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Porous Metal Organic Frameworks as Multifunctional Catalysts for Cyclohexane Oxidation

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Catalysis drives the conversion of substrates to the wanted products under amenable reaction conditions. In this context, one reaction that is particularly important from the industrial point of view is cyclohexane aerobic oxidation to a mixture of the corresponding cyclohexanone and cyclohexanol. This industrial oxidation is key for the production of Nylon 6 and Nylon 6,6, two polyamides of growing production. The industrial process is clearly unsatisfactory since it is run at low cyclohexane conversions to avoid the formation of complex

mixtures, difficult to isolate. The present review shows the progress made in the use of metal-organic frameworks as solid catalysts for this important reaction, with emphasis in the intrinsic activity of metal nodes, tuning of the polarity of the internal voids or incorporation of active metal nanoparticles. It is shown that using MOFs as catalysts, it is possible to reach high cyclohexane conversions, while the combined alcohol + ketone selectivity still close to the 90% limit.

1. Introduction

Cyclohexane aerobic oxidation is among the less-efficient large-scale industrial process carried out nowadays.^[1–5] Industrial cyclohexane oxidation is carried out under pressure at about 150 °C with a cyclohexane conversion of about 5% with a selectivity to the cyclohexanol and cyclohexanone mixture (KA oil) over 90%.^[6] The reaction mechanism is a radical chain type I aerobic oxidation that is promoted by cobalt naphthenate. This catalyst is an ill-defined mixture of Co(II)-carboxylates of naphthalenecarboxylic isomers. As in other aerobic oxidations, the main problem is the difficulty in controlling substrate selectivity of the radical attack in the presence of reaction products, resulting in overoxidation of the initial primary products. As cyclohexane conversion increases, overoxidation results in very complex reaction mixtures of very difficult purification, impurities being highly detrimental for the subsequent use of cyclohexanone.^[7]

Cyclohexanone is a bulk chemical, precursor of polyamide fibres of growing production, such as Nylon-6 and Nylon-6,6.^[5,8] Thus, although the use of oxygen as oxidizing agent is very appealing due to its availability, the lack of selectivity in the

aerobic oxidation forces to run the process at very low cyclohexane conversion, with the penalty of having to separate and recycle very large volume of starting materials.^[9] The present review focuses on this single oxidation reaction namely, the conversion of cyclohexane into KA oil catalysed by metal organic frameworks (MOFs) with the aim to show the advantages that these materials offer as oxidation catalysts and the recent progress in this field.

MOFs^[10–13] consisting in crystalline porous solids with metal nodes coordinated with rigid bi- or multipodal organic linkers defining an open lattice have become among the most researched solid catalysts due to the combination of favourable properties.^[14–19] The large transition metal content of the materials and the presence of exchangeable coordination positions^[20,21] or defects around the metal sites make these solids to exhibit general Lewis acidity^[22] that can promote not only acid-base reactions,^[23–25] but also can activate a series of oxidizing agents, including H₂O₂ and organic hydroperoxides.^[26,27] In this way, due to the presence of Lewis acid character, these MOFs behave as oxidation catalysts^[28–32] without really being involved in electron transfer processes, just by increasing the electrophilicity of oxygen atoms in (hydro)peroxides. The large percentage of transition metal in the composition of MOFs in comparison to Lewis acid zeolites or mesoporous aluminosilicates makes MOFs very appropriate as solid catalysts, particularly considering the large accessibility of active sites derived from their open structure and high porosity.^[33,34]

Besides the nature of the metal and accessibility to the active sites, one important parameter to consider in cyclohexane oxidation is the polarity of the internal voids in where the reaction taking place. In fact, one of the most powerful tools that has been proposed to increase cyclohexane oxidation selectivity preventing KA oil overoxidation is the control on the polarity of the reaction space.^[35,36] Embedding the active site in a hydrophobic reaction cavity with low polarity

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favours adsorption and reaction of apolar cyclohexane preferentially vs. the reaction products that are more polar and with increased hydrophilicity. It will be shown in this article that this concept of tuning the hydrophobicity of the MOF micropores has worked well to favour the selective oxidation of cyclohexane, although there is still room for improvement, particularly when oxygen in combination with other oxidizing agents is involved in the process.

When revising the literature and comparing the performance of different catalysts for cyclohexane oxidation, several comments must be considered. The first one refers to the mass balance and possible over estimation of cyclohexane oxidation. Since cyclohexane boiling point is low and frequently the reactions are carried out in batch under a certain pressure, opening of the system results in unavoidable cyclohexane release that can mislead quantification, being accounted as higher cyclohexane conversion if the number of moles of unreacted cyclohexane and all the combined reaction products are not quantified.

Another aspect refers to product distributions determined by gas chromatography (GC) analysis. Cyclohexylhydroperoxide (CHHP), a common intermediate and product of cyclohexane oxidation, if present in the reaction mixture will decompose during the GC analysis, again misleading the product distribution. Other case is adipic acid, the overoxidation product of cyclohexanone, that due to the very different physical proper-

ties, is generally not detectable by GC even if formed as one of the reaction products.

Since the reaction mechanism involves a radical chain pathway, comparison between different catalysts can also be misleading if TON values are used without considering the reaction conditions. Thus, it can be that uncatalyzed long reaction chain with oxygen could appear as indicating an efficient catalyst, while in reality it is just acting as an initiator generating the first radicals in the system, but not really participating in the formation of each product molecule.

Hydrophobicity has been achieved by selecting appropriate ligands for the synthesis of MOFs, but also by post-synthetic modifications. Post-functionalization has the advantage that can be applied when the material has been already synthesised by conventional methods, since in many cases hydrophobicity requires the presence of substituents and groups that are not compatible with most of the common solvothermal procedure for MOF synthesis.

Due to the above commented properties of MOFs, these solids have been reported for oxidation reactions. In one of these examples, the activity of porphyrin-based MOFs as heterogeneous catalyst for wide range of oxidation reactions using different substrates like cyclohexane, ethylbenzene, styrene and phenolic derivatives has been summarized.^[37] In another review, the oxidation of cyclohexane with different solid catalysts, like carbons, zeolites and MOFs was presented.^[38] Although these reviews have discussed large number of



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Sergio Navalón was born in Valencia (Spain) in 1979. He graduated in Chemical Engineering in 2003 and obtained his PhD in 2010 at the Technical University of Valencia (UPV). Currently, he is working as Associate Professor at the Chemistry Department of UPV. His research area includes the development of heterogeneous (photo)catalysts based on metal-organic frameworks, carbon-based materials and metal nanoparticles for the chemical industry, energy and environmental applications. He is the recipient of a Medal of the Real Academia de Ingeniería (Spain) as young researcher. He has co-authored more than 100 publications and holds one patent.



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examples with carbons and zeolites as catalysts, the discussion with MOF as catalysts was limited.^[38] In the present review article, we wish to exclusively focus on the use of MOFs as solid catalysts for the oxidation of cyclohexane with different active sites. This would provide readers a complete survey on this important reaction using MOFs as solid catalysts. In addition, this review also includes a section on the light-assisted oxidation of cyclohexane using MOFs as photocatalysts.

The present article is organized by first showing the examples of cyclohexane oxidation promoted by the activity of MOF metal nodes, followed by those cases in which the ligand has been modified for the purpose of controlling the oxidation reaction and, then, by those reports in which the activity derives from metal nanoparticles (NPs) that have been hosted inside MOF micropores. This classification is somehow flexible, since in several cases it has been shown that both metals and ligands cooperate in the oxidation process. Also, metal complexes adsorbed/attached to the MOF could be classified in both sections. The final section provides our view on the challenges remaining ahead and the expected developments in the future.

2. Metal nodes as active sites in cyclohexane oxidation

This section compiles those examples in where MOFs have been reported as heterogeneous solid catalysts for the oxidation of cyclohexane based on the catalytic activity of metal nodes. The existing literature is organized based on the nature of metal. Table 1 summarizes the examples that have been reported as heterogeneous catalysts for cyclohexane oxidation, summarizing the reaction conditions, conversion level, selectivity and stability evidence. This would certainly provide the readers an overview of cyclohexane oxidation using MOFs as well as the existing gaps in terms of material stability or conversion/selectivity data.

