduced by pre-/post-synthetic modification¹⁸. By using the “ship-in-bottle” approach, catalytically active metal complexes, polyoxometallic clusters or nanoparticles can be encapsulated inside the MOF cavities^{17a,19}. Furthermore, by pre-/post-synthetic modification on the organic linker, complementary catalytic activity can be introduced²⁰. With all these

efforts, MOF materials can, in principle, combine different catalytic functions in which the unsaturated metal centers can provide Brönsted or Lewis acidity and basicity, or redox active centers. The fine-tunable cavity size (from microporous to mesoporous) permits shape selectivity by avoiding the formation of undesired intermediates or product.

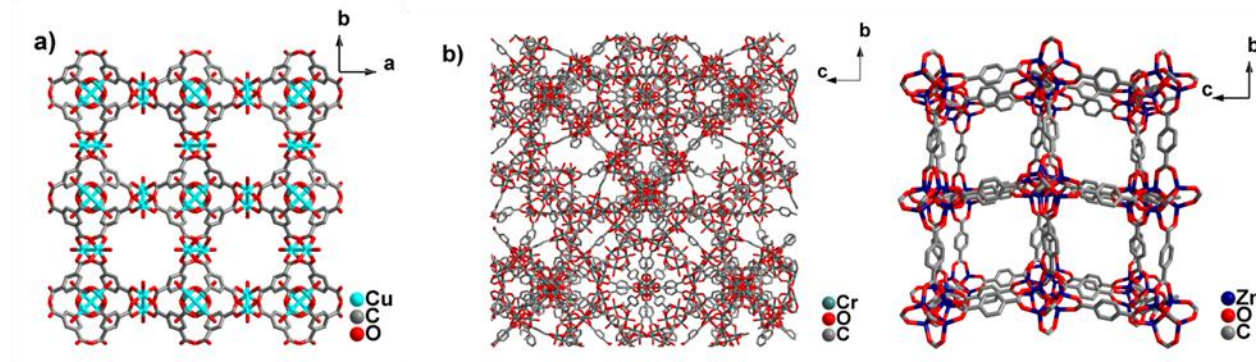


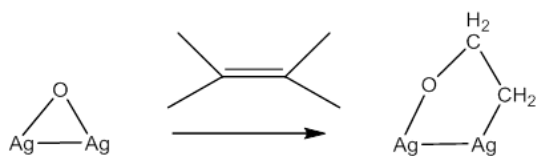
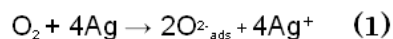
Figure 2. some examples of MOFs used as catalysts for selective oxidations reactions: a) HKUST-1¹⁶, b) MIL-101¹⁵, c) MOF-5 (IRMOF-1)^{7a}.

Despite of their unique features, MOFs also possess some limitations which restrict their use in heterogeneous catalysis. MOFs have a limited thermal and chemical stability (the majority cannot survive temperatures higher than 350 °C) and MOFs have shown to hold a limited stability towards water and moisture. A few MOFs however are very stable in moist atmosphere and water, the most important topologies are UiO-66 (Zr) and MIL-100/MIL-101 (especially the Cr-variants).

The use of MOFs as heterogeneous catalysts in a very broad field has been covered in several reviews in the range of 2009~2011^{14,21}. In 2011, the group of Garcia²² has selectively summarized the use of MOFs as heterogeneous catalysts in oxidation reactions employing hydroperoxides or dioxygen. Very recently, the same group published a mini-review on the use of MOFs as heterogeneous catalysts for the production of fine chemicals²³. In this present review we want to present a comprehensive overview of metal-organic frameworks for selective and chiral oxidation catalysis. We will provide empirical formulas as simplified representations of the MOF structures since considerable information is usually required to well describe the structure, meanwhile the reader is referred each time to the original publication for a better understanding of the structure. Firstly the different oxidants will be described as each oxidant will lead to different reaction pathways. Secondly an overview of the reported MOFs in catalyzing different types of oxidation reactions will be presented.

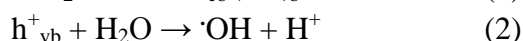
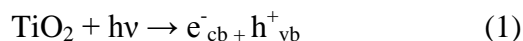
2.1 Oxidation in the presence of pure O₂ and/or H₂O

Clearly gaseous O₂, often referred to as molecular oxygen or dioxygen, is the most desired oxidant due to its availability and low cost. The most known catalytic system that can use molecular oxygen directly and efficiently is bulk silver²⁴. This is achieved by dissociative adsorption into atomic oxygen species (Scheme 1), which will give rise to selective epoxidation products.



Scheme 1. Oxametallacycle mechanism for Ag catalysts, adapted from ref²⁴.

By illumination of semi-conductors by an artificial or natural light in water (=photo catalysis), highly oxidizing OH^\cdot radicals can be created, which can be good oxidants. In Scheme 2, the basic mechanism of photo catalysis is shown for TiO_2 . Many efforts have been devoted to clarify the oxidizing species generated at the irradiated TiO_2 surface. Oxidizing species, which have been suggested, include holes, $\cdot\text{OH}$ and O_2^\cdot radicals, among others²⁵. In first instance, in the basic process of photo catalysis, an electron is ejected from the valence band (VB) to the conduction band (CB) of the TiO_2 semiconductor, creating a h^+ hole in the valence band (eq. 1 Scheme 2) due to UV irradiation of TiO_2 with an energy equal or superior to the band gap. This is followed by formation of extremely reactive radicals (like $\cdot\text{OH}$) and direct oxidation of the organic reactant. Furthermore, the ejected electrons react with electron acceptors such as molecular oxygen, which is dissolved in water (eq. 3 Scheme2)²⁶. These can in turn be oxidizing species.



Scheme 2. Basic process of photo catalysis²⁶.

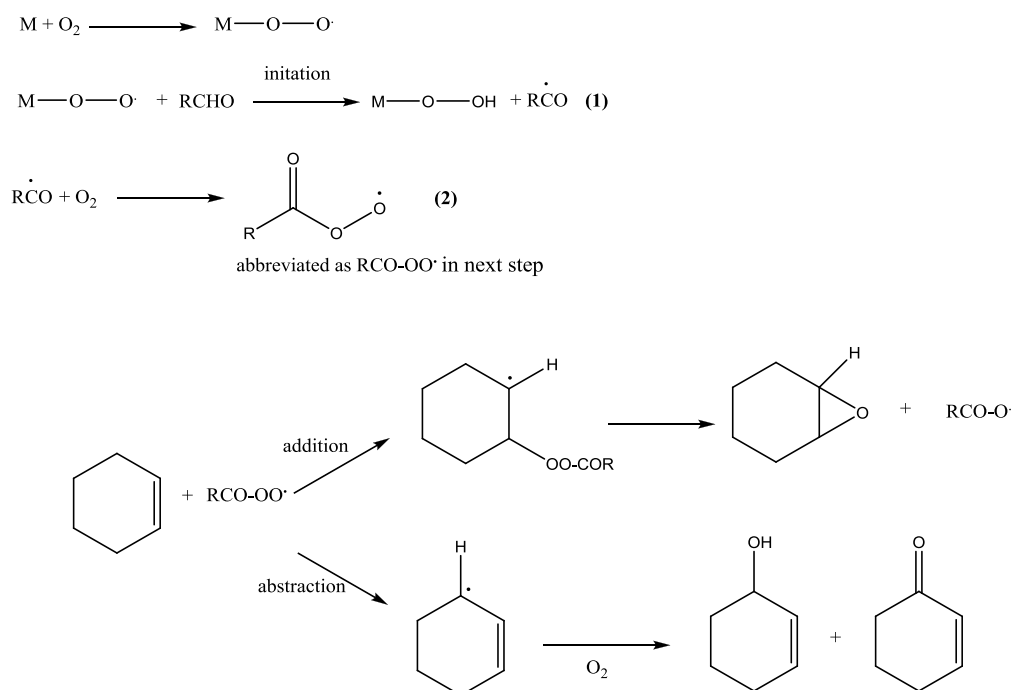
2.2 Oxidation in the presence of O_2 and aldehyde

The oxidation of alkenes in the presence of an aldehyde and O_2 appears to proceed via a mechanism related to aldehyde autoxidation, as can be seen in Scheme 3. In other words, the aldehyde plays a sacrificial role and undergoes co-oxidation (see eq.1 and 2 Scheme 3). From literature, it is concluded that the predominant oxidizing species is an acylperoxy radical (see eq. 2 Scheme 3)²⁷. These radicals are known to preferentially react with the double bonds of alkenes yielding epoxides, whereas hydroxyl and alkylperoxy radicals tend to abstract allylic hydrogens, resulting in allylic oxidation products.

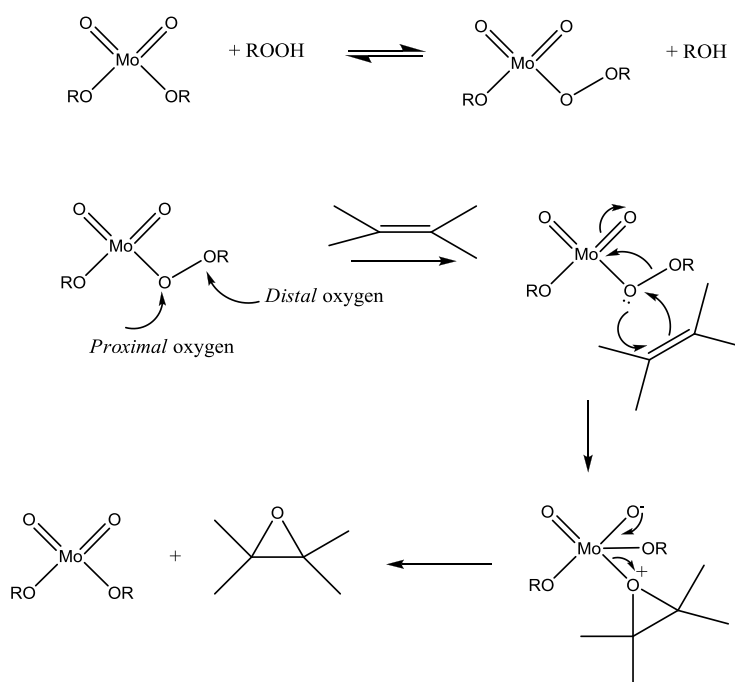
2.3 Oxidation in the presence of hydrogen peroxide or organic peroxides

In most catalytic systems the oxygen needs to be activated in some form. Examples of products of direct activation are hydrogen peroxide or organic peroxides like *tert*-Butyl hydroperoxide (TBHP), which retain the O-O bond. Hydrogen peroxide is an environmental friendly oxidant because the only by-product is water. It is, however, very hazardous to handle. In Scheme 4 an epoxidation mechanism is shown for a Mo based catalyst in the presence of H_2O_2 . Early transition metal ions in their highest oxidation state, such as Ti(IV), V(V), W(VI) and Mo(VI), tend to be stable toward changes in their oxidation state.

Consequently, in epoxidation reactions with H_2O_2 or alkylhydroperoxides, they form adducts (M-OOH and M-OOR). These adducts are the key intermediates in the epoxidation, and the role of the metal ion is that of a Lewis acid. The metal center acts as a Lewis acid by removing charge from the O-O bond, facilitating its dissociation, and activating the nearest oxygen atom (*proximal* oxygen) for insertion into the olefin double bond, whereas the *distal* oxygen constitutes a good leaving group in the form of -OH or -OR (see Scheme 4)²⁴.



Scheme 3. General mechanism for the oxidation of cyclohexene with O_2 and aldehyde (RCHO) inspired by ref ^{27b}.



Scheme 4. Alkylperoxo mechanism of Mo-catalyzed epoxidation with hydroperoxides adapted from ref. ²⁴.

2.4 Oxidation in the presence of N_2O , iodosyl aromatics and hypochlorite

Other examples of oxidants are N_2O , iodosyl aromatics and hypochlorite, which contain a single oxygen atom in a highly activated state. With these oxidants, a single oxygen atom is transferred to a metal ion to form a high oxidation state metal-oxo species ($\text{M}=\text{O}$), which in turn delivers the same oxygen to the reactant. These single oxygen transfers are seen in certain coordination compounds of Fe, Mn, and Cr, in which the metal undergoes successive oxidation state changes²⁴.

3. MOFs in oxidation catalysis

3.1 Oxidation of cycloalkanes and benzylic compounds

The selective oxidation of saturated hydrocarbons is one of the most challenging and interesting subjects in catalytic chemistry, due to the inertness of the C-H bond and the huge added value of the functionalized products. In particular, the oxidation of cyclohexane towards cyclohexanol or cyclohexanone (KA oil) is a very important industrial process. In conventional industrial methods, the oxidation of cyclohexane is performed by a cobalt-based homogeneous catalyst. In recent years heterogeneous systems have been developed, using either metal nanoparticles or metalloporphyrins²⁸. In an ideal case, these systems can activate molecular oxygen under mild conditions.

Similar reasonings apply to benzylic compounds. A variety of homogeneous and heterogeneous catalysts have been investigated for the oxidation of benzylic compounds (often the relevant oxidation of tetralin to α -tetralone) using environmentally friendly oxidants. A large number of metals (Cr, Mn, Fe, Co, Ni, Cu, Pd) have been tested in homogeneous systems, particularly with the metal coordinated to N-donor ligands, such as porphyrins, phthalocyanines and phenantrolines²⁹.

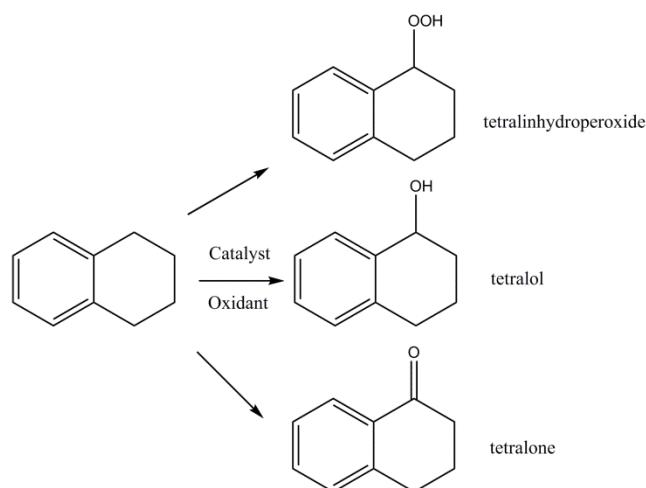
Important progress in this area can be made if MOFs can be developed that contain either immobilized (ship in a bottle) analogues of such complexes or MOFs that actually have such ligands as struts in their structure.