Thus, Cu-MOFs exhibit general catalytic activity to promote cyclohexane oxidation using H₂O₂ and other oxidizing reagents. In one of the earlier works in the field, the Cu-based MOF ([Cu₃(μ₃-OH)(μ-pz)₃(EtCOO)₂(H₂O)] (pz: pyrazolate) was prepared and its activity was tested in the cyclohexane oxidation using HNO₃ and H₂O₂ in acetonitrile.^[39] Under these conditions, the activity of this solid was 27.9% yield of cyclohexanol and cyclohexanone. Although the reaction conditions were optimized to achieve higher yields of the oxidation products, no efforts were made to characterize the solid after the catalytic

Table 1. List of MOFs as heterogeneous catalysts for the oxidation of cyclohexane.

Catalyst	Reaction conditions	Con. [%]	Sel. [%]	Stability evidence	Ref.
[[Cu ₃ (μ ₃ -OH)(μ-pz) ₃ (EtCOO) ₂ (H ₂ O)]	Cyclohexane (1 mmol), catalyst (10 μmol), HNO ₃ (0.10 mmol), 30% H ₂ O ₂ (5 mmol), CH ₃ CN (4 mL), RT	–	27.9 ^[a]	Not reported	[39]
[Cu ₆ (Hmdea) ₆ Fe(CN) ₆](NO ₃) _{2n} ·7nH ₂ O	Cyclohexane (1 mmol), catalyst (1 μmol), CH ₃ CN (4 mL), HNO ₃ (0.10 mmol), 30% H ₂ O ₂ (5 mmol), RT, 6 h	–	22 ^[a]	Not reported	[40]
[Cu ₃ (μ ₃ -4-ptz) ₄ (μ ₂ -N ₃) ₂ (DMF) ₂] _n ·(DMF) _{2n}	Cyclohexane (5 mmol), catalyst (2.5–5 μmol), H ₂ O ₂ (10 mmol), RT, 10 h	–	40 ^[a]	4 reuses, FT-IR	[41]
Cu ₃ (BTC) ₂	Cyclohexane (0.5 mL), catalyst (0.03 g), 30% H ₂ O ₂ (2 mL), CH ₃ CN (4 mL), 70 °C, 24 h	52	100	–	[42]
copper-phenylsilsesquioxane	Cyclohexane (0.46 M), catalyst (5 × 10 ⁻⁴ M), H ₂ O ₂ (2 M aq. 50%), CH ₃ CN (2 mL), 60 °C, 2.5 h	–	20 ^[a]	Not reported	[43]
Cu-MOF-808(Ce)	Cyclohexane (4.3 mL), catalyst (1 μmol), TBHP (1.4 mL), 65 °C, 16 h	–	–	Not reported	[44]
MIL-101(Cr)	Cyclohexane (4.6 mmol), catalyst (5 mg), TBHP (4 mmol), 70 °C, 8 h	36	83	5 reuses, XRD, FT-IR	[45]
Zr-PCN-221(Fe)	Cyclohexane (10 mL), catalyst (5 mg), TBHP (14 μL), 65 °C, 22 h	–	92.3	Not reported	[46]
Fe ₂ -MOF-5	Cyclohexane (1 mL), catalyst (0.1 g), 30% H ₂ O ₂ (1 mL), CH ₃ CN (13 mL), 80 °C, 4 h	40	95.4	Not reported	[47]
MIL-100(Fe)-2	Cyclohexane (11 mmol), catalyst (80 mg), 4 M H ₂ O ₂ in CH ₃ CN (1.1 mmol), CH ₃ CN (9 mL), 65 °C, 3 h	–	–	Reuse, SEM, FT-IR	[48]
PCN-222(Fe)-F7	Cyclohexane (0.1 mmol), catalyst (20 mg), O ₂ (1 bar), CH ₃ CN (2.5 mL), AgBF ₄ (25.6 mg), 80 °C, 24 h	50.2	90	3 reuses, XRD	[49]
Fe ₂ (dotpdtctBu)	Cyclohexane (0.3 mL), catalyst (5 mg), ^t BuSO ₂ PhIO (0.073 mmol), CD ₃ CN (1 mL), RT, 1.5 h	–	82 ^[a]	Mössbauer spectroscopy	[50]
Zr-MOF-Fluorinated	Cyclohexane (1 mmol), catalyst (20 mg), O ₂ purged, CH ₃ CN (2.5 mL), AgBF ₄ (26 mg), 60 °C, 24 h	21	84	2 reuses, XRD	[51]
Mn-TMPyP encapsulated in rho-ZMOF	Cyclohexane (10 ml), catalyst (88 mg), TBHP (77 μmol), 65 °C, 24 h	–	91.5 Y	11 reuses, UV-Vis	[52]
[Zn ₂ (MnOH-TCPP)-(DPNI)]·0.5DMF·EtOH·5.5H ₂ O	Cyclohexane (50 mmol), catalyst (0.0025 mmol), PhIO (100 mmol), CH ₃ CN (50 mL), RT, 20 h	94	100	6 reuses	[53]
Co-TCPPCu	Cyclohexane (200 mmol), catalyst (16 mg), O ₂ (1 MPa), 120 °C, 8 h	5.31	93	Not reported	[54]
Co(L)(PTA) ₂	Cyclohexane (10 mL), catalyst (2%), TBHP (0.31 mmol), 60 °C, 22 h	88	100	4 reuses, XRD, ¹ H-NMR, SEM	[55]
NENU-MV-1	Cyclohexane (5 mL), catalyst (50 mg), O ₂ (1 MPa), 150 °C, 2 h.	24.6	99	5 reuses, XRD	[56]

[a] total yield of cyclohexanol and cyclohexanone; TBHP: t-butylhydroperoxide.

reaction. It is essential to perform reusability studies and leaching tests to ascertain the catalyst stability, especially when highly corrosive reagent, such as HNO_3 , is used.

Three-dimensional heterometallic $\text{Cu}^{\text{II}}/\text{Fe}^{\text{II}}$ MOFs, $[\text{Cu}_6(\text{H}_2\text{tea})_6\text{Fe}(\text{CN})_6]_n(\text{NO}_3)_{2n}\cdot 6n\text{H}_2\text{O}$ (tea: triethanolamine) and $[\text{Cu}_6(\text{Hmdea})_6\text{Fe}(\text{CN})_6]_n(\text{NO}_3)_{2n}\cdot 7n\text{H}_2\text{O}$ (Hmdea: N-methyldiethanolamine) were synthesised by reacting copper(II) nitrate with tea or H_2mdea , respectively.^[40] The activity of these solids was checked in the oxidation of cyclohexane under mild conditions using hydrogen peroxide as oxidant and HNO_3 as promoter. Among the various experimental conditions screened, the total yield (based on cyclohexane) and turnover number (TON) were 22% and 470, respectively, with $[\text{Cu}_6(\text{Hmdea})_6\text{Fe}(\text{CN})_6]_n(\text{NO}_3)_{2n}\cdot 7n\text{H}_2\text{O}$ as catalyst. No data were reported regarding the stability of these solids under these experimental conditions, something that, as it has been commented in the previous paragraph, is a prerequisite for any further application at larger scale.

Microwave has been employed as a tool to synthesize a Cu-based MOF, namely $[\text{Cu}_3(\mu_3\text{-}4\text{-ptz})_4(\mu_2\text{-N}_3)_2(\text{DMF})_2]_n \cdot (\text{DMF})_{2n}$ (4-ptz : 5-(4-pyridyl)tetrazolate), and its catalytic performance was examined in the oxidation of cyclohexane with aqueous H_2O_2 at room temperature without any added solvent or additive.^[41] Under these conditions, the oxidation of cyclohexane took place to the corresponding KA oil reaching 40% yield with TON of 396 and turnover frequency (TOF) of 40 h^{-1} . The solid catalyst was recycled at least four consecutive cycles, retaining 90% of its initial activity. No structural changes from the fresh to the reused sample were observed by FT-IR spectroscopy. However, further characterization is essential to ascertain the structural integrity of the reused solid in this type of oxidation reaction, particularly chemical analysis to ascertain the absence of metal leaching from the solid to the liquid phase.

In another precedent, the activity of $\text{Cu}_3(\text{BTC})_2$ (BTC: 1,3,5-benzenetricarboxylate) was tested in the cyclohexane oxidation using 30% H_2O_2 as oxidizing reagent at 70°C .^[42] Under these conditions, the conversion was 52% at 24 h with the selectivity of cyclohexanol and cyclohexanone of 40 and 60%, respectively. No reusability data and stability tests were reported.

Synthesis of ionic ethylenediamine-containing copper-phenylsilsesquioxane was performed through the direct interaction of Cu,Na -silsesquioxane with ethylenediamine (Figure 1) and the activity of the resulting complex was studied in the cyclohexane oxidation using H_2O_2 as an oxidant.^[43] The total yield of the oxygenated products was 20% with respect to cyclohexane after 2 h at 60°C .

In one of the recent studies, the rate of catalytic oxidation of cyclohexane was four times higher with Cu supported on Ce- or Zr-based MOFs.^[44] The advantage of this approach to host Cu species inside the pores of a robust MOF is to combine the higher stability due to the structure with the inherent redox catalysis of Cu. This is particularly important, since the structural stability of most $\text{Cu}^{[2+]}$ is not remarkable. In this way, the reaction between $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and MOF-808(Ce) ($[\text{Ce}_6\text{O}_4(\text{OH})_{10}(\text{BTC})_2(\text{H}_2\text{O})_6]$, or MOF-808(Zr) $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BTC})_2(\text{HCOO})_6]$) resulted in $\text{Cu}\text{-MOF-808}(\text{Ce})$ and $\text{Cu}\text{-MOF-808}(\text{Zr})$, respectively (Figure 2). The catalytic perform-

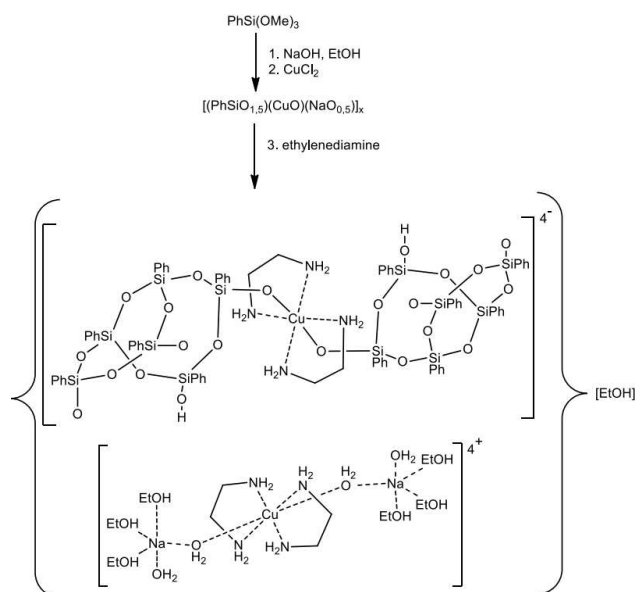


Figure 1. Synthesis of copper-phenylsilsesquioxane complex. Reproduced with permission from ref. [43] Copyright 2020 American Chemical Society.

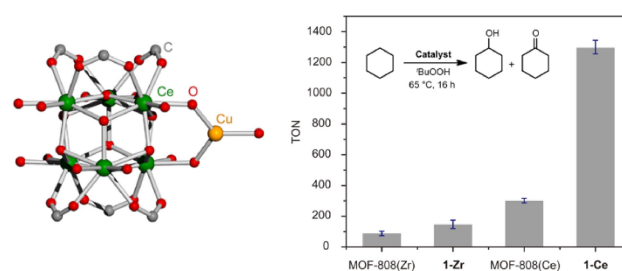


Figure 2. Illustration of the coordination sphere of copper atoms in $\text{Cu}\text{-MOF-808}(\text{Ce})$ (left). Cyclohexane oxidation with $\text{Cu}\text{-MOF-808}(\text{Ce})$ (1-Ce), $\text{Cu}\text{-MOF-808}(\text{Zr})$ (1-Zr), MOF-808(Ce) and MOF-808(Zr) (right). Reproduced with permission from ref. [44] Copyright 2020 American Chemical Society.

ance of these solids was tested in the cyclohexane oxidation using TBHP as oxidant at 65°C for 16 h. The activity of $\text{Cu}\text{-MOF-808}(\text{Ce})$ was significantly higher, affording in the formation of KA oil the highest TON compared to $\text{Cu}\text{-MOF-808}(\text{Zr})$ and with the pristine solids (Figure 2). The enhanced activity of $\text{Cu}\text{-MOF-808}(\text{Ce})$ was ascribed to the differences in the nature of the Cu species, proposing based on XAS studies that MOF-808(Ce) favours mononuclear Cu active sites, while Zr support stabilizes higher nuclearity Cu species.

Besides Cu, other transition metals in MOF metal nodes can also promote cyclohexane oxidation. Thus, MIL-101(Cr) is among the most stable MOFs. In one of the seminal works, MIL-101(Cr) and MIL-101(Fe) samples were tested as heterogeneous catalysts for the oxidation of cyclohexane.^[45] Among the various experimental conditions optimized, MIL-101(Cr)/TBHP afforded 36% conversion of cyclohexane with 83% selectivity to KA oil at 70°C . Under identical conditions, MIL-101(Fe)/TBHP/ O_2 resulted in 38% conversion of cyclohexane with 49% selectivity of KA oil and 51% CHHP. Furthermore, MIL-101(Cr) was reused

five cycles with no decay in its activity. The structural integrity of the reused solid was confirmed by powder XRD and FT-IR spectroscopy.

Metal porphyrins are known as oxidation catalysts.^[57–60] However, as soluble complexes they exhibit a poor TON, due to self oxidation and decomposition.^[60] Zr-PCN-221(Fe) was prepared and its catalytic performance was examined in the cyclohexane oxidation using TBHP as oxidant at 65 °C.^[46] Under optimized experimental conditions, cyclohexane was converted to cyclohexanone and cyclohexanol with yields of 86.9 and 5.4%, respectively. In contrast, no conversion of cyclohexane was observed with Zr-PCN-221(no metal). The high reactivity and selectivity was attributed to the presence of high-density of accessible active porphyrinic iron(III) centers within the porous framework. No data were shown regarding the catalyst stability under the optimized reaction conditions.

Mixed-metal MOFs offer the opportunity to improve further the catalytic activity by combining two metals with complementary redox properties.^[61–63] In a study addressing the influence of two metals on the catalytic activity, a series of mixed metal MOFs (Fe₄-MOF-5, Fe₂-Zn₂-MOF-5 and Fe_{0.9}-Zn_{3.1}-MOF-5) were prepared, characterized and their activity was examined in the oxidation of cyclohexane using H₂O₂ in acetonitrile at 80 °C.^[47] Among these solids, the highest conversion of cyclohexane (40%) was observed with Fe₄-MOF-5 with the selectivity of 48.3% for cyclohexanol and 47.1% for cyclohexanone. In addition, 4.6% of CHHP was also detected. However, catalyst stability was not reported. This is one of the issues to be addressed since the reaction conditions make use of oxidant, and hence, there is a possibility for catalyst damage and metal leaching. Besides, the potential benefits of having more than one metal in the MOF were not realized, probably due to the fact that Zn²⁺ being a d¹⁰ transition metal does not exhibit general redox activity. For this reason, the catalytic activity of the mixed metal MOF is disfavoured respect to the monometallic Fe-MOF.

Besides mixed metal MOFs, the same metal can be present in two different oxidation states. This is the case of MIL-100(Fe) in which, depending on the activation conditions, there is a spontaneous thermal reduction of Fe(III) ions present in the as-synthesised material to Fe(II). The fraction of redox-active Fe(II/III) sites in MIL-100(Fe) was tuned by different pretreatment temperatures (MIL-100(Fe)-1 and MIL-100(Fe)-2) (Figure 3).^[48] The activity of these solids was tested in the cyclohexane

oxidation at 65 °C using 30% H₂O₂ as oxidant in acetonitrile. The catalytic data revealed that MIL-100(Fe)-2 exhibited much higher activity than MIL-100(Fe)-1 in the cyclohexane oxidation. This was due to the fact that MIL-100(Fe)-2 was activated at 250 °C, thus containing higher population of Fe^{II} sites, while MIL-100(Fe)-1 exclusively contains Fe^{III} sites, since the sample was activated at 150 °C. Furthermore, the enhanced activity of MIL-100(Fe)-2 was due to the rapid decomposition of CHHP in the presence of high Fe^{II} sites, which is consistent with Haber Weiss reaction. Reusability experiments indicated that the activity of MIL-100(Fe)-1 was slightly decreased in the second cycle, but retained in the third cycle. In contrast, MIL-100(Fe)-2 showed identical product yields during three cycles. However, SEM and FT-IR analyses of the fresh and reused solids of MIL-100(Fe)-1 and MIL-100(Fe)-2 did not show any changes in their pattern and morphology. Clearly this strategy of using the same metal in two different oxidation states deserves further exploration as well as deeper understanding of the origin of the synergy between the two oxidation states.