The investigated MOFs for the oxidation of cycloalkanes and/or benzylic compounds are presented in Table 1. Still many reports use TBHP as oxidant (entries 1,3-5,7,13,17 Table 1). However, some studies discuss the oxidation under aerobic conditions (entries 2,6, 9,10, 12,14,15, 18 Table 1) or use H_2O_2 as an oxidant (entry 8,11 Table 1). From Table 1 it can be seen that tetralin is the most commonly used reactant (see Scheme 5).

First of all, Cr-MIL-101 has been evaluated for the oxidation of tetralin using TBHP or molecular oxygen in combination with trimethylacetaldehyde as an oxidant (entry 1 Table 1)³⁰. The use of TBHP afforded higher conversion, whereas higher selectivities toward 1-tetralone were obtained with molecular oxygen (93 vs. 86%). In another study on the oxidation of tetralin, air was applied as the oxidant for the evaluation of the catalytic performance of a Cu and Co MOF (entry 2 Table 1)²⁹. A remarkable difference was detected between both catalysts due to the different catalytic behaviour of the central metal ions. Very recently, quantum chemical calculations were performed on these two MOFs to investigate the decomposition of the hydroperoxide, suggesting that surface catalysis may be dominant³¹.

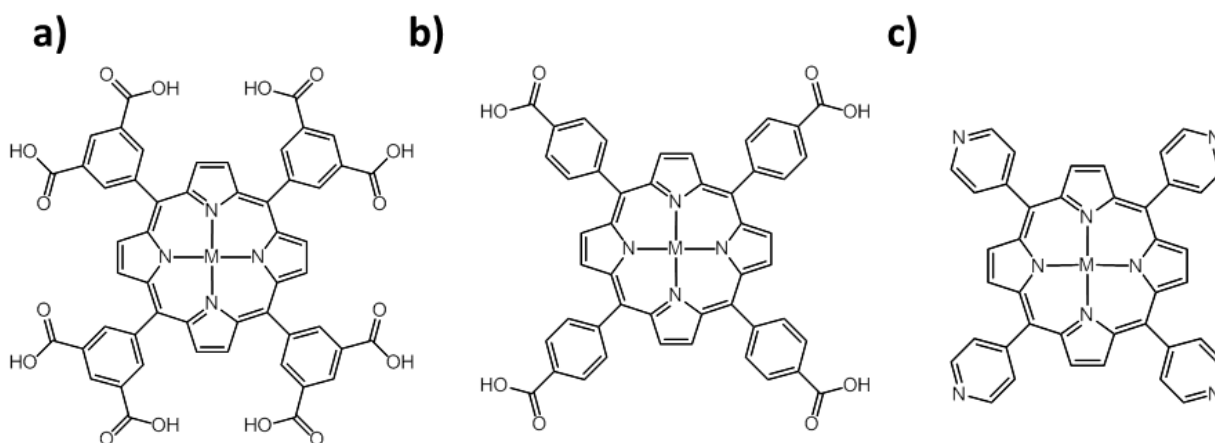
The influence of the metal ion on the oxidation performance was confirmed by the study of Dhakshinamoorthy *et al.*³² (entry 3 Table 1) in which a significant difference in activity between $\text{Fe}(\text{BTC})$, $\text{Cu}_3(\text{BTC})_2$ and $\text{Al}_2(\text{BDC})_2$ was noticed. Furthermore, this report corroborated that the nature of the oxidant plays a crucial role. By means of O_2 and H_2O_2 almost no oxidation of xanthene took place, while TBHP was a good oxidizing reagent in terms of the percentage yield to xanthone. Later

on, these authors examined the influence of the particle size of Fe(BTC) on the oxidation performance. They concluded that for the bulky substrate, triphenylmethane, the average crystal size had a major impact on the activity: the smaller the particle size, the larger the initial reaction rate³³. This evidences that in this case the reactant is unable to enter the pores of the MOFs matrix and the catalytic activity is only on the crystal surface.



Scheme 5. Oxidation of tetralin toward tetralinhydroperoxide, tetralol and tetralone.

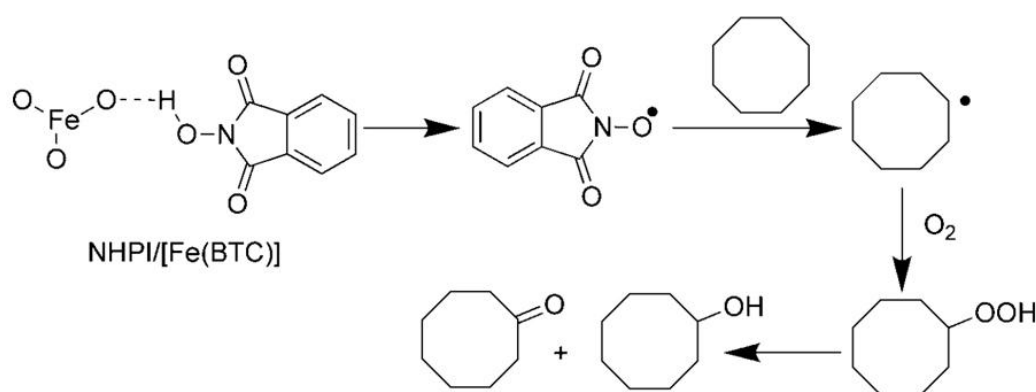
Instead of studying the influence of the metal centers, Wang *et al.*³⁴ studied the influence of the anion exchange on the oxidation of diphenylmethane and tetralin for Cu based MOFs (entry 4 Table 1). As can be observed, a similar conversion of tetralin was obtained for both MOFs, whereas for the oxidation of the larger diphenylmethane a significantly higher conversion was detected for the Cu-MOF-NO₃ in comparison to the Cu-MOF-SiF₆, suggesting a certain size and shape selectivity. The authors stated that the openings of the channels may display a distinct recognition and response to different reactants, so in other words the catalytic activity is controlled by the size of the channels of the Cu-MOFs with the counter anion varying from SiF₆²⁻ to NO₃⁻.



Scheme 6. a) 5,10,15,20-tetrakis(3,5-biscarboxyphenyl)porphyrin metalloligands; b) Tetrakis(4-carboxyphenyl) porphyrin metalloligands (M^{III}-TCPP); c) 5,10,15,20-tetra(4-pyridyl)-porphyrin metalloligands (M^{IV}-TPyP)

Furthermore, some modified MOFs, obtained by the incorporation of species into the framework, were examined for the oxidation of cycloalkanes and/or benzylic compounds. Firstly, 4 POM based MOFs were tested for the oxidation of ethylbenzene (entry 5 Table 1)³⁵. Also, this report demonstrated that the metal center, more specifically the valence of the metal ion in the POM, can significantly influence the activity of the framework.

Secondly, *N*-hydroxyphthalimide (NHPI), a radical initiator, was embedded in Fe(BTC) which was explored for the oxidation of several benzylic compounds and alkanes (see entry 6 Table 1)³⁶. The authors assumed the occurrence of a radical oxidation mechanism with the aid of NHPI and the metal site of the MOF, which is widely known for the auto-oxidation of alkanes (see Scheme 7)³⁷. Besides the oxidation of benzylic compounds and other alkanes, the NHPI@Fe(BTC) was also examined in the aerobic oxidation of benzylamines (entry 10 Table 1). Under mild conditions without the presence of a cosolvent, very good conversions (comparable with supported gold nanoparticles) were obtained³⁸. Later on, the group of Garcia incorporated the same radical initiator in a Co-based MOF matrix (entry 9 Table 1) as it is well known that NHPI in combination with Co²⁺ salts is a strong homogeneous catalyst in oxidation catalysis³⁹. In comparison with their former study, the Co-host exhibited a lower activity but a higher selectivity toward the ol/one was observed at the same substrate conversion^{39b}.



Scheme 7. Proposed mechanism for the oxidation of cyclooctane catalysed by NHPI@Fe(BTC) reproduced with permission from ref ³⁶. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Very interestingly, several porous metalloporphyrinic frameworks have been designed for certain catalytic applications.⁴⁰ For instance, X. L. Yang *et al.*⁴¹ used carboxylate porphyrin metalloligands as the functional ligand (Scheme 6a) to build a series of porous metalloporphyrinic frameworks in *tbo* topology (same topology as HKUST-1, pore window ~11.5 Å, pore cage ~21.3 Å). This open structure allows various substrates to reach the unsaturated metal centers. These metalloporphyrinic catalyst are highly efficient and show selective catalytic activity in the oxidation of alkylbenzenes. The porous catalyst shows substrate-selective properties. C. Zou *et al.*⁴² reported 4 other metalloporphyrinic frameworks build up from M'₂(COO)₄ (M'=Zn or Cd) paddle-wheel subunits bridged by M^{III}-TCPP (M= Fe or Mn) (Scheme 6 b) and formate ligands. Such MOFs show interesting catalytic properties in the selective epoxidation of olefins. The Mn-porphyrinic MOFs show full epoxidation of styrene in CH₂Cl₂ at RT within 6h, while the Fe-porphyrinic MOFs are quickly deactivated by self-oxidation (entry 28, Table 4). They are also active in the oxidation of cyclohexane (20.6% conversion) (entry 19 Table 1).

Recently, Xamena, Corma and co-workers⁴³ reported several MOFs with Cu²⁺ centers linked to four nitrogen atoms from azaheterocyclic compounds. These materials are active catalysts for the aerobic oxidation of activated alkanes. Furthermore, a tandem reaction was designed using Cu-MOF combined with silylated Ti-MCM-41 as solid catalyst, in which Cu-MOF first catalyzed cumene oxidation to form cumene hydroperoxide as major product. Subsequently the intermediate hydroperoxide, together with silylated Ti-MCM-41 further catalyzed 1-octene to obtain 1-octene oxide. However, at high temperature (90 °C) the presence of Cu-MOF will catalyze the oxidation of 1-octene at allylic position. Therefore, to increase the selectivity to the epoxide product, 1-octene and the Cu-MOF were kept in separate reactors.

Finally, the report of Alkordi *et al.*^{19h} described the encapsulation of a Mn-metallated porphyrin complex in an indium-imidazoledicarboxylate based MOF, *rho*-ZMOF (entry 7 Table 1). The resulting catalyst was explored for the oxidation of cyclohexane with TBHP as an oxidant, yielding a conversion of 91.5% after 24 hours of catalysis.

Entry	Catalytic MOF	Reactant	Oxidant	Reaction parameters	Conversion (%)	Main product (selectivity)	Take home message	Ref.
1	Cr-MIL-101	Tetralin	TBHP/ O ₂ +aldehyde	60~100°C, 8h in chlorobenzene	55-73	Tetralone (86-93%)	Solvent and oxidant: influence on activity and selectivity	30
2	[Cu(2-pymo) ₂]	Tetralin	Air	Tetralin/metal molar ratio: 2000, 90°C, air flow:0.5mL/s	52	Tetralinhydroperoxide	No induction period, low selectivity toward ketone	29
	[Co(PhIM) ₂] (ZIF-9)				23	Tetralone	Induction period, high selectivity toward ketone	
3	Fe(BTC) /Cu ₃ (BTC) ₂ / Al ₂ (BDC) ₂	Xanthene	TBHP	70°C, 24 h in CH ₃ CN	42-90	Xanthone (85-99%)	O ₂ and H ₂ O ₂ : inefficient to promote oxidation, Influence of the metal ion on the activity: Fe>Cu>Al	32
	Fe(BTC)	Benzylic compounds (tetralin, cyclooctane,...)		70°C, 24~88h in CH ₃ CN	28-96	Ketone (26-99%)		
4	Cu ^{II} (bped) ₂ (H ₂ O) ₂ (SiF ₆)	Tetralin/ Diphenylmethane	TBHP	60°C, 36 h in CH ₃ CN	88-92	Tetralone (71-77%)/ Benzophenone	Influence of the anion exchange: activity is regulated by the size of the surface openings of Cu-MOFs	34
	Cu ^{II} (bped) ₂ (H ₂ O) ₂ (NO ₃)				28-47			
5	{[Cu ₂ (4,4'-bipy) ₄ (H ₂ O) ₄](SiW ₁₂ O ₄₀)(H ₂ O) ₁₈] _n {[Cu ₂ (4,4'-bipy) ₄ (H ₂ O) ₄](SiW ₁₂ O ₄₀)(4,4'-bipy) ₂ (H ₂ O) ₄] _n {[Cu ₂ (4,4'-bipy) ₄ (H ₂ O) ₄](PW ₁₂ O ₄₀)(H ₂ O) ₁₈] _n {[Cu ₂ (4,4'-bipy) ₄ (H ₂ O) ₄](PMO ₁₂ O ₄₀)(H ₂ O) ₁₈] _n	Ethylbenzene	TBHP	40~70°C, 6~24h in CH ₃ CN, ratio TBHP/substrate= 1~3 70°C, 12 h in CH ₃ CN	37.9-56.8	Acetophenone (80.1-88.1%)	The activity is influenced by the valence of the metal	35
6	NHPI@Fe(BTC)	Benzylic compounds, Linear alkanes	O ₂	120°C, 2~24 h	7-33	Ketone	No solvent, high selectivity toward alcohol and ketone Undergoes desactivation (formation of FeO nanoparticles)	36
7	Mn-porphyrin@rho-ZMOF	Cyclohexane	TBHP	65°C, 24 h	91.5	Cyclohexanone	Stable up to 11 cycles	19h
8	[Cu ₃ (μ ₃ -OH)(μ-pz) ₃ (EtCOO) ₂ (H ₂ O)] [Cu ₃ (μ ₃ -OH)(μ-pz) ₃ (EtCOO) ₂ (EtOH)]	Cyclohexane/ cyclopentane	H ₂ O ₂	RT, 6h in CH ₃ CN+HNO ₃	27.9/25.4 25.6/31.0	Alcohol	In absence of nitric acid: no activity	44
9	NHPI@[Co(DMA) ₆] ₃ [(Co ₄ Cl) ₃ (BTT) ₈ (H ₂ O) ₁₂] ₂ . 12H ₂ O	Cycloalkanes and benzylic compounds	O ₂	120°C, 1~29 h	7-48	Ketone	Higher selectivity toward ol/one compared to former study (entry 16-18)	39b
10	NHPI@Fe(BTC)	Benzylamines	O ₂	100°C, 10~24 h	7-99	Benzylimines	Catalysis under mild and neutral conditions without any cosolvent	38
11	Cu-BTC and Cu-BTC-PyDC	Toluene	H ₂ O ₂	40~80°C, 1~18 h in CH ₃ CN	0.14-4.91	-	High selectivity toward <i>ortho</i> and <i>para</i> product	17c

12	N(FePc ^t Bu ₄) ₂ @MIL-101 FePcF ₁₆ @MIL-101 RuPcF ₁₆ @MIL-101	Tetralin	O ₂	50~130 °C, 6~10bar, 1~24h, solvent free	5100* 24200* 30900*	1-tetralone	Higher activity of the complex@MOF than the homogeneous complex	45
13	Mn ₅ Cl ₂ (Mn ^{III} Cl-OCPP ZJU-18,)	namely Alkylbenzenes	TBHP	65°C 18h in CH ₃ CN	16~>99	Phenyl ketones	ZJU-18 shows highly selective oxidation of ethylbenzene to acetophenone in >99% yield,	41
14	Au-Pd/MIL-101	Toluene	O ₂ (1MPa)	120 °C, solvent free, 48h; substrate/Metal =2200 (Pd: Au molar ratio 1.5:1)	75.6	Benzylbenzoate (93%)	High activity and selectivity are due to the presence of bimetallic nanoparticles(activating O ₂) as well as the lewis acidity of the MOF support(activate the methyl group of toluene). Meanwhile, the Lewis centre inhibits the further oxidation of benzaldehyde to benzoic acid.	46
		Aromatic hydrocarbons(xylene, methoxytoluene, Fluorotoluene)	O ₂ (1MPa)	120 °C, solvent free, 48h; substrate/Metal =3000 (Pd: Au molar ratio 1.5:1)	25.5~45.5	Substituted benzylbenzoate (62~71%)		
15	Al(OH)(bpydc) =MOF-253 (bpydc=2,2'-bipyridine-5,5'-dicarboxylate)	Various alkanes e.g. cyclohexane	O ₂ (1MPa)	150 °C, solvent free, 4h;	59.9	Cyclohexanone (48.1)	MOF-253(Al) can efficiently activate molecular O ₂ at high temperature	47
16	Cu(im) ₂ (im = imidazole) together with silylated Ti-MCM-41	Tandem 1) cumene and 2) 1-octene epoxidation	O ₂ and TBHP	Two pot setup 1) 90 °C, 4h 2) 90 °C 24h	Cumene: 31 Octene 18.1	Cumene hydroperoxide (24%) 1-octene oxide (100%)	To increase the selectivity to the epoxide product, 1-octene and the Cu-MOF was kept at separate reactors	43
17	V-CatBrO MOF	Tetralin	TBHP	50 °C, in chlorobenzene 24h Tetralin: TBHP: catalyst molar ratio 100:100:1	45	Tetralone (~75%)	Vanady(monocatecholate) are incorporated into a dipyridyl struts of a Zn-MOF, providing the unsaturated V centers for catalysis.	48
18	Au/MIL-53(Cr), Au/MIL-101(Cr)	cyclohexane	O ₂ (1.2MPa)	130 °C, 6h, solvent free.	30.5~31.3	Cyclohexanone(81.9%~87.7%)	Both Cr ions from MOF framework and Au nanoparticles act as catalytic sites for the reaction.	49
19	(CH ₃) ₂ NH ₂][Zn ₂ (HCOO) ₂ (Mn ^{III} - TCPP) (H ₆ TCPP= tetrakis(4- carboxyphen yl) porphyrin)	cyclohexane	PhIO (iodosobenzene)	RT, 6h in CH ₂ Cl ₂	20.6%	Cyclohexanone	Catalysis happens on exterior sufaces due to the M ^{III} sites are ligated by formate pillars.	42

*TON value

Table 1 Overview of the MOFs studied for the oxidation of cycloalkanes and/or benzylic compounds.

3.2 Oxidation of alcohols and hydroxylation of phenol

Oxidation of alcohols

The oxidation of alcohols to carbonyl compounds is one of the most fundamental processes in organic synthesis⁵⁰. During the last decade, a number of green heterogeneous catalytic systems have been developed that use molecular oxygen or air as the oxidant⁵¹. These typically employ metal-based heterogeneous catalysts containing ruthenium, gold or platinum. However, many of these systems require harsh reaction conditions and substrate selectivity can be difficult to control. Oxidation reactions at room temperature in appropriate solvents are necessary for alcohols with high melting points or low stability at high temperatures, but examples of these room-temperature reactions are very limited⁵². Oxidation catalysis with MOFs has been particularly productive over the past several years. The majority of these transformations have employed either metal nodes or encapsulated nanoparticles in the MOF as catalysts.

In Table 2 an overview is presented of the MOFs that have been examined for the oxidation of alcohols (including phenol). There is one report of a Pd based MOF, denoted as [Pd(2-pymo)₂]_n, studied for the aerobic oxidation of 3-phenyl-2-propen-1-ol (entry 1 Table 2)⁵³. A complete conversion of the alcohol was observed after a reaction time of 20 h, with a selectivity of 74% toward the cinnamylaldehyde, which is comparable to other palladium-catalyzed oxidation reactions of allylic alcohols⁵³. Furthermore, the research group of Zou^{20b} reported for the first time the post-synthetic coordination of a Ru-complex onto MOF-253⁵⁴ (entry 8 Table 2). The resulting Ru@MOF-253 was examined in the oxidation of a variety of alcohols exhibiting high selectivities for ketones and aldehydes (up to 99%) under mild reaction conditions. This is remarkable, as the selective oxidation of primary alcohols to aldehydes at room temperature with heterogeneous catalysts is still rather limited and represents a challenging area in green chemistry⁵⁵.

Most other studies describe the loading of Au or Pt nanoparticles on a MOF. One report describes the gas-phase deposition of MOF-177 with Pt nanoparticles, denoted as Pt@MOF-177, which was studied for the aerobic oxidation of allylic and aliphatic alcohols at room temperature in a base and solvent-free medium (entry 2 Table 2)⁵⁶. For most reactants very high conversions and selectivities were observed. However, it was not possible to recycle the catalyst. Due to the presence of water (which is a by-product in the oxidation of alcohols), the host framework was destroyed making the Pt particles inaccessible for further reaction⁵⁶.

Also Dhakshinamoorthy *et al.*⁵⁷ applied O₂ as an oxidant to examine the catalytic performance of Cu₃(BTC)₂ in combination with the radical initiator TEMPO as a co-catalyst (entry 3 Table 2). The authors observed a somewhat low reactivity for some substituted benzylic alcohols and other alcohols, which they attributed to the inability of reactants to reach the active sites and to catalyst deactivation by poisoning and/or pore blocking.

All the Au@MOF materials were studied for the oxidation of benzyl alcohol, a typical benchmark reaction. Very different conditions were used in the catalytic tests. Firstly, there is a lot of debate on the question if a base is required. For example, Müller *et al.*⁵⁸ showed that if no base was added to the reaction mixture, the Au@MOF catalysts were inactive whereas in the presence of the base K₂CO₃, the oxidation reaction is accelerated by deprotonation of the alcohol. Nevertheless, in the report of Liu *et al.*⁵⁹ on Au@MIL-101 (entry 7 Table 2), the catalyst already showed a high catalytic performance in

the absence of a base which was the result of a high dispersion of the Au nanoparticles combined with a synergetic effect of the MIL-101 host matrix. It is suggested that the support may play a crucial role, either direct or indirect, in the determination of the activity of gold^{2,60}. The influence of the support is also illustrated in the work of Ishida *et al.*⁶¹ in which large differences in alcohol conversions are observed for the Au@MOF-5, Au@Al-MIL-53 and Au@Cu₃(BTC)₂ (entry 4 Table 2). Also in the work of Esken *et al.*^{21a} (entry 5 Table 2), it was suggested that the Au nanoparticles may chemically interact with the functionalities on the organic linker. They observed a remarkable difference in catalytic activity between Au@ZIF-8, which exhibit a good conversion of 81% benzyl alcohol, whereas the Au@ZIF-90 shows a very weak activity (13%). The latter is due to in situ oxidation of the aldehyde functions of ZIF-90 by means of the Au nanoparticles imbedded in the MOF, making the active Au sites inaccessible for further reaction.^{21a}

Hydroxylation of Phenol

For the hydroxylation of phenol, completely different catalysts are required. Phenol hydroxylation is an oxidation of phenol by hydrogen peroxide to produce two benzenediols: catechol (benzene-1,2-diol) and hydroquinone (benzene-1,4-diol). They can be produced in industrial scales by using homogeneous acid catalysts at 40–90 °C, but the homogeneous catalysts are difficult to separate from the reaction mixture making their recovery and recycling almost impossible⁶².

Several researchers have tried to develop heterogeneous catalysts for phenol hydroxylation. Transition metal oxides such as iron (Fe), copper (Cu) and cobalt (Co) on various support materials have been tested and Fe has been the most widely investigated. When supported on various zeolites including ZSM-5, NaY, MOR, the phenol conversions were less than 40% in all Fe catalysts and only Fe/MOR gave 100% catechol selectivity. This information inferred that the shape and size of pores of the supports influenced the product selectivity⁶³.

Most reports that discuss the hydroxylation of phenol, use H₂O₂ as an oxidant (entry 9-12, Table 2). Some reports discuss the use of a metal-phenanthroline based complex encapsulated in a MOF (entry 10-11, Table 2). Besides the use of a similar homogeneous complex, some other common conclusions can be drawn from these studies⁶⁴. Firstly, almost no activity was observed applying 1-naphthol as substrate. The authors attributed this finding to the large dimensions of the substrate, preventing its diffusion through the framework. Secondly, a remarkably high selectivity toward hydroquinone was noticed which was contrary to the selectivity of the homogeneous catalyst. The authors assumed that the reaction took place in the channels of the framework and concluded a reactant shape selectivity.

Apart from these studies, Bhattacharjee *et al.*⁶⁵ (entry 9, Table 2) examined Fe-MOF-74 in the oxidation of phenol, showing a high selectivity towards catechol (68%) whereas the study of Jian *et al.* (entry 12, Table 2) applied a Cu-MOF which exhibited good selectivity towards benzoquinone. So far, however, the Fe-MOF systems have not yet proven to perform better than the Fe@mordenite zeolitic systems⁶⁶.

It should be noted that many metalloporphyrins present distinct photo catalytic activity in the homogeneous phase, however, investigation of the photo catalytic properties of metalloporphyrin-based MOFs are rare. Xie M.-H. *et al.*⁶⁷ reported a MOF which is constructed from 5,10,15,20-tetra(4-pyridyl)-tin(IV)-porphyrin (Sn^{IV}TPyP) (Scheme 6c) and formate linking up zinc atoms, which presents excellent photo catalytic activities for phenol and sulfide oxygenations (entry 16, Table 3). A selective

photo-oxygenation of 1,5-dihydroxynaphthalene in the presence of a tin(IV)-porphyrin based MOF was performed in the optimized solvent of CH₂Cl₂/MeOH (4:1, v/v). The substrate could be fully oxidized into 5-hydroxynaphthalene-1,4-dione, The high conversion is attributed to CH₂Cl₂ being able to prolong the lifetime of the singlet oxygen(¹O₂) (entry 16, Table 2).

The application of MOFs in photo catalysis is emerging as an interesting topic. However, a lot of MOFs need either the assistance of a sacrificial agent or UV-light as energy source. Recently, several research groups performed a photo catalytic study of an amine-functionalized Zr-MOF, UiO-66-NH₂ (Figure 2d). For instance, J. Long *et al.*⁶⁸ reported that under visible light irradiation, UiO-66-NH₂ catalyzes the aerobic oxidation of alcohols, olefines and cyclic alkanes. In benzyl alcohol, cyclohexanol and hexyl alcohol oxidation catalysis, 100% selectivity is achieved for these substrates (entry 13, Table 2) , but the conversion rate highly depends on the activation energy of α -C-H bonds. The authors also studied the influence of solvents, the result shows that polar organic media play a crucial role in stabilizing the intermediate epoxides and active oxygen species. The mechanism of the photo catalytic process was proposed based on the in-situ EPR characterization, which determine the active intermediates, the O₂⁻ formed during irradiation are adsorbed on Zr³⁺ sites, and can be stabilized in the cavities of UiO-66-NH₂ its interaction with the amine groups and/or organic solvents, which consequently benefits the photo catalytic process.

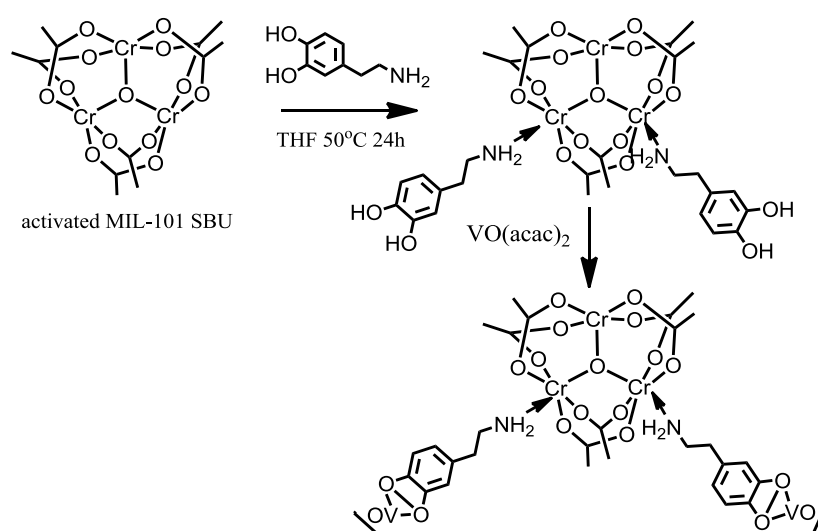
Table 2. Overview of the MOFs investigated for the oxidation of alcohols and hydroxylation of phenol.