As commented earlier, one of the merits of using MOFs as heterogeneous catalysts is their ability to adjust the nature of active sites by engineering the pore walls of the framework. Control of the hydrophilic/hydrophobic nature of the catalyst surface is known to be important to favour cyclohexane adsorption and decrease consecutive oxidation reactions of the KA products by disfavoring they adsorption near the active sites.^[64] In this aspect, hydrophobic engineering of pore walls of an iron-porphyrinic MOF, PCN-222(Fe) was performed by post-synthetic treatment with perfluorinated alkylcarboxylic acids and their catalytic activity was tested in cyclohexane oxidation.^[49] Among the modified PCN-222(Fe) solids, PCN-222(Fe)-F7 afforded 50.2% of cyclohexane conversion with 90% selectivity of KA oil using TBHP as oxidant and AgBF₄ as cocatalyst in O₂ at 80 °C. Under identical conditions, the activity of PCN-222(Fe) was 20.5% conversion with 81% selectivity of KA oil. In contrast, the homogeneous iron porphyrin complex was inactive for this reaction. It was proposed that grafting of perfluorinated alkylcarboxylate units on the pore walls significantly increased the hydrophobicity, thereby facilitating the preferential adsorption of cyclohexane in the confined space in comparison with its more polar reaction products. Remarkably, the use of AgBF₄ creates a weak coordination between the BF₄⁻ and Fe(III) sites, facilitating the formation of an active Fe(IV)-oxo species. Furthermore, PCN-222(Fe)-F7 was used in three consec-

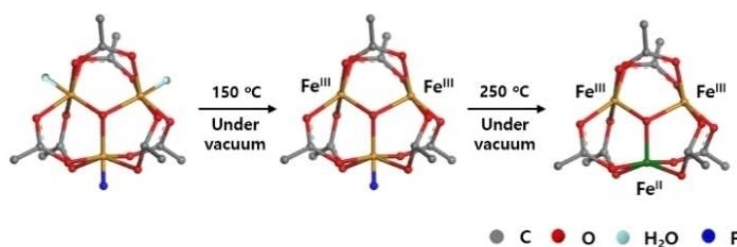
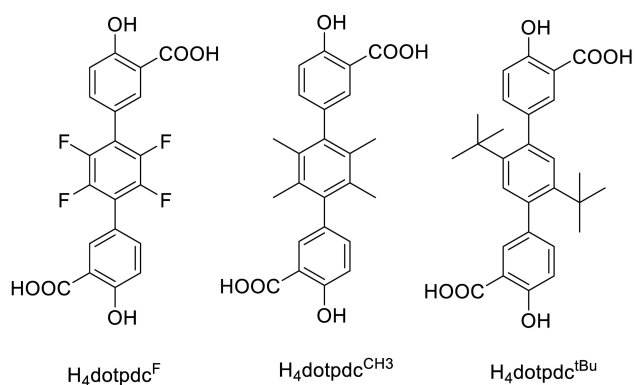


Figure 3. Spontaneous reduction of nodal Fe^{III} to Fe^{II} in MIL-100(Fe) and formation of coordinatively unsaturated sites on Fe. Reproduced with permission from ref. Reproduced with permission from ref. [48] Copyright 2019 Wiley.

utive reactions with no decrease in its conversion and KA selectivity. Also, the structural stability of the used solid was checked by powder XRD, without observing difference in the crystalline pattern between the fresh and the reused sample.

In another related study tuning the hydrophilicity of the internal voids, the MOFs were synthesised with hydrophobic groups attached to the ligands and their influence on the catalytic activity of MOFs in the cyclohexane oxidation was reported. In this work, three new MOFs were prepared based on $\text{Fe}_2(\text{dotpdc})$ (dotpdc: dihydroxy-[1,1':4',1''-terphenyl]-3,3''-dicarboxylic acid) in which the central ring is substituted with tetrafluoro-, tetramethyl-, or 1,4-di-*tert*-butyl groups (see Scheme 1) to obtain $\text{Fe}_2(\text{dotpdcR})$ ($\text{R}=\text{F}$, CH_3 , and ^tBu), respectively.^[50] The series also included the parent, unfunctionalized $\text{Fe}_2(\text{dotpdc})$ MOF. Interestingly, these solids did not



Scheme 1. Structures of terphenyl derivatives used as linkers to prepare the series of $\text{Fe}_2(\text{dotpdcR})$ MOFs.

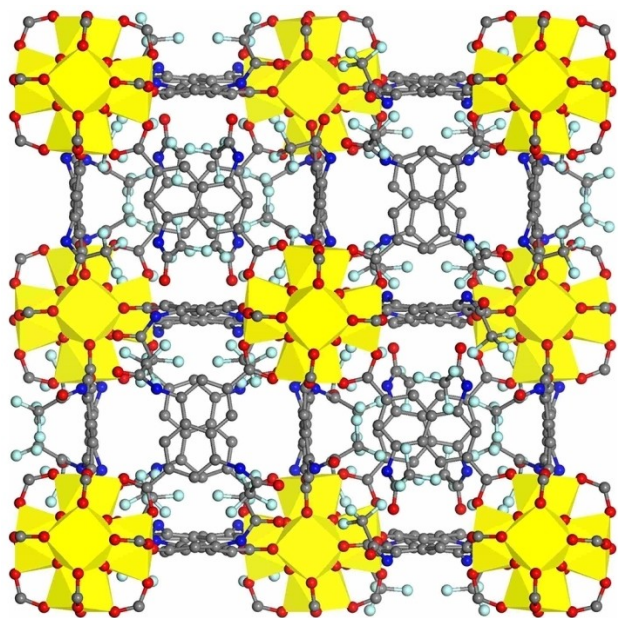


Figure 4. Simulated cubic framework structure of DUT-52- NHCOCF_3 MOF in a ball and stick model. Reproduced with permission from ref. [51] Copyright 2021 American Chemical Society.

exhibit many differences in the surface areas and pore size. All these solids behaved as heterogeneous catalysts as evidenced by leaching tests and no evidences were observed for the loss of crystallinity. However, these four $\text{Fe}_2(\text{dotpdcR})$ solids showed significantly different selectivity of KA oil ratio and TONs. The order of increasing activity of MOFs with the functional groups is $\text{H} < \text{F} < \text{CH}_3 < ^t\text{Bu}$ with a 3-fold increase in A:K ratio (from 2.8:1 to 8.4:1) and a 5-fold increase in TON (from 4 to 19). It was found that $\text{Fe}_2(\text{dotpdcCH}_3)$ and $\text{Fe}_2(\text{dotpdc}^t\text{Bu})$ solids were partially deactivated. Based on Mössbauer spectroscopy, it was proposed that deactivation derives from the oxidation of the active Fe(II) form to the inactive Fe(III) hydroxide or alkoxide species, rather than framework collapse or ligand degradation.

A Zr-MOF with face-centred cubic topology having a DUT-52 (DUT: Dresden University of Technology) structure was prepared with 1-(2,2,2-trifluoroacetamido)naphthalene-3,7-dicarboxylic acid ($\text{H}_2\text{NDC-NHCOCF}_3$) ligand (Figure 4) and its catalytic performance in the cyclohexane oxidation in acetonitrile using AgBF_4 as cocatalyst under aerobic condition at 60°C was examined.^[51] Under these conditions, the aerobic oxidation of cyclohexane with Zr-MOF (21% conversion) was higher compared to analogous DUT-52 without fluorine groups (6% conversion) solid under identical conditions. These catalytic data indicate again the benefits of hydrophobic cavities of Zr-MOF in achieving higher conversion of cyclohexane with high KA oil selectivity. Zr-MOF was reused in two consecutive cycles and powder XRD of the reused sample did not show any change respect to the fresh solid.