Entry	Catalytic MOF	Reactant	Oxidant	Reaction parameters	Conversion (%)	Main product (selectivity)	Take home message	Ref.
1	[Pd(2-pymo) ₂] _n	3-phenyl-2-propen-1-ol	Air	90°C, 20 h in toluene	>99	3-phenylprop-2-enal (74%)	Selectivity similar to Pd based catalysts	53
2	Pt@MOF-177	Allylic and aliphatic alcohols	Air	Solvent- and base-free, RT, 24 h	>99	Ketone or aldehyde	RT, solvent- and base-free conditions, not recyclable	56
3	TEMPO/Cu ₃ (BTC) ₂	Benzyl alcohol	O ₂	40~75 °C, 22~44h in CH ₃ CN+ Na ₂ CO ₃	90	Benzaldehyde (>98%)	Deactivation by poisoning and/or pore blocking	57
4	Au@MOF5 / Au@Al-MIL-53 Au@Cu ₃ (BTC) ₂	Benzyl alcohol and 1-phenylethanol	O ₂	80 °C, 30 min in MeOH+ K ₂ CO ₃ at 5 bar	56-99 70	Methyl benzoate Benzaldehyde	Influence of MOF support on the activity	61, 58
5	Au@ZIF-8 and Au@ZIF-90	Benzyl alcohol	O ₂	80 °C, 24 h in MeOH at 5 bar	13-81	Methyl benzoate (50-98%)	Side reaction: oxidation of functional groups in framework by Au	21a
6	Au/ZnO@MOF-5 and Au/TiO ₂ @MOF-5	Benzyl alcohol	O ₂	80 °C, 30 min in MeOH+ K ₂ CO ₃ at 5 bar	68-74	Methyl benzoate	Au/oxide@MOF-5: higher activity and selectivity than Au@MOF-5	58
7	Au@MIL-101	Benzylic alcohols, allylic alcohols and aliphatic alcohols	O ₂	80 °C, 1 atm, 1~35h in toluene	23-99	Aldehyde or ketone (>99%)	High activity, selectivity, recyclability in absence of base or water	59
8	Ru@MOF-253	Primary/secondary alcohols	PhI(Oac) ₂	22~40°C, 1.5~5 h in CH ₂ Cl ₂	55-99	Ketone or aldehyde	At RT: high conversions and selectivities (>90%)	20b
9	Fe-MOF-74	Phenol	H ₂ O ₂	Mol ratio phenol:H ₂ O ₂ = 1:0.33~1:1, 1h, 20 °C in H ₂ O	60	Catechol (68%)	Higher conversion to useful products and lower induction period compared to Fe-MCM-41, FeO _x -MCM-41	65
10	[Mn ^{II} (H ₂ O) ₆].[Mn ^{II} (phen) ₂ (H ₂ O) ₂] ₂ .2BTC [Cu ^{II} (H ₂ O) ₆].[Mn ^{II} (phen) ₂ (H ₂ O) ₂] ₂ .2BTC [M ^I (H ₂ O) ₆].[M ^{II} (phen) ₂ (H ₂ O) ₂] ₂ (BTC) ₂ with M ^I , M ^{II} : Co(II), Ni(II), Cu(II), Zn(II), Mn(II)	Phenol	H ₂ O ₂	25~35°C, 9~12h in EtOH	14-21	Hydroquinone	The encapsulated Mn complex is responsible for the activity, no activity of the host	64a,b
11	[Co(phen) ₂ (H ₂ O) ₂] ₂ [M(H ₂ O) ₆] ₂ .2BTC (M=Co, Cu, Mn) [Zn(phen) ₂ (H ₂ O) ₂] ₂ [Mn(H ₂ O) ₆] ₂ .2BTC	Phenol	H ₂ O ₂	30~40°C, 8 h in EtOH	20.2~24.2	Hydroquinone	The encapsulated complex is responsible for the activity, no activity of the host	64c
12	[Cu ₂ (BPTC)(Im) ₄ (H ₂ O)(DMF)] _n	Phenol+functionalized derivates	H ₂ O ₂	30~50°C, 2-10 h in H ₂ O, acetone or EtOH	15-62	Benzoquinone	Selectivity toward single diphenols and the yield of products are still lower than classic catalysts	69
13	UiO-66-NH ₂	Benzyl alcohol Cyclohexanol Hexyl alcohol	O ₂ 1atm	12h, 0 °C, Solvent: CH ₃ CN/ TBT/ Acetone/CHCl ₃ /DMF; 420-450 nm light irradiation	8~13.1 1.6~2.8 0.9 (depend on different solvents)	Benzaldehyde Cyclohexanone Hexanal	polar organic media play a crucial role in stabilizing the intermediate epoxides and active oxygen species	68
14	0.35%Pd/MIL-101(Cr)	Cinnamyl alcohol	O ₂ 1atm (20ml min ⁻¹)	80°C, 0.5h in toluene	97	Cinnamyl aldehyde (99%)	Recyclable up to 5 times without significant loss of cativity.	70

15	$\text{Fe}_2\text{O}_3/\text{MIL-101}(\text{Cr})$	Benzyl alcohol+derivates	H_2O_2 (50wt.%)	3~15min,in water, 100~120 °C, (8.3~13.4bar) Microwave assisted(300W)	86~99	Corresponding benzaldehydes (92~99%)	Microwave assisted oxidation reaction; Recyclable up to 3 times with over 90% of its initial activity.	⁷¹
16	$[\text{Zn}_2(\text{H}_2\text{O})_4\text{Sn}^{\text{IV}}(\text{TPyP})(\text{HCOO})_2]_3 \cdot 4\text{NO}_3$	1,5-Dihydroxynaphthalene	O_2	3.5h, RT, solvent: $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (4:1, v/v), 350W Xe lamp irradiation	>99.9	5- hydroxynaphthalene- 1,4-dione	the mixed solvents can prompt photo-oxygenation smoothly	⁶⁷

3.3 Oxidation of thiols and sulfides

The few MOFs that have been studied for thiol and sulfide oxidations focused on the selective production of fine chemicals (Table 3) or on ODS (Oxidative Desulfurization). Dhakshinamoorthy *et al.*^{21b} examined the commercially available Fe(BTC), F300, for the oxidation of thiophenol. The catalyst showed moderate to high conversions at RT (44% of reactant conversion) and 70°C (87% of reactant conversion) in air using acetonitrile as solvent (entry 1, Table 3), whereas, Cu₃(BTC)₂ and Al₂(BDC)₃ exhibit a poor catalytic performance of 28% and 4% respectively. Song *et al.*^{21d} examined a POM@HKUST-1 material for the chemo- and shape- selective oxidation of a variety of thiols to disulfides (entry 2 Table 3). The authors observed a synergistic stabilization of both the MOF and the POM and this synergy between the two structural components was extended to the catalytic activity of the POM. Similar studies using POM@MOF or POM based MOFs for catalyzing ODS reaction have been reported in several recent papers (entry 11,12 Table 3).



Scheme 8 : Illustration of the post-synthetic modification of MIL-101(Cr) by grafting of dopamine, then followed by by metallation of VO(acac)₂ to create V(dop)-MIL-101(Cr). The bracket around [VO] denotes the presence of a vanadium oxo moiety.⁷²

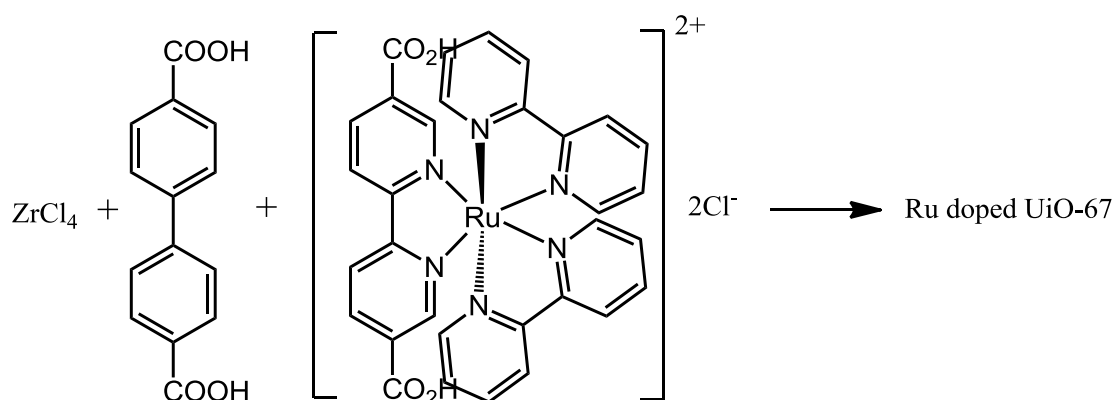
Besides the report on Cr-MIL-101 (entry 8, Table 3), or encapsulate phosphotungstic acid/ vanadium oxide in MIL-101 framework (entry 13, 15 Table 3) Nguyen and coworkers⁷² use Cr-MIL-101 as a model platform for the post-synthesis incorporation of catechols, which is further metallated with VO(acac)₂ for oxidation. The postmodification procedure is illustrated in Scheme 8. The obtained V(dop)-MIL-101 has been investigated in the oxidation of thioanisole using TBHP as the oxidant. The catalyst shows catalytic activity to oxidize thioanisole to the corresponding sulfoxide and sulfone (entry 14). The catalyst can be recovered and reused up to 3 runs. Interestingly, a slight increase in the selectivity to sulfoxide is observed, which is due to the gradual conversion of the starting V^{IV} to V^V.

Rare-Earth based MOFs are often used for the oxidation of sulfides. They can be divided into 2 main groups: the Yb and Sc based MOFs. For all these rare- earth MOFs, H₂O₂ was applied as the oxidant. The Yb based MOF of Bernini *et al.* (entry 3 Table 3) has been examined for the oxidation of methylsulfanylbenezene. After an induction period, a moderate conversion of 50% in the first run was observed. The authors state that the noted induction period is due to the Ln-O-OH species that are

formed during the first run, which are the real active species in the additional runs ^{21e}. The presence of a peroxo complex that acts as the active intermediate was suggested in their earlier report on Ln MOF based catalysts (entry 9 Table 3) ^{18b}. Furthermore, the same group reported much higher conversions for 2 other based Yb MOFs (entry 4 Table 3) ¹⁴. Although the kinetic profile of both MOFs was different, complete conversion (>99%) was obtained, using methylphenylsulfide as the reactant.

The latter reactant was also applied for the catalytic evaluation of the Sc based MOFs. Comparison of the Sc-terephthalate (entry 5 Table 3) with the Sc-succinate (entry 6, Table 3) shows that the reaction proceeds faster and more selectively for the terephthalate based framework under the same reaction conditions ⁷³.

The group of Monge presented in 2009 the synthesis of a novel Sc and Y-MOF, using 1,5- and 2,6-naphthalenedisulfonates as organic linkers ⁷⁴. Although the reaction takes place at the surface of the materials, better results were obtained in comparison to their earlier reports (entries 5-6 Table 3) with conversions up to 100 % in 60 minutes (entry 7 Table 3).



Scheme 9. Synthesis of Ru doped UiO-67(an extended framework of UiO-66, Figure 1a)

A novel photo catalytic system was developed for the aerobic oxidation of thioanisole by the Lin group in 2011 (Scheme 9) ^{19f} with methanol as the solvent. The Ru-doped UiO-67 successfully catalyzed the selective aerobic oxidation of thioanisole to methyl phenyl sulfoxide. No sulfone (the possible overoxidized byproduct) was detected by ^1H NMR, demonstrating a high degree of selectivity of this reaction.

Entry	Catalytic MOF	Reactant	Oxidant	Reaction parameters	Conversion (%)	Main product (selectivity)	Take home message	Ref.
1	Fe(BTC) Cu ₃ (BTC) ₂ Al ₂ (BDC) ₃	Thiophenol	Air/O ₂	70°C, 1 h in CH ₃ CN	44-87 28 4	Diphenyldisulfide	Activity: Fe>Cu>Al	21b
2	[CuPW ₁₁ O ₃₉] ⁵⁻ @HKUST-1	Linear and cyclic thiols	Air/O ₂	45°C, 62 h in chlorobenzene	27-95	Disulfide (99%)	Synergistic stabilization of both the MOF and the POM	21d
3	[Yb(C ₄ H ₄ O ₄) _{1.5}]	Methylsulfanylbenzene	H ₂ O ₂	60 °C, 6 h in CH ₃ CN	50	Methyl phenyl sulfoxide (92%)	In first run: induction period due to formation of the active species	21e
4	[Yb ₄ (OH) ₁₀ (H ₂ O) ₄][2,6-AQDS] [Yb(OH)(2,6-AQDS)(H ₂ O)]	Methylphenylsulfide	H ₂ O ₂	60°C, 30 min in CH ₃ CN	>99	Methyl phenyl sulfoxide (>99%)	Higher charge density yields in poorer activity	14
5	[Sc ₂ (C ₈ H ₄ O ₃) ₃]	Methylphenylsulfide and (2-ethylbutyl)phenylsulfide	H ₂ O ₂	50°C, 4 h in CH ₃ CN	~90	Sulfoxide (85%)	No loss in activity or selectivity for at least 4 runs	73a
6	[Sc ₂ (C ₄ H ₄ O ₄) _{2.5} (OH)] [Y ₂ (C ₄ H ₄ O ₄) ₃ (H ₂ O) ₂].H ₂ O [La ₂ (C ₄ H ₄ O ₄) ₃ (H ₂ O) ₂].H ₂ O	Methylphenylsulfide and (2-ethylbutyl)phenylsulfide	H ₂ O ₂	40°C, 6 h in CH ₃ CN, H ₂ O ₂ / substrate:2.5	~85 >99 and 95 >99 and 86	Sulfoxide (90-99%) Sulfoxide (90-95%) Sulfoxide (90-95%)	Every MOF: total conversion in 60 min. to the sulfoxide	73b
7	[Sc ₂ (nds)(OH) ₄] _n [Y(1,5-nds)(OH)(H ₂ O)] _n	Methylphenylsulfide	H ₂ O ₂	60°C, 1 h in CH ₃ CN	>99	Methyl phenyl sulfoxide (>99%)	The catalysts could be reused at least four times with neither loss of activity nor selectivity	74
8	Cr-MIL-101	Benzenethiol, diphenylsulfide and isopropyl phenylsulfide	H ₂ O ₂	25°C, 12 h in CH ₃ CN, ratio H ₂ O ₂ / benzyl phenyl sulfide:2	88-99	Sulfoxide (>99%)	Reactants with electron-releasing groups enhance the activity	75
9	[Ln ₂ (C ₁₇ H ₈ F ₆ O ₄) ₃] with Ln= Yb, Er, Gd, Sm, Nd, La	Methylphenylsulfide	H ₂ O ₂	RT, 3~5 h in CH ₃ CN, H ₂ O ₂ / substrate:3	78-92	Sulfoxide	Presence of peroxo complex: active species	18b
10	[Zn ₂ (bdc)(L-lac)(dmf)].DMF	Tetrahydrothiopyran	H ₂ O ₂	RT, 24 h in CH ₃ CN/CH ₂ Cl ₂ , ratio substrate/H ₂ O ₂ =1:1	72	Sulfone (98%)	No sulfone formation in the initial period of reaction	76
11	Tb(PW ₁₁) ₂ @MIL-101(Cr)	Dibenzothiophene, 1-benzothiophene or 4,6-dimethyldibenzothiophene	Air 1atm (initiated by 75μl H ₂ O ₂)	50 °C, 5h, biphasic system (equal volume of oil+ MeCN)	100	-	POM@MOF catalysed ODS using biphasic system , complete desulfurization achieved in 5h.	77
12	H[Ln(H ₂ O) ₄] ₂ [MnV ₁₃ O ₃₈] (Ln = La or Ce)	Variable sulphide	TBHP	50 °C, 3~6h in CH ₂ Cl ₂ TBHP: substrate=5:1	98.8~99.5	Corresponding sulfone	[MnV ₁₃ O ₃₈] ⁷⁻ is the redox catalytic active center for ODC process, it is heterogenized into a POM based porous framework	78
13	PTA-MIL-101(Cr)	Benzothiophene, dibenzothiophene or 4,6-dimethyldibenzothiophene	H ₂ O ₂	50 °C, 1-5h, in n-heptane Oxidant/substrate=50	72~91	-	The sulphide oxidation process are contributed from both PTA and Cr ³⁺ in the presence of large excess of H ₂ O ₂	79
14	V(dop)-MIL-101(Cr)	Thioanisole	TBHP in nonane	RT, 8h, in CH ₂ Cl ₂ . oxidant : substrate: catalyst =100:100:1	83	Sulfoxide (69%) Sulfone (31%)	The catalytic activity is attributed to the vanadium actecholate species.	72
15	4.2%V@MIL-101(Cr)	Sulphide	H ₂ O ₂	RT, 0.5~3h, H ₂ O ₂ : substrate=8:1 Solvent: EtOH or CH ₃ CN	87~98(in EtOH) 92~98 (in CH ₃ CN)	sulfoxide(in EtOH) sulfone (in CH ₃ CN)	Changing solvent from EtOH to CH ₃ CN results in different product formation.	80
16	[Zn ₂ (H ₂ O) ₄ Sn ^{IV} (TPyP)(HCOO) ₂] 3 4NO ₃	Various sulfides	O ₂	12h, RT, solvent: CH ₂ Cl ₂ /MeOH(4:1,	93~>99.9	Corresponding sulfoxides	Sn porphyrin based MOF shows better selectivity to sulfoxide than homogeneous	67

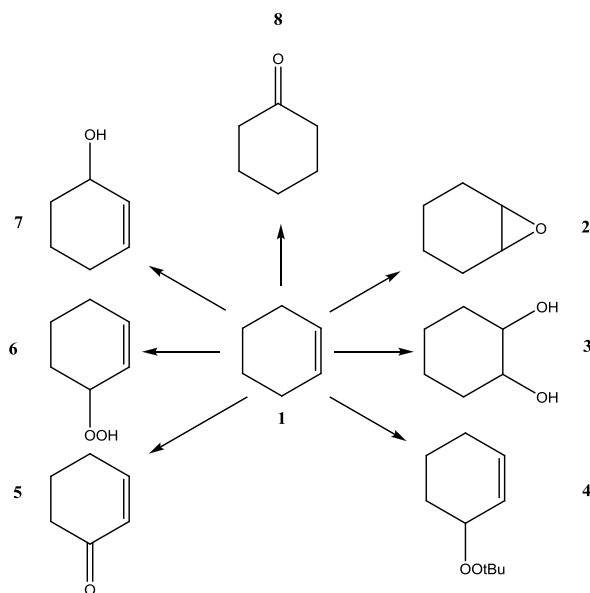
17	Ru doped UiO-67	Thioanisole	light	v/v), 350W Xe lamp irradiation RT, 22h, Solvent: MeOH	72	methyl phenyl sulfoxide	Sn-porphyrin complex, the latter let the sulfide partially converted to sulphone. The conversion after 22 h is comparable to that of the corresponding homogeneous catalytic system	19f
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Table 3. Overview of the MOFs studied for the oxidation of thiols and/or sulfides.

3.4 Oxidation of cycloalkenes and linear alkenes

Ethylene oxide is produced aerobically using a silver catalyst⁸¹, but a similar efficient process for the aerobic epoxidation of other (cyclo)alkenes has not been yet implemented. Nice progress in this field has been achieved by using supported gold catalysts⁸². In general, selective epoxidation of alkenes using molecular oxygen instead of peracids or peroxides still remains a challenge in catalysis and green chemistry. Next to epoxidations, allylic oxidations are also relevant in the synthesis of fine chemicals. For asymmetric or chiral epoxidations, transition metal complexes containing redox active transition metals like Cu, Co, Mn and Fe with Schiff-base ligands are important homogenous catalysts which can oxidize alkenes with oxygen. The most efficient is the Mn-salen complex, also known as the Jacobsen catalyst⁸³. The use of MOFs in chiral and asymmetric oxidations will be discussed in the next paragraph.

Evidently, catalytic studies on MOFs for the epoxidation of the C=C bond have received considerable attention as can be inferred from Table 4. Commonly investigated (non prochiral) reactants are cyclohexene, cyclooctene and styrene. During the oxidation of cyclohexene, many products can be formed, as can be seen from Scheme 10.



Scheme 10. Oxidation of cyclohexene **1** toward the products: cyclohexene oxide **2** cyclohexane-1,2-diol **3**, *tert*-butyl-2-cyclohexenyl-1-peroxide **4**, 2-cyclohexene-1-one **5**, cyclohexene hydroperoxide **6**, 2-cyclohexen-1-ol **7** and cyclohexanone **8**.

From Table 4, principally 5 classes of MOFs, studied in the oxidation of alkenes, can be distinguished. More specifically, Cu-, Co-, rare-earth, V- and “linker-modified” MOFs. Each of these classes will now be discussed in more detail. There have been studies using other MOFs as well. Worth mentioning is the study of the group of Gascon and Kapteijn⁸⁴. The MIL-101(Cr) was immobilized on monoliths using seeding techniques followed by a secondary growth. A monolithic stirrer reactor has been used to explore reactivation procedures of MIL-101 in the selective oxidation of tetralin. However we will focus in the Table and discussion on the 5 classes mentioned above.

Table 4. Overview of MOFs examined for the oxidation of cyclic and/or linear alkenes.

Entry	Catalytic MOF	Reactant	Oxidant	Reaction parameters	Conversion (%)	Main product (selectivity)	Take home message	Ref.
1	[Cu(bpy)(H ₂ O) ₂ (BF ₄) ₂ (bpy)]	Cyclohexene	O ₂	45°C, 15 h, no solvent	8	Cyclohexene hydroperoxide (90%)	No solvent, high selectivity (90%) to cyclohexene hydroperoxide	⁸⁵
2	{[Cu(Pht)(Im) ₂].1.5H ₂ O} _n [Co(Pht)(Im) ₂] _n	Cyclohexene	H ₂ O ₂	RT, 1 h in acetone	75.2 40.6	2-cyclohexen-1-one (40.6-75.2%)	Yield of ketone: Cu-MOF>Co-MOF	⁸⁶
3	[Cu(H ₂ btec)(bipy)] _∞	Cyclohexene/ styrene	TBHP	75°C, 24 h in 1,2-dichloroethane in N ₂ atmosphere	61.8/26.9	Epoxide (68.4/70.2%)	Cyclohexene: higher conversion but lower selectivity, styrene: lower conversions but higher selectivity	^{87, 88}
4	[Cu ₂ (OH)(BTC)(H ₂ O)] _n .2nH ₂ O [Co ₂ (DOBDC)(H ₂ O) ₂].8H ₂ O	Cyclohexene	O ₂	80°C, 20h	20.8 32.8	2-cyclohexen-1-ol 2-cyclohexen-1-one	Solvent free catalysis	⁸⁹
5	[Co ^{II} (bpb)].3DMF	Cyclohexene	TBHP	80°C, 12h in CH ₂ Cl ₂	62	Tert-butyl-2-cyclohexenyl-1-peroxide (83%)	83% selectivity toward tert-butyl-2-cyclohexenyl-1-peroxide	⁹⁰
6	[Co ^{II} ₄ O(bdpb) ₃] = MFU-1	Cyclohexene	TBHP	70°C, 22 h, ratio substrate/TBHP:2	27.5	Tert-butyl-2-cyclohexenyl-1-peroxide (66%)	Reaction in the pores, high selectivity to allylic substitution product (66%)	¹¹
7	MFU-2 NHPI@MFU-1	Cyclohexene	TBHP Air	70°C, 22h, ratio substrate/TBHP:2 35°C, 24h in CH ₃ CN	16 35	Tert-butyl-2-cyclohexenyl-1-peroxide Cyclohexene hydroperoxide	high selectivities toward the allylic substitution product, MFU-2: leaching observed	⁹¹
8	Co-ZIF	Cyclooctene/ cyclohexene/ styrene	O ₂ +aldehyde	35 °C, 3~5 h in CH ₃ CN, O ₂ flow: 7-10mL/min	>99	Epoxide (98.5/ 70.3/ 60.2 %)	High selectivity to epoxide (99%): cooperative effect ligand and metal center	⁹²
9	Co-STA12	(E) stilbene	O ₂	100 °C, in DMF for 12 h, O ₂ flow: 50mL/min	95	Trans-stilbene oxide (90%)	Induction period, catalysis occurs mainly heterogeneous	⁹³
10	Ln _n (N ₃)(nic) _n (OH) _{1.5n} (Hnic) _{0.5} n=2 Ln =Y, Gd, Sm	Cyclooctene/ styrene/ substituted styrene derivatives and linear alkenes	TBHP	68~70°C, 24 h in CH ₃ CN	40-99	Cyclooctene oxide (>99%)/ Styrene oxide / Epoxide	Activity: MOF> rare- earth oxides	⁹⁴
11	[Nd(HCOO) ₃] _n [Pr(HCOO) ₃] _n	Cyclopentene/ Cyclooctene/ Styrene/ substituted styrene derivatives and linear alkenes	TBHP	65~68°C, 24 h in CH ₃ CN	38-99	Cyclopentene oxide (>99%)/ styrene oxide/ epoxide	Selectivity and conversion depends on steric hindrance of reactant	⁹⁵
12	MIL-47	Cyclohexene	TBHP in water /TBHP in decane	50 °C, molar ratio cyclohexene/oxidant= 1/2,, solvent: chloroform, inert atmosphere	55/30	Tert-butyl-2-cyclohexenyl-1-peroxide/ cyclohexene oxide	Stability and selectivity toward the epoxide increased by using TBHP in decane as oxidant	⁹⁶
13	COMOC-3	Cyclohexene	TBHP	50°C, molar ratio cyclohexene/oxidant= 1/2, 7h, solvent:chloroform, inert atmosphere	38	Cyclohexene oxide (82%)	Formation of an extra phase V ₄ O ₉ during the catalytic test	⁹⁷
14	TiO(acac) ₂ @NH ₂ -MIL-47	Cyclohexene	O ₂ +cyclohexanecarboxylic acid	40°C, O ₂ flow: 7mL/min, 6 h in	25	Cyclohexene oxide	Enhanced stability and activity in comparison to the non-modified	⁹⁸

			rbxalde hyde	CH ₃ CN			material	
15	Co-POM@Cr-MIL-101 Ti-POM@Cr-MIL-101 Ti-POM@Cr-MIL-101	α -pinene/ Cyclohexene/ Caryophyllene	O ₂ H ₂ O ₂ H ₂ O ₂	50°C, 2~5h in CH ₃ CN / 70°C, 6h in CH ₃ CN / 50°C, 4 h in CH ₃ CN	40-45/ 39/ 88	Verbenol (29%) Verbenol (32%)/ Ketone+alcohol/ epoxide(>99%)	O ₂ : catalyst is stable, H ₂ O ₂ : MIL-101 matrix is destroyed	99
16	5% PW ₄ /Cr-MIL-101 5% PW ₁₂ /Cr-MIL-101	Cyclohexene Cyclohexene/ other cyclic alkenes	H ₂ O ₂	50°C, 3~5h, CH ₃ CN,	76 72/ 30-76	Cyclohexene oxide (74%) Cyclohexene oxide (76%) Epoxide (71-99%)	Good selectivity toward epoxide (70- 80%): depends on POM loading	100
17	PTA@Cr-MIL-101	Caryophyllene	H ₂ O ₂	55°C, 5 min in CH ₃ CN, microwave power: 300mW	>90	Caryophyllene oxide	Utilization of microwave heating during the catalytic tests	101
18	Fe-MIL-101 Cr-MIL-101	Cyclohexene/Cycloh exane	O ₂ /TBHP+a ir	60°C, 10~16h/ 70°C, 8h	44/24 16/36	Cyclohexenyl hydroperoxide (46%)/ Cyclohexyl hydroperoxide (46%) 2-cyclohexene-1-one (56%)/ Cyclohexanone (75%)	Fe-MIL-101 is less stable in the oxidative medium than Cr-MIL-101 and product distribution depends on the nature of the active metal	102
19	NHPI@FeBTC	Styrene/ Substituted styrene derivates	O ₂	100°C, 1~10h in toluene	10/ 12-60	Benzaldehyde (60%)/ Aldehyde (63-75%)	Conversion increased by electron donating substituents	103
20	VO(acac) ₂ @IRMOF-3	Cyclohexene	TBHP	60°C, 72 h in THF	40	-	Low catalytic activity and stability	104
21	Mn(acac) ₂ @IRMOF-3	Cyclohexene/ Cyclooctene/ Styrene	O ₂ +aldehy de	40°C, 6 h in toluene, ratio substrate/aldehyd =1/2	52.3-67.5	Epoxide (92/ 95.8/ 80.7 %)	High selectivities toward the epoxide (>80%) and good stability	105
22	Mn(III)-porphyrin MOF	Styrene, stilbene	2-(<i>tert</i> - butylsulf onyl) iodosylbe nzene	RT, 3h in CH ₂ Cl ₂	-	-	Improvement of the catalytic activity and lifetime. Only the TON numbers are reported	106
23	Mn (III)-porphyrin Zn-MOF	Styrene	2-(<i>tert</i> - butylsulf onyl)iodo sylbenze ne	In CH ₃ CN	-	Styrene oxide	ZnMn-RPM MOF showed a TON of 2150 and stopped only because of depletion of oxidant	107
24	[Co ₂ (p ₁₂ -H ₂ O)(H ₂ O) ₄](Co- dcdbp).(H ₂ O) ₆ .(C ₂ H ₅ OH) ₁₂ .(D MF) ₁₂	Stilbene	TBHP	60°C, 24 h in CH ₃ CN	95.7	Stilbene oxide (87.1%)	Catalyst could be reused for 8 runs without significant drop in activity	108
25	[Ni ₂ (dhtp)(H ₂ O) ₂].8H ₂ O=Ni- CPO-27	Cyclohexene	H ₂ O ₂	60°C, 8 h in CH ₃ CN	75.4	Cyclohexene oxide (39.7%)	Only heterogeneous catalysis at RT	109
26	[Mn(μ -terph)(H ₂ O) ₂] _n	Cyclooctene/ Cyclohexene, norbornene, indene, Stilbene	H ₂ O ₂ +imi dazole	60°C, 24h in CH ₃ CN/60°C, 4~24h in CH ₃ CN	75/ 2-75	Epoxide	Good activity for epoxidation of cyclooctene, whereas aryl-substituted olefins gave a low yield , slow release of the active species	110
27	TMPyP@[Fe ₃ (BTC) ₂](TMPyP = meso-Tetra(N-methyl-4- pyridyl)porphine	Styrene trans- stilbene/ triphenylethylene	TBHP in H ₂ O	60°C, in CH ₃ CN for 10 h	85/ 40/ <5	Epoxide and benzaldehyde	Heterogeneous porph@MOF catalyst shows better conversion compare to homogeneous catalyst, size selective	111