MOFs can also be hosts of active molecular complexes. Compared with other microporous solids, MOFs offer some advantage related to larger porosity and the presence of structural metals and linkers. Thus, in one of the early works, Eddaoudi and co-workers encapsulated inside a crystalline MOF the Mn complex of the H_2RTMPyP (TMPyP: 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin) and reported its activity in the cyclohexane oxidation under neat conditions at 65°C with TBHP as oxidant.^[52] Under these conditions, the total yield of KA oil was 91.5% with a TON of 23.5. The activity of this solid catalyst based on MOF was much superior compared to other metalloporphyrins supported on zeolites or mesoporous silicates (Table 2). Interestingly, the solid catalyst was recyclable for at least 11 times by retaining its crystallinity, activity and selectivity. Also, no leaching of the metalloporphyrin was observed in the reaction mixture as evidenced from the UV-Vis spectrum. Further, the superior performance of Mn-TMPyP encapsulated in rho-ZMOF was attributed to the perfect stabilization of metalloporphyrin within the pores of MOFs by avoiding the formation of bridged μ -oxide dimers, whose formation is not possible in the rigid MOF lattice, and oxidative self-degradation, which is very common in homogeneous metalloporphyrin-based catalysts. Given the excellent performance of this catalyst, it would be important to confirm these results and even trying to optimize further the TON value by combining TBHP with O_2 to enhance the activity of this catalyst.

The synthesis of a porous $[\text{Zn}_2(\text{MnOH-TCPP})\cdot(\text{DPNI})] \cdot 0.5\text{DMF} \cdot \text{EtOH} \cdot 5.5\text{H}_2\text{O}$ (TCPP: tetrakis(4-carboxyphenyl)porphyrin); $\text{DPNI}=\text{N,N}'\text{-di}((4\text{-pyridyl})\text{-1,4,5,8-naph-$

Catalyst	T [°C]	Time [h]	Oxidant	TON	Yield [%]	Ref.
Fe(III)-Pd encapsulated in zeolite Y	r.t.	6	PhIO	7.6	38	65
Fe(III)-TMPyP encapsulated in zeolite X	r.t.	7.5	PhIO	10	60	66
Fe(III)-TMPyP supported on silica surface/matrix	r.t.	Not Reported	PhIO	2~20	2~20	67
Mn-TMPyP encapsulated in rho-ZMOF	65	24	TBHP	24	91.5	52

thalenetetracarboxydiimide) (Figure 5) was performed and its catalytic activity in the oxidation of cyclohexane was examined.^[53] The structural analysis of this MOF revealed that the basic $Zn_2-(COO)_4$ paddle-wheel clusters are bridged by metalloporphyrin to form two-dimensional sheets that are further bridged by the organic DPNI pillar resulting in a porous structure. This solid exhibited 94% conversion of cyclohexane with 100% selectivity to KA oil in acetonitrile at room temperature using PhIO as oxidant. Although the catalyst was recycled for six cycles, the reused solid exhibited a slight decay in its

conversion to 79%. However, the reasons for this decay in its activity were not addressed.

Two-dimensional MOFs consisting of two different active centres (Co–Cu, Co–Zn, Cu–Zn) were prepared employing also metalloporphyrins as organic linkers (Figure 6) and the activity of these solids was tested in the cyclohexane oxidation.^[54] The conversion of cyclohexane under aerobic conditions at 120 °C using the homogeneous metalloporphyrin complex was only 4.39%, while the conversion was 5.31% with Co-TCPPCu. The selectivity of cyclohexanol, cyclohexanone and CHHP under these conditions was 49, 44 and 2%, respectively. The enhanced

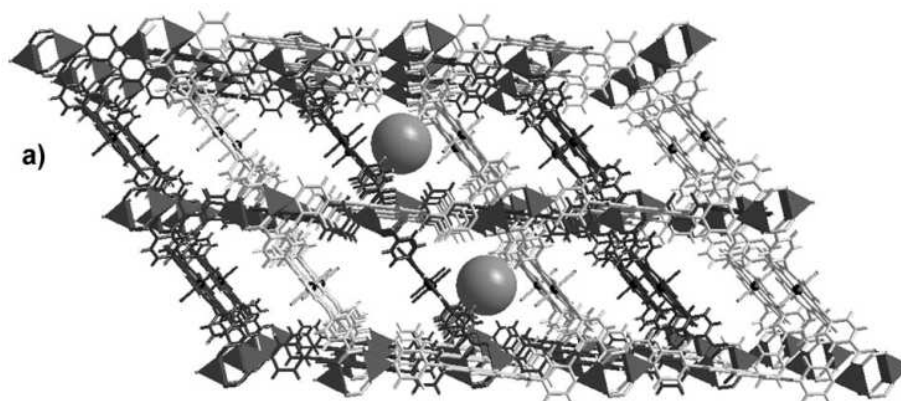


Figure 5. X-ray crystal structures of a) $[Zn_2(MnOH-TCPP)-(DPNI)] \cdot 0.5DMF \cdot EtOH \cdot 5.5H_2O$. Reproduced with permission from ref. [53] Copyright 2013 Wiley.

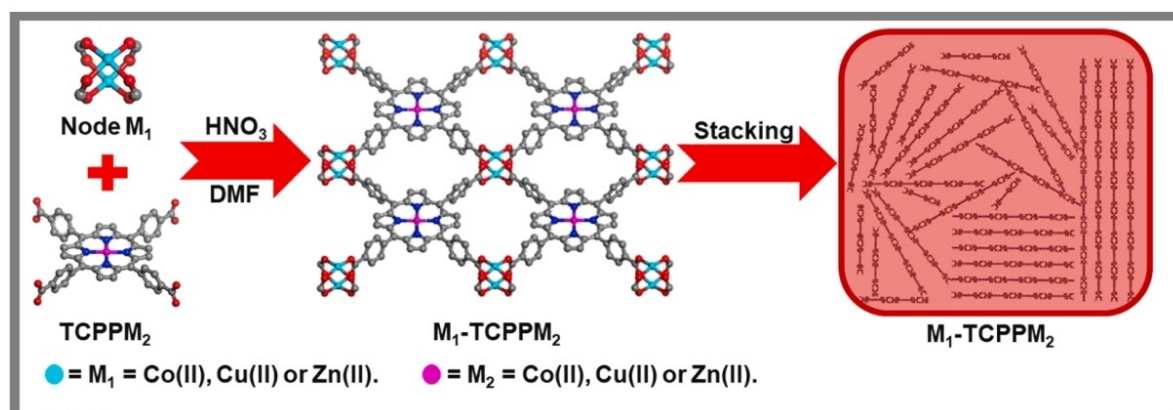


Figure 6. Schematic syntheses of 2D MOFs possessing bimetallic active centers. Reproduced with permission from ref. [54] Copyright 2022 Elsevier.

catalytic performance of Co-TCPPCu was mainly attributed to the decreased autoxidation of the partial oxidation products, the suppressed free radical diffusion in the 2D MOFs due to some confinement and the enhanced C–H bond oxidation with oxidation of CHHP intermediate. No data were shown for the stability of this catalyst. On the other hand, a mesoporous cobalt-containing silicate Co-TUD-1 was also reported as an efficient heterogeneous catalyst for the selective oxidation of cyclohexane to KA oil with very high stability with complete conversion of CHHP, without observing Co leaching.^[68] It is mandatory to establish the stability of solid catalyst in any of the oxidation reactions, especially oxidation of cyclohexane since there is always a possibility to produce adipic acid that acting as ligand as one of the by-products.

In another present, a 3D porous Co(L)(PTA)₂ (PTA: p-terephthalic acid; Scheme 2) MOF with coordinatively unsaturated metal sites was reported as an efficient heterogeneous solid catalyst for the oxidation of cyclohexane with TBHP as an oxidant at 60 °C after 22 h.^[55] Under these conditions, Co(L)(PTA)₂ afforded 88% conversion with complete selectivity to KA oil. Leaching test confirmed the absence of Co leaching from the solid. On the other hand, ¹H-NMR analysis showed no evidence for the presence of the ligand (L) in the filtrate of the solution, thus proving the stability of the catalyst. The catalyst was used five cycles with a conversion of 83% after fifth cycle. Powder XRD confirmed the crystallinity of the five times used solid catalyst. SEM images of the five times used solid showed identical morphology to the fresh catalyst.