	tetratosylate) (refer as Porph@MOM-4)							catalysis was observed based on the three substrates with different sizes. Efficient catalysts for selective oxidation of various hydrocarbons at RT.	
28	(CH ₃) ₂ NH ₂][Zn ₂ (HCOO) ₂ (M ^{III} -TCPP) (H ₆ TCPP= tetrakis(4-carboxyphenyl) porphyrin) (M =Fe or Mn)	Styrene / variable olefins	PhIO	RT. 6h in CH ₂ Cl ₂	>99 / 7~>99	Styrene oxide and epoxides			42
29	PW ₁₁ @MIL-101(Cr) SiW ₁₁ @MIL-101(Cr)	R-(+)-limonene	H ₂ O ₂	75 °C, in CH ₃ CN 6h. H ₂ O ₂ /substrate molar ratio: 4.5/1	~95	Limonene-1,2-epoxide Limonene-1,2-diol		The kinetic profile of PW11 and PW11@MIL-101 is similar. No selectivity concerning product distribution is given.	112
30	Fe ₂ O ₃ /MIL-101(Cr)	Alkenes cyclohexenes	H ₂ O ₂ (50 wt.%)	3~15min,in water, 100~120 °C, (8.3~13.4bar) Microwave assisted(300W)	88~95 92	Corresponding benzaldehydes (90~95%) cyclohexane-1,2-dione(86%)		Recyclable up to 3 runs. MIL-101 is a good catalyst/support for under pressure and oxidising conditions.	71
31	Zn ₄ O based MOFs (MOF-5, IRMOF-2, IRMOF-8, IRMOF-9)	Propene Propylene	O ₂	RT, 60min illumination, gas mixutre of 28.5 mol % propene and 14.3 mol % O ₂ from dry air. Flow rate 10ml/min (operando FT-IR)	- -	propanoic acid, ketones, aliphatic aldehydes acrylic acid, acrolein, acetone		The photo catalytic activity of the Zn ₄ O based clusters turned out to be higher than that of their MOF counterparts and that of zinc oxide in the oxidation of propene.	113 114

3.4.1 Cu based MOFs

Only a few studies have been carried out on Cu-MOFs for the oxidation of alkenes (entries 1-4 Table 4). In the first two reports pure O₂ was applied as an oxidant (entry 1 and 4, Table 4), whereas in the third report H₂O₂ (entry 2, Table 4) and in the last study TBHP was employed as an oxidant (entry 3, Table 4). In spite of the low cyclohexene conversion⁸⁵ (8%), very good selectivities toward cyclohexene hydroperoxide (Scheme 10, product **6**) were obtained (90%) using O₂. The use of H₂O₂ as an oxidant mainly gave the allylic oxidation product 2-cyclohexene-1-one (entry 2 Table 4).

Aguirre *et al.*⁸⁷ show that Cu-based MOFs can also possess a good selectivity towards the epoxide (entry 3 Table 4). Although a significant difference is observed in the conversion of both reactants (cyclohexene and styrene), a selectivity of approximately 70% toward the epoxide was detected in both cases. In an additional report, the authors proposed a mechanism for the formation of the epoxide and they ascribed the difference in conversion for cyclohexene and styrene to the mechanism involved in the oxidation reaction⁸⁸.

3.4.2 Co-based MOFs

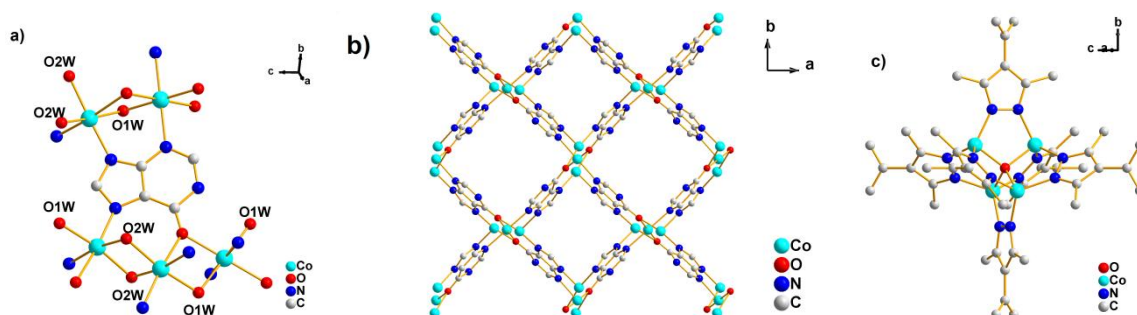
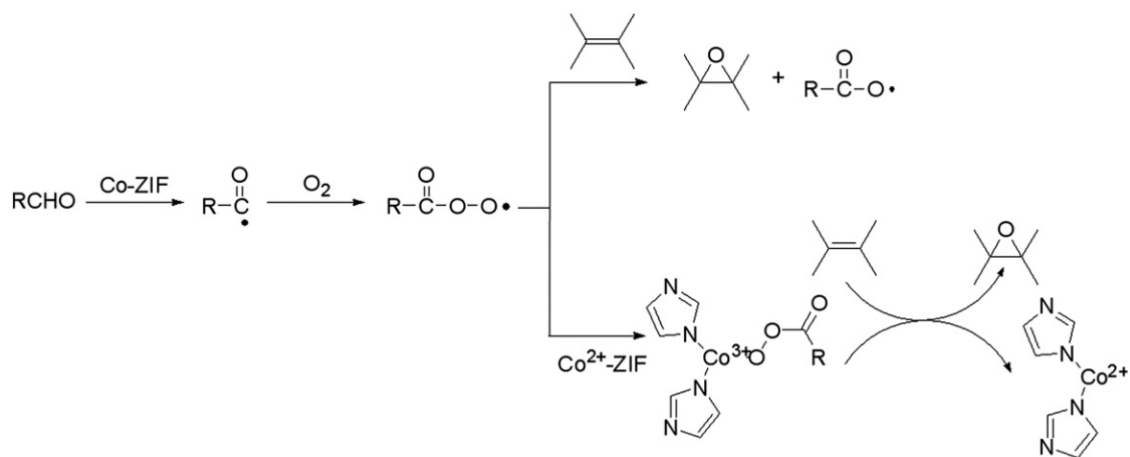


Figure 3 a,b) the coordination surroundings of Co in [Co₃(μ₂-OH)₄(I)₂] as well as the 3D porous framework¹¹⁵ c) the SBU of MFU-1 framework

Several Co containing MOFs have been evaluated for the oxidation of alkenes (entries 4-9 Table 4). Many attempts have been made to get novel structures containing unsaturated cobalt sites. As shown in Figure 3, two Co-MOF structures, [Co₃(μ₂-OH)₄(I)₂] and MFU-1 are given as examples. MFU-1 is designed by the group of Volkmer, they applied TBHP as an oxidant for the evaluation of their Co-MOFs (entries 5-6 Table 4)^{11,90}. In both studies very high selectivities were obtained toward the allylic substitution product, *tert*-butyl-2-cyclohexenyl-1-peroxide (83%) (Scheme 10, product **4**), suggesting a mechanism in which peroxy radicals are created by a reductive cleavage of *tert*-butyl hydroperoxo ligands coordinating to Co(III) metal centers.

In a later report⁹¹, more mechanistic insights were given and additional catalytic tests were executed. Whereas the MFU-1 material demonstrated to be a stable catalyst, the catalytic activity of MFU-2 was due to the slow leaching of the Co centers using TBHP as an oxidant (entry 7 Table 4)⁹¹.

Zhang *et al.* applied O_2 combined with the sacrificial isobutyraldehyde to test a Co-ZIF for the oxidation of various alkenes (entry 8 Table 4)⁹². Under these conditions, the epoxide product was formed with very high selectivities (98.5%). The authors ascribed these results to a combined effect of the basic ligand and the unsaturated metal center, since epoxides are fairly stable in a basic medium⁹². They suggested a radical mechanism (see Scheme 11). In first instance, an *in situ* acylperoxy radical was created as a result of the reaction of isobutyraldehyde with O_2 initiated by Co-ZIF. In a second step, the acylperoxy radical is able to follow 2 possible pathways, it can either react with the olefin to produce the epoxide, or with the Co-ZIF to form Co-peroxy species, which on their turn can transfer an oxygen atom directly to the olefins.



Scheme 11. Proposed pathway by Zhang *et al.* for the selective epoxidation of olefins catalyzed by Co-ZIF. Reproduced with permission from ref⁹². Copyright 2011 Elsevier.

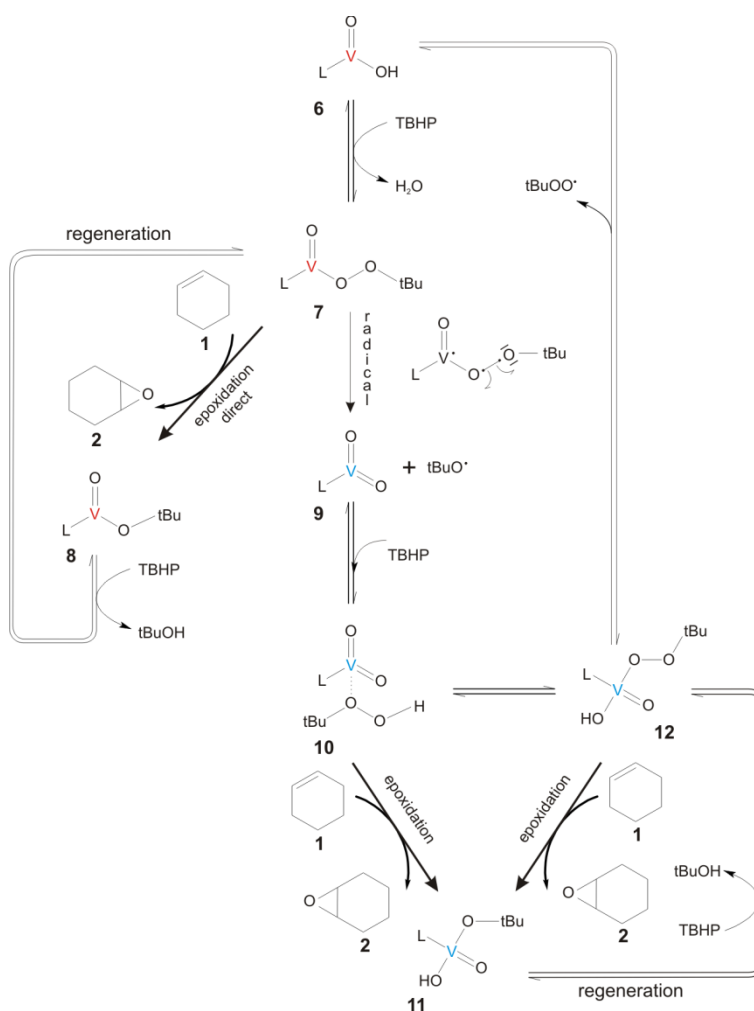
In a report of Beier *et al.*⁹³, pure O_2 was applied as an oxidant with DMF as a solvent (entry 9 Table 4). Former studies on Co-catalysts revealed that in the presence of DMF, a Co-DMF complex is formed that reacts with O_2 giving rise to Co-superoxo species¹¹⁶. As mentioned earlier, these species will afterwards transfer the oxygen to the olefin, resulting in the epoxide product. The catalytic evaluation of Co-STA-12 resulted in the formation of the epoxide with an excellent selectivity of 90%, which was in agreement with the proposed mechanism⁹³.

3.4.3 Rare-earth based MOFs

Although homogenous rare-earth salts have already shown to possess good catalytic performance for the oxidation of olefins, the reports using rare-earth MOFs in the epoxidation of alkenes are very scarce¹¹⁷. Rare earth metals act as Lewis acids, forming adducts with the peroxo groups of H_2O_2 or TBHP similar to early transition metals in a high oxidation state. In recent years, Sen *et al.* reported two papers concerning the use of rare-earth based carboxylate MOFs in the oxidation of alkenes (entries 10-11 Table 4)⁹⁴⁻⁹⁵. Similarities between both studies were observed. Firstly, TBHP was seen as the most appropriate oxidant. Very little or no catalytic activity was observed when H_2O_2 or sodium hypochlorite was applied. Moreover, in both cases a higher conversion was noted for the MOF based catalysts than for the corresponding metal oxides.

3.4.4 V based MOFs

Our own research efforts were mainly focused on the catalytic evaluation of V-MOFs. MIL-47, a V(IV) terephthalate MOF with completely coordinatively saturated V-nodes was tested in the oxidation of cyclohexene employing TBHP in water or TBHP in decane as oxidant (entry 12 Table 4)^{96a}. With the water based oxidant, a similar cyclohexene conversion and product distribution was observed in comparison with the geometrically and structurally wise homogeneous catalyst VO(acac)₂. Nevertheless, a significant leaching of V-species into the solution (12.8 % after one hour of reaction) was detected. If the TBHP was dissolved in decane as solvent the leaching of V becomes negligible and the catalyst was reused for at least 4 runs without loss of the structural integrity of the framework. Theoretical calculations were carried out to elucidate the active species and to propose a plausible reaction pathway (Scheme 12). At least two catalytic cycles are co-existing: one with V^{+IV} sites and one with pre-oxidized V^V sites. In the first cycle a direct epoxidation pathway is proposed that leads to the formation of cyclohexene oxide **2**, whereas the second cycle follows a radical based mechanism. In this route, +V vanadium-complexes **9** are generated by a homolytic cleavage of the peroxy linkage which can be activated with TBHP. The generated V^V-activated complexes **10** and **12** can on their turn produce cyclohexene oxide ^{96c}.



Scheme 12. Two competitive cyclohexene epoxidation pathways for MIL-47 (direct and radical) (V^{+IV} is shown in red, V^{+V} is shown in blue and V^{+III} is represented in black). Reproduced with permission from ref ^{96c}. Copyright 2012 Elsevier

Another V^{IV} terephthalate, denoted as COMOC-3, exhibiting the non-porous MIL-69 topology, was also examined in the oxidation of cyclohexene applying TBHP in decane as the oxidant (entry 13 Table 4)^{97,118}. A similar cyclohexene conversion was observed for COMOC-3 as for the porous MIL-47-catalyzed reaction under the same conditions. This suggests that the activity is driven by surface defect sites. A new V_4O_9 phase was detected, probably due to the surface activation and bond breaking during catalysis in combination with the oxidizing atmosphere during the regeneration of the catalyst⁹⁷.

3.4.5 MOFs as hosts for POMs or complexes

POM@MOF

Co and Ti –monosubstituted Keggin heteropolyanions were inserted into the nanocages of Cr-MIL-101⁹⁹. During the catalytic evaluation of the resulting POM@MOF materials, two types of oxidant were applied: O_2 for the Co-POM and H_2O_2 for the Ti-POM (entry 15 Table 4). Both systems gave foremost the allylic product in the oxidation of α -pinene. In addition, in the oxidation of cyclohexene over Ti-POM@MIL-101, the allylic oxidation products cyclohexene-2-ol and cyclohexene-2-one were the main products as well. In turn, the oxidation of caryophyllene mostly gave the epoxide product. The authors state that this could be due to the deprotonation of the Ti-POM during the encapsulation within the host matrix preventing the acid-sensitive epoxide for the ring opening reaction⁹⁹.

Later on, the same group reported on the incapsulation of the polyoxotungstates $[PW_4O_{24}]^{3-}$ (PW_4) and $[PW_{12}O_{40}]^{3-}$ (PW_{12}) into MIL-101 which were examined for the oxidation of cyclohexene and other cyclic alkenes by means of H_2O_2 as an oxidant (entry 16 Table 4)¹⁰⁰. For these POM@MOF materials, not the allylic but the epoxide product was observed as the main product. Furthermore, the authors witnessed an enhanced stability of the immobilized POM in the presence of H_2O_2 .

The Hatton group made a PTA@Cr-MIL-101 (PTA=phosphotungstic acid) material (entry 17 Table 4) for which much higher TOF values are reported (approximately 22-fold higher) than the TOF obtained for Ti-POM@MIL-101 under identical reaction conditions (entry 15 Table 4)¹⁰¹. They attributed this to the use of microwave heating and its effect on the grain size.

complex@MOF

Dhakshinamoorthy *et al.* reported the NHPI@FeBTC for the aerobic oxidation of styrene and derivatives (entry 19 Table 4)¹⁰³. In earlier times this MOF was already investigated for the aerobic oxidation of cyclooctane and other benzylic compounds (see entry 6 Table 1)³⁶. A similar mechanism was proposed (Scheme 7) with the generation of phthalimide *N*-oxyl radicals acting as precursors of C-centered radicals that would undergo auto-oxidation. Ingleson *et al.*¹⁰⁴ reported the two steps modification of IRMOF-3 to an imine grafted $VO(acac)_2$ complex (entry 20 Table 4). The authors carried out a preliminary catalytic investigation on this modified MOF structure for the oxidation of cyclohexene with TBHP as the oxidant. However, the $VO(acac)_2$ @IRMOF-3 showed a rather low catalytic activity and stability¹⁰⁴. The group of Ahn reported a more straightforward one step functionalization of the IRMOF-3 with a manganese complex (entry 21 Table 4)¹⁰⁵. Instead of using TBHP as an oxidant they utilized O_2 in combination with trimethylacetaldehyde as a co-oxidant. Good conversions (even for the

more bulky cyclooctene) were obtained with very high selectivities toward the epoxide (>80%)¹⁰⁵. Very recently, we performed a similar post-modification of NH₂-MIL-47, with TiO(acac)₂. The catalytic performance of V/Ti-MOF was examined for the oxidation of cyclohexene using O₂ as oxidant in combination with cyclohexanecarboxaldehyde as co-oxidant. A significantly higher cyclohexene conversion (25%) was observed for the bimetallic catalyst compared to the non-functionalized material (14.1%). The catalyst could be regenerated for at least 2 additional cycles without loss of activity and stability (entry 14 Table 4)⁹⁸.

The success of the immobilization of a homogeneous catalyst was once more demonstrated in the report of Lee *et al.*¹⁰⁶ in which a Mn(III)-porphyrin based MOF was synthesized resulting in an increased catalytic activity and lifetime in comparison to its homogeneous counterpart (entry 22 Table 4). Also the Hupp group synthesized a MOF incorporating a series of metalloporphyrins (Al³⁺, Zn²⁺, Pd²⁺, Mn³⁺ and Fe³⁺ complexes) in which the Mn containing MOF exhibited promising results for the oxidation of styrene (entry 23, Table 4) and the hydroxylation of cyclohexane¹⁰⁷.

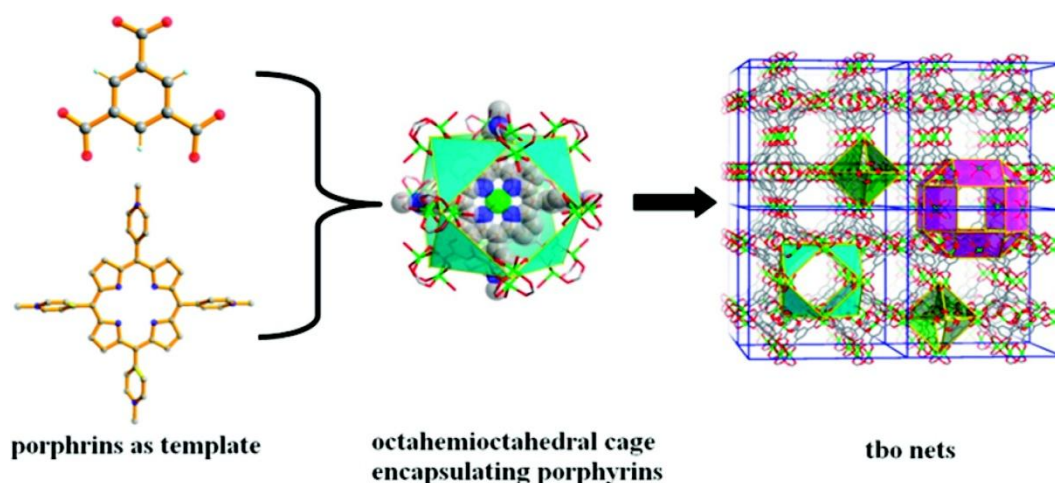
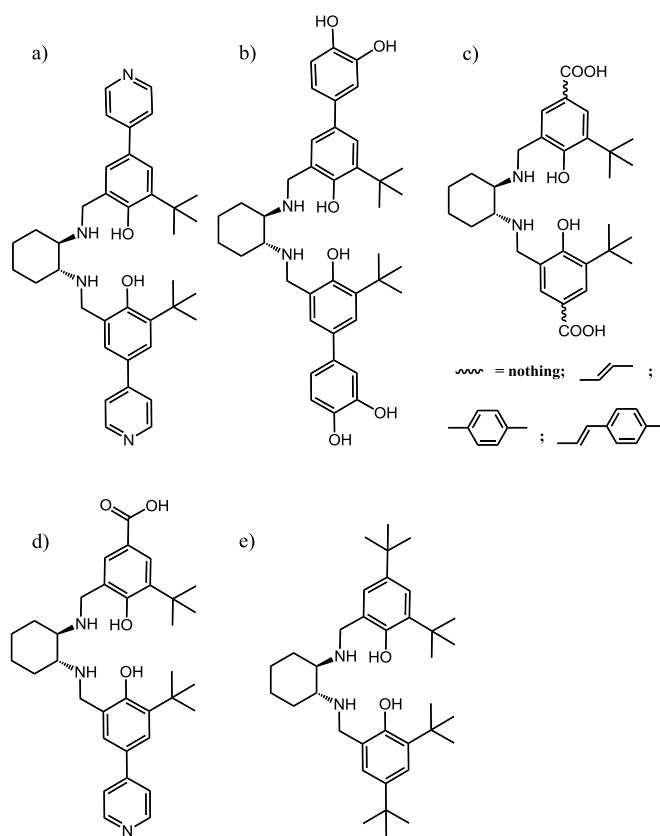


Figure 4 (right) Polyhedral cage framework of porph@MOM-4, -5, and -6 containing three distinct cages: large rhombihexahedral cages (pink), medium-sized octahemioctahedral cages (turquoise), and small tetrahedral cages (green). (middle) TMPyP cation encapsulated in the octahemioctahedral cage. (left) Structures of BTC and TMPyP. Reprinted with permission from Ref.¹¹¹ Copyright (2012) American Chemical Society

More recently, Z. Zhang *et al.*¹¹¹ reported a “ship-in-a-bottle” encapsulation of metalloporphyrins in a series of MOFs. As shown in Figure 4, the metalloporphyrins are located in the octahemioctahedra cages and serves as size-selective catalysts for oxidation of olefines (entry 27 Table 4).

3.5 MOFs in chiral oxidation catalysis

In Table 5 an overview is presented of the MOFs examined in the chiral oxidation of different substrates. Besides their use in oxidation catalysis, chiral MOFs have already been tested for a variety of reactions (diethylzinc additions, transesterifications, aldol reactions, hydrogenation, cyanosilylation reactions...). As the discussion of each type of catalytic reaction falls beyond the scope of this review the reader is referred to the recent and comprehensive overview of Kim *et al.*¹¹⁹. We will here focus on chiral oxidation catalysis.



Scheme 13. Various metalated salen /salan ligands used in this chapter to construct MOFs for chiral oxidation catalysis. a) 6,6'-(((1R,2R)-cyclohexane-1,2-diylbis(azanediyl))bis(methylene))bis(2-(tert-butyl)-4-(pyridin-4-yl)phenol); b) 5',5'''-(((1R,2R)-cyclohexane-1,2-diylbis(azanediyl))bis(methylene))bis(3'-(tert-butyl)-[1,1'-biphenyl]-3,4,4'-triol); c) 5,5'-(((1R,2R)-cyclohexane-1,2-diylbis(azanediyl))bis(methylene))bis(3-(tert-butyl)-4-hydroxybenzoic acid) and its derivatives; d) 3-(tert-butyl)-5-(((1R,2R)-2-((3-(tert-butyl)-2-hydroxy-5-(pyridin-4-yl)benzyl)amino)cyclohexyl)amino)methyl)-4-hydroxybenzoic acid; e) 6,6'-(((1R,2R)-cyclohexane-1,2-diylbis(azanediyl))bis(methylene))bis(2,4-di-tert-butylphenol)

The very first report on chiral oxidation catalysis was presented by Cho *et al.*¹²⁰ in which an Zn based MOF containing a Jacobsen-type salen(Mn) catalyst (salen ligand is shown in scheme 13a) showed promising results in the asymmetric epoxidation of 2,2-dimethyl-2*H*-chromene applying 2-(*tert*-butylsulfonyl)iodosylbenzene as oxidant (entry 4, Table 5). The polymerized salen complex exhibited an enhanced lifetime and only a minor selectivity degradation (82% ee) in comparison to the homogeneous complex (88% ee). The authors attributed the difference in enantioselectivity to electronic effects, more specifically to the presence of electron-withdrawing groups, whereas the research group of Snurr ascribed the decreased enantioselectivity to sterical hindrance between the substrate and the framework along with a decreased flexibility of the salen complex¹²¹.

In a later report of Cho *et al.* another salen based coordination polymer was described (Scheme 13 b, entry 3, Table 5). In contrast to their previous work, this catalyst could be recycled up to ten times with only a slight leaching percentage in the first 6 cycles¹²². Furthermore, they presented a porous, noncatenated analogue (denoted as Mn^{III}SO-MOF) of their first Jacobsen catalyst based Zn-MOF (entry 8, Table 5). Evaluation of the latter in the asymmetric epoxidation of 2,2-dimethyl-2*H*-chromene gave very high TON values (nearly 4000)¹²³. Additionally, removal of the Mn ions of the Mn^{III}SO-MOF material and subsequently remetalation was carried out. A comparison of the Mn^{III}SO-MOF with the remetalated Mn^{II}SO-MOF (entry 9, Table 5) demonstrated that for the latter a longer

induction period was observed due to the fact that the Mn^{II} center needs to be oxidized to Mn^{III} before catalysis can occur^{19b}.