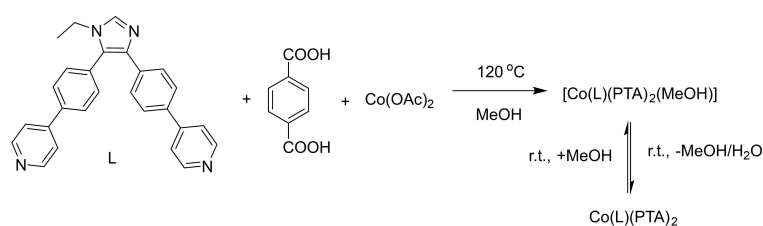
Recently, Luo and co-workers have shown that the catalytic cyclohexane oxidation under aerobic conditions can be facilely altered through rational size regulation by employing mixed-valence (V₁₆) cluster-based MOF (NENU-MV-1).^[56] The average particle size of NENU-MV-1 was altered from 25 μm to 500 nm by changing the reaction temperature, precursor concentration and molar ratio between metal and ligand during the

solvothermal synthesis. Notably, NENU-MV-1 with 500 nm particle size gave the highest cyclohexane conversion (24.6%; 228.6 h⁻¹) with KA oil selectivity of 99% at 150 °C under aerobic conditions. Under identical conditions NENU-MV-1 with 1–5 μm, 1–15 μm and 1–25 μm particle sizes afforded 18.5 (156.2 h⁻¹), 15.7 (137 h⁻¹) and 9.63% (76.2 h⁻¹) conversions, respectively. In contrast, the activity of bulk crystalline NENU-MV-1 was 5.25% cyclohexane conversion with TOF value of 60 h⁻¹, which is significantly lower than the above catalysts. Furthermore, NENU-MV-1-500 nm solid was reused five times with no loss in its activity and selectivity. On the other hand, the structural integrity of the reused solid was identical to the fresh catalyst as evidenced by powder XRD.

3. Ligand functionalized MOFs

This section provides the examples in where the ligands in MOFs were functionalized with metal complexes or metal complexes were encapsulated within the pores of MOFs. The activity of these resulting solids was tested as heterogeneous catalysts for the oxidation of cyclohexane. The following examples are grouped under this category mainly to illustrate the readers that these solid catalysts do have more than one active site. Hence, Table 3 summarizes the catalytic performance of these catalysts for the cyclohexane oxidation by indicating the reaction conditions, cyclohexane conversion, product selectivity and evidence for catalyst stability.

A series of MOF-based catalysts possessing metal-salen complexes incorporated into amino-functionalized MIL-101 matrices was obtained by condensation of salicylaldehyde to the amino group of the linker, followed by subsequent coordination of the metal ions (Figure 7).^[69] In this way, a cooperation between the metal ion of the salen complex and the other present in the MOF structure can be possible. The



Scheme 2. Synthesis of Co(L)(PTA)₂.

Table 3. Functionalized MOFs as heterogeneous catalysts for oxidation of cyclohexane.

Catalyst	Reaction conditions	Con. [%]	Sel. [%]	Stability evidence	Ref.
NH ₂ -MIL-101(Cr)-Sal-Co	Cyclohexane (10 mL), catalyst (0.1 g), TBHP (60 μL), O ₂ (1 MPa), 130 °C, 6 h.	36.1	91	4 reuses, XRD	[69]
CuPhen/MIL-100(Al)	Cyclohexane (9.5 mmol), catalyst (0.05 g), 30% H ₂ O ₂ (38 mmol), 70 °C, 3 h	11.1	100	3 reuses	[70]
NHPI/Fe(BTC)	Cyclohexane (1 mL), catalyst (75 mg), O ₂ (6 bar), 160 °C, 24 h	6	72	XRD	[71]
PCN-224(Mn)-H ₂ L	Cyclohexane (1 mmol), catalyst (20 mg), TBHP (8 μL), CH ₃ CN (2.5 mL), AgBF ₄ (25.6 mg), 80 °C, 24 h	51.3	90	3 reuses, XRD	[72]
UiO-67-KVO(O ₂) ₂	Cyclohexane (8 mmol), catalyst (10 mg), TBHP (8 mmol), CH ₃ CN (8 mL), 70 °C, 12 h	9.4	77	Leaching test	[73]

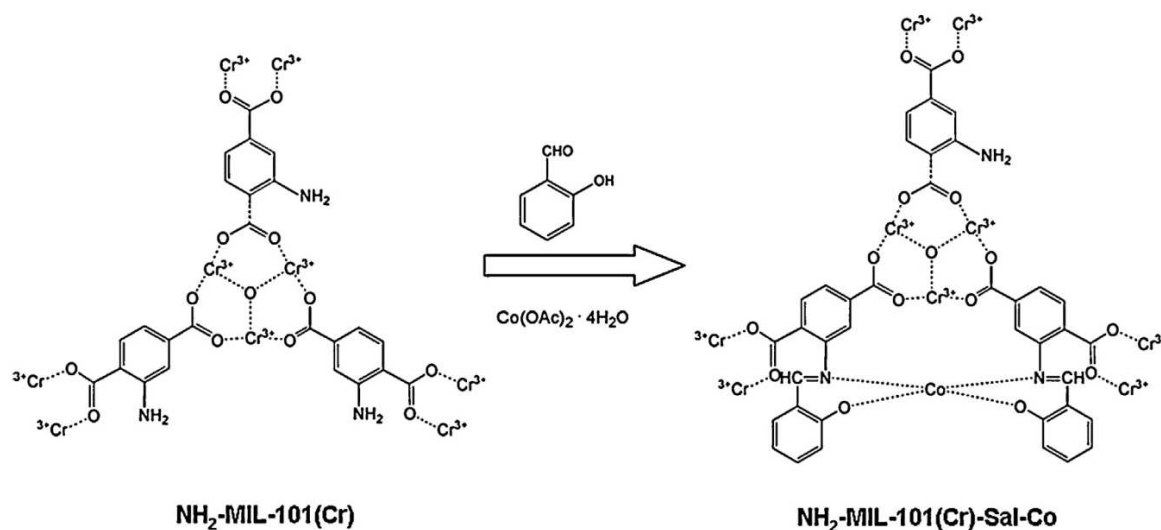


Figure 7. Synthesis of NH₂-MIL-101(Cr)-Sal-Co. Reproduced with permission from ref. [69] Copyright 2013 Elsevier.

activity of the as-prepared solid catalysts was checked at 130 °C in the oxidation of cyclohexane using O₂/TBHP as oxidant. The activity of NH₂-MIL-101(Cr), NH₂-MIL-101(Cr)-Sal-Co, NH₂-MIL-101(Cr)-Sal-Mn and NH₂-MIL-101(Cr)-Sal-Zn was 19.6, 36.1, 35.3 and 18.5%, respectively. The selectivity of KA oil was around 91 % for these catalysts. The superior performance of NH₂-MIL-101(Cr)-Sal-Co among other solids was due to the activity of the salen-Co(II) attached to the MOF structure effectively promoting the generation of new radicals from CHHP, while the Cr³⁺ ions located within the framework catalyze the dehydration of CHHP intermediate to improve KA oil selectivity. In addition, NH₂-MIL-101(Cr)-Sal-Co was reused in four consecutive reactions without any decay in its activity and KA oil selectivity. Powder XRD of the reused solid was identical to the fresh catalyst.

In another work, metal complex formation within the pores of MIL-100(Al) was achieved in a stepwise manner. Initially, Cu²⁺ metal ions were adsorbed over MIL-100(Al) and the resulting Cu²⁺/MIL-100(Al) was further reacted with tris-1,10-phenanthroline (phen) to form CuPhen complex within the pores of MIL-100(Al) (CuPhen/MIL-100(Al)).^[70] The oxidation ability of CuPhen/MIL-100(Al) (TON: 467) in the oxidation of cyclohexane using 30% H₂O₂ at 70 °C was higher compared to that of homogeneous CuPhen (TON: 71) and CuPhen encapsulated over zeolite Y (TON: 195). CuPhen/MIL-100(Al) was reused three times without observing any decrease in its activity. The enhanced activity of CuPhen/MIL-100(Al) was due to the large supercages of MIL-100(Al) hosting CuPhen complex (2.5 and 2.9 nm), which can facilitate the diffusion of cyclohexane and the generation of the active transition state compared to zeolite Y (1.3 nm).