Other Salen based MOFs were developed by the group of Lin who synthesized an isorecticular series of Mn-Salen based Zn-MOFs, denoted as CMOF-1 to CMOF-5 (Scheme 13c) (entry 2, Table 5). This family of isorecticular chiral MOFs was examined in the epoxidation of different olefins affording good to excellent yields and ee's¹²⁴. Furthermore they noticed that the rates of the epoxidation reaction strongly depend on the channel sizes. Nevertheless, the inherent instability of the CMOFs (7.5% Mn leaching) limits their use in enantioselective epoxidation reactions. In another recent work of Lin a different Mn(salen) ligand was applied to synthesize a chiral MOF having the same SBU as in one of their previous works (entry 1, Table 5)¹²⁵ which was the first MOF catalyzing sequential alkene epoxidation/epoxide ring-opening reactions.

Huang *et al.* reported a more stable chiral functionalized nickel Salen based MOF (Scheme 13a) which was insoluble in water and other common organic solvents (entry 7, Table 5)¹²⁶. The latter compound showed a similar catalytic activity as the homogeneous catalyst and could be recycled for at least 3 runs without loss in epoxide selectivity and only a minor loss in conversion¹²⁶.

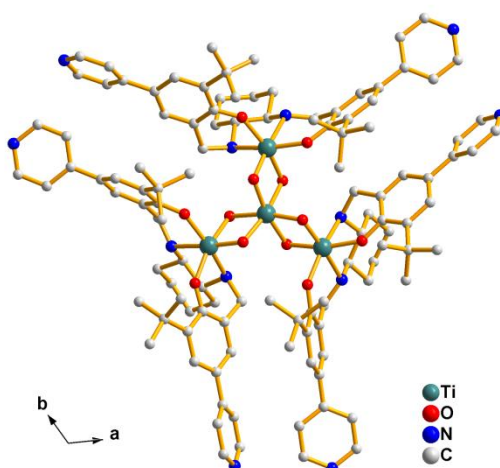


Figure 5. $\text{Ti}_4\text{O}_6\text{L}_3$ cluster as the basic building unit of a salen based MOF structure, salen ligand H_2L are shown in Scheme 13a

An interesting salen based MOF structure has been reported by the research group of Cui¹²⁷, as shown in Figure 5, The framework containing salen-bound Ti_4O_6 clusters which act as the building unit as well as the active catalytic center. The MOF is shown to be an efficient and recyclable heterogeneous catalyst for the oxidation of thioethers to sulfoxides by aqueous H_2O_2 (up to 82% ee) (Table 5, entry 11), displaying markedly enhanced enantioselectivity over the homogeneous catalyst by providing a cavity confinement effect. A similar approach has been employed by the same group using another Ti-based salen complex (Scheme 13d) to form a salen complex based MOF structure, the obtained MOF catalyst also shows good selectivity (up to 62% ee) in the oxidation of sulfides to sulfoxides (Table 5, entry 12).¹²⁸

Whereas the previous studies report on the application of chiral MOFs in the epoxidation of alkenes, Dybtsev *et al.* examined a homochiral Zn MOF in the size- and chemoselective oxidation of thioethers (entry 5, Table 5)¹²⁹. The chiral MOF exhibited a reasonable conversion (58-64%) for the smaller

thioethers whereas for the bulkier thioethers a very poor conversion was noted. Although the authors could recycle the catalyst for 30 catalytic cycles, they failed to observe any asymmetric induction in the catalytic sulfoxidation. In a later report this MOF was applied at the same time as a catalyst and as a chiral stationary phase for a column to obtain enantiomerically pure sulfoxides¹³⁰. However, the enantioseparation of the bulkier sulfoxides could not be obtained due to the relative small pore dimensions of the MOF. To overcome this problem, the same research group synthesized 2 isoreticular homochiral MOFs applying bigger linkers which could be used in the sulfoxidation of bulkier thioethers (entry 6, Table 5)¹³¹.

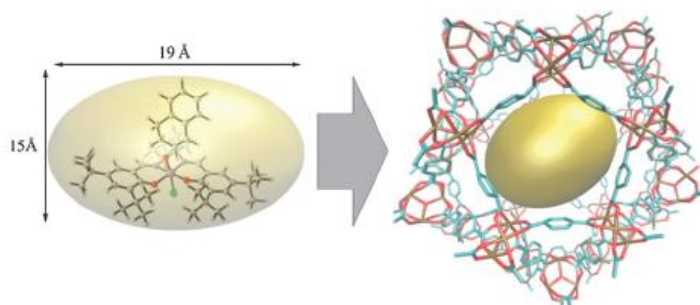


Figure 6. Schematic representation of the transition state contained in the small (2.9 nm diameter) cage of MIL-101. The space needed for transition state to be contained in the cage is represented by an ellipsoid with radii of 19 and 15 Å.

This fits readily in the MIL-101 cage. Reproduced by permission of The Royal Society of Chemistry [ref¹³²]

In order to overcome the stability problems that many MOFs with chiral struts are dealing with, our group has recently published a Jacobsen salen complex (Scheme 13e), that was immobilized inside the pores of an NH₂-MIL-101(Al), using a “bottle around the ship” approach¹³². This, by the way, also prevents the dimerization of the Mn-salen complex, rendering it useless and inactive. As shown in Figure 6, the dimensions of the Jacobsen salen complex (approximately 1.7 x 1.2 x 0.5 nm) allow it to reside in the cages (2.9–3.4 nm, connected by windows of 1.2 and 1.6 nm) without being able to pass through the windows, thus effectively immobilizing the complex. The trapping of the active complex without any covalent or coordinative bonds keeps the structure in the optimal shape needed for achieving the high selectivity. This catalyst was tested for up to four runs with a minimal decrease in activity and complete retention of the selectivity. We also calculated that the transition state (that determines the selectivity) fits the pores of the host unhindered, allowing the reaction to exhibit the same behavior as with the homogeneous catalyst.

Table 5. Overview of MOFs examined for in chiral oxidation catalysis

Entry	Catalytic MOF	Reactant	Oxidant	Reaction parameters	Conversion (%)	Main product (ee%)	Take home message	Ref.
1	CMOF-1 [Zn ₄ (μ ₄ -O)(L) ₃], L= Mn-Salen complex	2,2-dimethyl-2 <i>H</i> -chromene and derivatives/ 1,2-dihydronaphthalene/ 1 <i>H</i> -indene	2-(<i>tert</i> -butylsulfonyl)iodosylbenzene	RT, 0.5h in CH ₂ Cl ₂ , 0.5 equiv. of oxidant	60-83/ >99/ 96	Epoxide (72-84/ 31/ 22)	Obtained <i>ee</i> values are comparable with the homogeneous Mn-Salen catalyst	¹²⁵
2	CMOF- <i>n</i> (<i>n</i> =1~5) [Zn ₄ (μ ₄ -O)(L) ₃] Mn-salen complex	1 <i>H</i> -indene (CMOF-1,3,5)	2-(<i>tert</i> -butylsulfonyl)iodosylbenzene	RT, 0.5h in CH ₂ Cl ₂ , 0.5 equiv. of oxidant	54~80	(1 <i>R</i> ,2 <i>S</i>)-indene oxide (47~64)	Rate of epoxidation reaction depend on the CMOF	¹²⁴

		Unfunctionalized alkenes (CMOF-4,5)			60-99	Epoxide (39-92)	open channel size (7.5% of the Mn-salen complex was leached out).	
3	poly(Cu-1)=Cu-linked(salen)Mn-polymer poly(M-1) with M= Cr, Mn, Fe, Co, Ni, Zn, Cd, Mg	2,2-dimethyl-2H-chromene	2-(tert-butylsulfonyl)iodosylbenzene	Molar ratio olefin/oxidant/catalyst= 100/150/1, 2h in CH ₂ Cl ₂	79 22-89	Epoxide (76) Epoxide (20-76)	Recycled up to 10 times with little loss in activity and no loss in enantioselectivity	122
4	Zn ₂ (bpdC) ₂ (L) ₁₀ DMF.8H ₂ O with L= salen(Mn) struts	2,2-dimethyl-2H-chromene	2-(tert-butylsulfonyl)iodosylbenzene	Molar ratio olefin/oxidant/catalyst= 4000/2000/1, 2h in CH ₂ Cl ₂	66-71	Epoxide (82)	Higher stability, easier separation, recyclability and substrate size selectivity	120
5	[Zn ₂ (bdc)(L-lac)(dmf)].(DMF)	Thioethers with small and bulkier substituents	Urea hydroperoxide/H ₂ O ₂	RT, 16 h in CH ₂ Cl ₂ , CH ₃ CN or CH ₂ Cl ₂ /CH ₃ CN	3-99	Sulfoxide	Could be reused at least 30 times, however no asymmetric induction was observed	129
6	[Zn ₂ (ndc){(R)-man}{dmf}].3DMF [Zn ₂ (bpdC){(R)-man}{dmf}].2DMF	2-NaphSMe/PhSCH ₂ Ph	H ₂ O ₂	RT, 16h in CH ₃ CN	78/70 57/78	Sulfoxide		131
7	[Ni ₃ (bpdC)(RR-L) ₂ .(DMF)] _n with L= Salen(Ni)complex	Styrene/cyclohexene	NaClO	RT, 24h in CH ₂ Cl ₂	22/34	Epoxide	Catalytic activity similar to the homogeneous counterpart	126
8	Mn ^{III} SO-DMF	2,2-dimethyl-2H-chromene	2-(tert-butylsulfonyl)iodosylbenzene	In CH ₂ Cl ₂	4000*	Epoxide(80)	Very high TON, stopping only due to the depletion of the oxidant	123
9	Mn ^{II} SO-DMF	2,2-dimethyl-2H-chromene	2-(tert-butylsulfonyl)iodosylbenzene	In CH ₂ Cl ₂	750*	Epoxide (37)	Long induction period due to oxidation of Mn ^{II} to Mn ^{III}	19b
10	Mn-salen@MIL-101(Al)	Dihydronaphthalene	meta-chloroperoxybenzoic acid (MCPBA) and N-methylmorpholine N-oxide(NMO)	RT, 2h in CH ₂ Cl ₂	69	Epoxide (70)	One-pot encapsulation strategy, the encapsulation have no effect on the ee% of the homogeneous catalyst.	132
11	[H ₂ NMe ₂] ₂ [Cd ₃ {TiO ₆ (TiL) ₃ }(BPDC) ₃ (H ₂ O) ₃ (H ₂ L= salan ligand (scheme 13a),)	Sulfides	30% H ₂ O ₂	0°C, 72h, Solvent: CH ₂ Cl ₂ , Substrate: oxidant=1:1.2	23~90	sulfoxides (67-82)	The MOF is stable in boiling H ₂ O or 30% aqueous H ₂ O ₂ for 3days)	127
12	Cd ₃ (m ₃ -OH)Br[(TiLOMe) ₂ O] ₂ (H ₂ L= salan ligand, (scheme 13d),	Sulfides	30% H ₂ O ₂	0°C, 16h, Substrate: oxidant=1:1.15	54~90	sulfoxides (23~62)	Recycled upto 4runs. The MOF catalyst shows improved enantioselect	128

										ivity relative to the homogeneous catalyst	
13	chiral, salen/[Cu ₂ (mand) ₂ (hmt)]	dimeric	Cr ^{III} –	trans-methyl cinnamate	NMO	RT, 72h, solvent: EtOH/H ₂ O (5:1)	Et ₃ N,	38.5~48.5	methyl 3-phenylglycidate (67.6~99.9)	Stable catalyst, no leaching observed. The presence of a donor ligand, Et ₃ N, the reaction rate is accelerated.	133

* TON value

4 Conclusions and perspectives

From this review, it can be concluded that there is an enormous growth of reports on MOFs in oxidation catalysis. Different types of substrates have already been examined (alcohols, alkenes, alkanes, thiols and sulfides..) in which MOFs were examined as such (e.g. MIL-101, Fe(BTC), MIL-47..) or served as a matrix for the incapsulation or post-modification with a homogeneous catalyst. In many of these reports the MOFs showed promising results in terms of activity, selectivity and stability. Nevertheless, to be able to compete with the industrial catalysts and to explore their industrial relevance, it is important that longer and more catalytic cycles are carried out in contrast to the few cycles (3-10 runs) presented now. At this moment, very few papers address the comparison of the MOF material with catalysts used in industry (e.g. zeolites, zeotypes, silica based materials). Most of the reports compare the catalytic activity of the MOF with the homogeneous counterpart or metal oxides.

In addition to this, more in depth studies are definitely required on the nature of the active site. In other words, a combined experimental and theoretical study to elucidate the catalytic mechanism is of a paramount importance. Within the concept of green chemistry, more efforts should be carried out to perform the oxidation reactions with clean oxidants like H₂O₂ or oxygen. Their use is probably hampered due to the very few MOFs which are known to be stable in water or air. We witness therefore a shift in research focus: in contrast to the original aim to design MOFs with unsaturated metal sites for catalytic applications, research groups are performing nowadays more efforts to enhance the intrinsic stability of the framework. This can be done by selecting a more rigid SBU or by performing a post-modification of a known stable framework. Only a few very stable frameworks have been reported, they include amongst others the UiO-66 (Zr) and several variants for the MIL-101 and MIL-100 (Cr, Al).

At this moment, the use of MOFs as chiral oxidation catalysts is still in an early stage, nevertheless the results reported so far show promising results in terms of an enhanced lifetime of the chiral MOF catalyst and similar *ee* values in comparison to the homogeneous counterpart. We believe that chiral and selective catalysis for the production of fine chemicals will be one of the most promising directions, hereby heterogenizing the fragile homogeneous complexes that are now used. In these mild, liquid phase conditions, catalyst attrition will be minimal and we have discussed in this review several studies that have shown that the *ee* or selectivity can be retained with respect to the original complex, the activity drops only marginally and the catalysts are reusable multiple times. Two distinct routes are

possible: one can create exciting chiral MOF structures with chiral struts and designed pore size to outperform the homogeneous complexes, one can also follow very simple encapsulation routes in pore designed MOFs, with complete retention of selectivity. The big advantage of designability and functionalizability of MOFs compared to zeolites should be more and more exploited by employing reactants in which chemo, regio and stereo selectivity aspects can be achieved.

Acknowledgments

Ying-Ya Liu acknowledges the Ghent University BOF postdoctoral Grant (Nr. 01P02911T) and the Fundamental Research Fund for the Central Universities of China (DUT13RC(3)85). Karen Leus acknowledges the Ghent University GOA Grant (Nr. 01G00710) and the Ghent University BOF postdoctoral Grant (Nr. 01P068135).

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