In a related work, N-hydroxyphthalimide (NHPI) was adsorbed onto commercial Fe(BTC) (NHPI/Fe(BTC)) and its catalytic performance was checked in the aerobic oxidation of cyclohexane at 160 °C.^[71] The use of NHPI/Fe(BTC) resulted in 6% conversion with 72% selectivity to KA oil. The presence of 13% of CHHP in the reaction mixture was also found and adipic

acid was also formed in 8%. Further, powder XRD of the fresh NHPI/Fe(BTC) and reused solids were identical, thus the structural integrity is retained during the oxidation reaction.

Substituents on the organic linker can be used to tune the hydrophilicity of the internal pores. In one example, the influence of hydrophobic environments within the pores of MOFs was studied by selecting PCN-224 (Zr TCPP). In this study, PCN-224 was first synthesized and subsequently free-metal porphyrin linkers were complexed by Mn³⁺ ions to form PCN-224(Mn). Later, PCN-224(Mn) was treated with 2,2'-bis(trifluoromethyl)-4,4'-diphenylphthalate (H₂L) linker with two carboxyl groups and fluorine-containing groups to partially substitute some porphyrin linkers within the framework of PCN-224(Mn) to obtain a hydrophobic porphyrinic MOF of PCN-224(Mn)-H₂L (Figure 8). The catalytic performance of PCN-224(Mn)-H₂L was tested in the oxidation of cyclohexane.^[72] The activity in acetonitrile using TBHP as oxidant with AgBF₄ as cocatalyst at 80 °C was relatively higher for PCN-224(Mn)-H₂L that afforded a conversion of 51.3% and a selectivity of KA oil to 90% compared to PCN-224(Mn) (16.7% conversion) and higher than that of the homogeneous metalloporphyrin catalyst (Mn-TCPP, <2% conversion). PCN-224(Mn)-H₂L was reused three times with no changes in activity and selectivity. Powder XRD pattern of the reused PCN-224(Mn)-H₂L remained unchanged after three reactions, however, the crystallinity of PCN-224(Mn)-H₂L was slightly decreased.

Oxidoperoxo transition metal complexes (MoO(O₂)₂, WO(O₂)₂, and KVO(O₂)₂) have been incorporated in the framework of UiO-67 and the activity of the resulting solids in the cyclohexane oxidation was examined.^[73] The robust structure of UiO-67 was not altered upon loading of these oxidoperoxo transition metal complexes. Among these heterogeneous catalysts, the highest activity was observed for UiO-67-KVO(O₂)₂ that reached 9.4% cyclohexane conversion with 77% KA oil selectivity using TBHP as oxidant at 70 °C. On the other hand, UiO-67-MoO(O₂)₂ and UiO-67-WO(O₂)₂ exhibited <1 and 1.6%

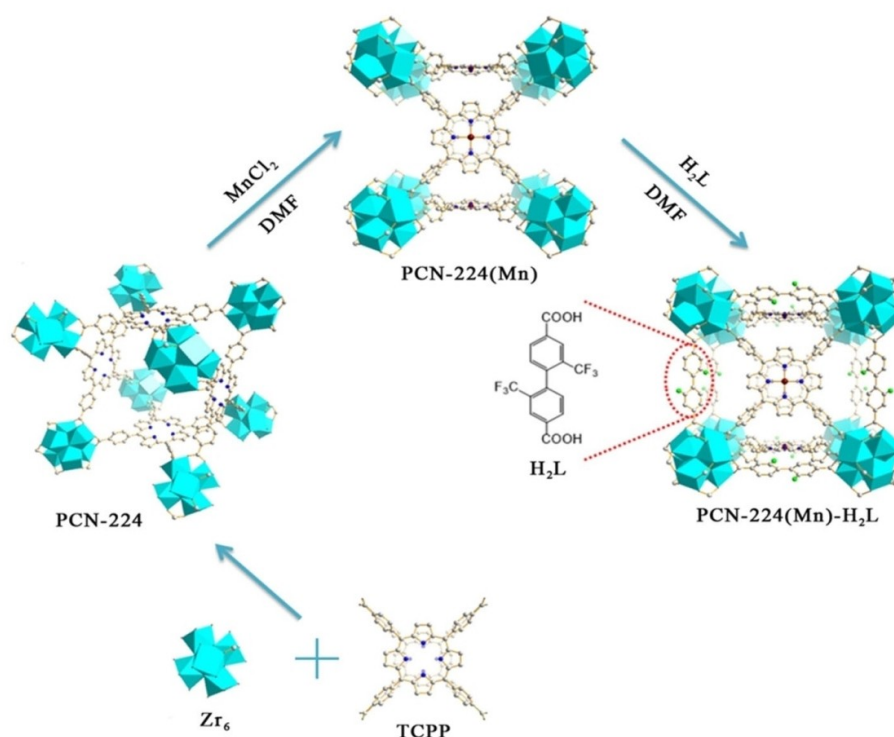


Figure 8. Synthesis of PCN-224(Mn)-H₂L by post-synthesis modification. Reproduced with permission from ref. [72] Copyright 2020 Wiley.

conversions under identical conditions. The catalytic process was heterogeneous and no leaching of the metal was observed.

4. Metal NPs supported on MOFs

This section discusses the catalytic performance of MOFs containing metal NPs for the oxidation of cyclohexane. Further, Table 4 lists the examples that have been reported for this reaction, providing information about the reaction conditions, conversion/selectivity data and evidence for catalyst stability.

Au/MIL-53(Cr) and Au/MIL-101(Cr) solid catalysts were synthesised through urea deposition-precipitation method (Figure 9).^[74] MIL-53(Cr) is a unidirectional MOF with flexible parallel channels, while MIL-101(Cr) is a tridirectional structure with two type of cages of 2.9 and 3.4 nm dimension. The resulting Au NPs were highly dispersed on Au/MIL-53(Cr) with the average particle size of 4.8 ± 2.9 nm. Most of the Au NPs were dispersed on the external surface of MIL-53(Cr). In contrast, the average particle size of Au NPs in Au/MIL-101(Cr) was 1.8 ± 0.6 nm,

which are mostly confined within the pores of MIL-101(Cr). The catalytic activity of these two solids was examined in the aerobic cyclohexane oxidation to KA oil under neat conditions without any initiator at 130 °C. MIL-53(Cr) and MIL-101(Cr) afforded 23.3 and 24.1 % cyclohexane conversions with 84.6 and 83.8% KA selectivity, respectively under the above conditions. On the other hand, the aerobic oxidation of cyclohexane with Au/MIL-53(Cr) and Au/MIL-101(Cr) was 31.3 and 30.5% conversions with the selectivity of KA oil to 81.9 and 87.7%, respectively under similar conditions. These catalytic data indicate that both, framework Cr ions and Au NPs, are acting as catalytic sites for this oxidation. Recyclability data indicated that both solids did not show any decrease either in the conversion of cyclohexane or in the selectivity of KA oil after five cycles. Further, ICP analysis did not detect the presence of Cr and Au, thus indicating the stability of these solids under these conditions. These results indicate that there is no gain in this case by encapsulation of Au NPs within the MOF lattice, probably due to the polarity of the micropores compared to the external surface.

Table 4. List of examples of metal NPs embedded over MOFs for oxidation of cyclohexane.

Catalyst	Reaction conditions	Con. [%]	Sel. [%]	Stability evidence	Ref.
Au/MIL-101(Cr)	Cyclohexane (10 mL), catalyst (0.1 g), O ₂ (1.2 MPa), 130 °C, 6 h	30.5	87.7	4 reuses, ICP	[74]
Au-Pd/MIL-101(Cr)	Cyclohexane (10 mL), catalyst (50 mg), O ₂ (1–1.5 MPa), 150 °C, 4 h	50.8	39.6 ^[a]	3 reuses, TEM	[75]

[a]: total yield of cyclohexanol and cyclohexanone.

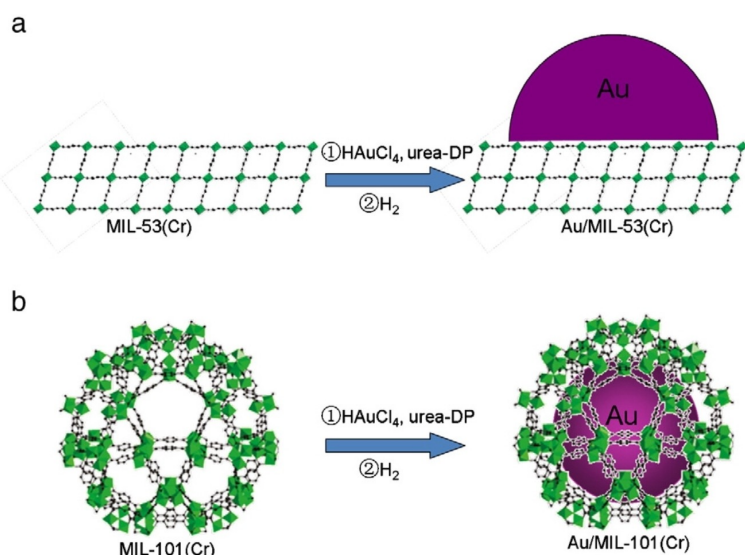


Figure 9. Preparation of Au/MIL-53(Cr) (a) and Au/MIL-101(Cr) (b) solids. Reproduced with permission from ref. [74] Copyright 2012 Elsevier.

In one of the notable works in the field, Au and Pd NPs dispersed on MIL-101(Cr) (Au–Pd/MIL-101(Cr)) were prepared, characterized and the activity of Au–Pd/MIL-101(Cr) was tested in the oxidation of cyclohexane under aerobic oxidation at 150 °C.^[75] Au and Pd were mostly in the form of bimetallic alloy on the MIL-101(Cr) support. TEM analysis revealed that the Au–Pd NPs were uniformly dispersed on MIL-101(Cr) with the average particle size of 2.40 ± 0.63 nm, small enough to be occluded within the MOF cages. Under these conditions, the conversion of cyclohexane was 50.8% with the KA oil of 39.6% yield. Interestingly, the TOF value achieved with this catalyst for the conversion of cyclohexane to KA oil was 19000 h^{-1} after 2 h, which is comparable to the highest TON values and TOF rates reported for the liquid phase oxidation of cyclohexane with Au NPs supported over mesoporous silica.^[76] Furthermore, the catalytic data indicated that the use of Au–Pd alloy catalyst showed much superior activity compared to pure metal counterparts and Au and Pd physical mixture. The high activity and selectivity observed for Au–Pd/MIL-101(Cr) in cyclohexane aerobic oxidation was due to the operation of synergistic effect of bimetallic Au–Pd alloy NPs. Au–Pd/MIL-101(Cr) was used four cycles without any decrease in activity and selectivity. TEM analysis of the four-times used solid indicated agglomeration of the particle size to average size: 2.59 ± 0.51 nm.

It has to be commented that noble metal NPs supported on large surface area solids are general oxidation catalysts^[77–79] for aerobic oxidation reaction, including cyclohexane oxidation.^[80,81] In this regard, encapsulation of metal NPs on MOFs should exhibit advantages in terms of higher reaction rate, conversion and selectivity to be competitive with alternative noble metal NPs supported on metal oxides.^[82] Confinement and polarity effects together with synergistic effects of having near the noble metal NPs^[83] with Lewis acid sites should be exploited to show the superiority of MOFs compared to these simpler systems. It must be reminded that encapsulation of metal NPs inside MOFs have resulted frequently in the formation of very small (< 3 nm) noble metal NPs that remain stable without growing under reaction conditions.^[84]

5. Photocatalytic cyclohexane oxidation

This section summarizes the photocatalytic data obtained from the use of MOFs as catalysts/supports for the oxidation of cyclohexane to KA oil. Performance data indicate that the number of reports for cyclohexane oxidation under photocatalytic conditions is still low, being necessary to develop processes with higher cyclohexane conversion and high product selectivity (Table 5).

Table 5. List of the MOF catalysts that have been reported for the light-assisted cyclohexane oxidation.

Catalyst	Reaction conditions	Con. [%]	Sel. [%]	Stability evidence	Ref.
$[(\text{Cu}(\text{NPY})_2(\text{DMF}))_2(\text{W}_{10}\text{O}_{32})] \cdot \text{DMF} \cdot 3\text{CH}_3\text{CN}$	Cyclohexane (200 μmol), catalyst (2 μmol), O_2 (101 kPa), CH_3CN (1.5 mL), Xe lamp (500 W), RT, 12 h	87.2	1.05 ^[a]	2 reuses, XRD	[85]
$\text{NH}_2\text{-MIL-125}(\text{Ti})/\text{P25-4}$	Cyclohexane (10 mL), catalyst (50 mg), O_2 , CCl_4 (10 mL), Xenon lamp, 25 °C, 5 h	0.74	99	3 reuses, XRD, FT-IR	[86]

[a]: total molar ratio of cyclohexanol and cyclohexanone.

The reaction consisting of $[(n-C_4H_9)_4N]_4[W_{10}O_{32}]$, 3-amino-4,4'-bipyridine (NPY) and $Cu(ClO_4)_2 \cdot 6H_2O$ resulted in 3D decaying-state-based MOF, namely, $[(Cu(NPY)_2(DMF))_2(W_{10}O_{32})] \cdot DMF \cdot 3CH_3CN$ (DT-NPY, Figure 10) possessing one-dimensional hydrophilic/hydrophobic channels.^[85] DT-NPY exhibited 87.2% conversion of cyclohexane with the molar ratio of KA oil of 1.05 using Xe lamp under aerobic conditions. This solid was used three consecutive runs with no decay in its activity and selectivity. XRD of the three times used solid showed no changes in its crystalline pattern.

In another report, a series of NH_2 -MIL-125(Ti)/ TiO_2 (P25) composites with different MIL to TiO_2 molar ratios were synthesised and tested as visible-light photocatalysts for the selective oxidation of cyclohexane using molecular oxygen as oxidant at room temperature.^[86] Among these composites, NH_2 -MIL-125(Ti)/P25-4 (4 represents the molar ratio of Ti^{4+} ions in P25 derived from tetrabutyltitanate) exhibited 0.74% conversion of cyclohexane with 99% selectivity to KA oil in acetonitrile while the conversion of NH_2 -MIL-125(Ti) was 0.096% with KA selectivity to 71% in CCl_4 as solvent. This activity difference between these solids is due to the energy band alignment and intimate interfacial contact between NH_2 -MIL-125(Ti) and TiO_2 , which improves the photon-generated charge transfer, minimizing the recombination of electron-hole pairs. Further, the catalyst was used four cycles with no decrease in its conversion/selectivity performance. XRD and FT-IR results of the four times used solids showed no changes compared to the fresh solid.

6. Conclusions

From the reports presented above it is clear that aerobic cyclohexane oxidation is still far from achieving the target of any catalytic reaction, i.e. to reach complete product selectivity at complete conversion using the simplest reagents. However, in some cases the cyclohexane conversion was very high (close to be complete) with high stability of the catalyst, but using costly oxidizing agents. In these cases, a comparison with analogous homogeneous catalysts, giving compelling evidence

of the advantages that MOFs offer should have been given. In addition, most of the studies carried out so far have been performed under batch conditions and a clear step forward in the field will be to develop process under continuous flow. It has been shown that the combination of oxygen with H_2O_2 can be a suitable and convenient way to minimize the use of peroxide reagent, while still reaching high product selectivity at high conversion. Considering that cobalt naphthenates, the current commercial catalyst, contain active sites in where the Co(II) ions are coordinated to carboxylate group, the structure of this current cobalt catalyst is not much different from that encountered in many MOF materials having aromatic polycarboxylate linkers. This similarity suggests the suitability of MOFs as heterogeneous solid catalysts for the process, with the advantage of being possible to tune the adsorption properties of the reaction cavities. In this regard, an obvious line of research would be to mimic cobalt naphthenates in a MOF design to have similar active sites, but providing the required polarity to enhance cyclohexane oxidation over the reaction products. In fact, MOFs offer a considerable flexibility in design and synthesis that should be fully exploited for the purpose of having a material with potential catalytic sites in the appropriate reaction cavity. In this regard, it can be easily anticipated that MOFs will continue to be the catalyst choice for cyclohexane oxidation reaction with the long-term aim of developing a MOF-based catalytic system that can be commercially implemented. Towards this goal of MOF scalability, cost of preparation, regeneration of active sites and high TON values when the material becomes exhausted, are major considerations to be taken into account for opting MOFs among the other possible catalytic systems.

Life cycle assessment (LCA) in which all the aspects regarding preparation of the catalyst and its disposal after complete deactivation, reagents, solvents, energy and the impact to the environment are considered in comparison with the current industrial process are necessary before implementation at large scale.

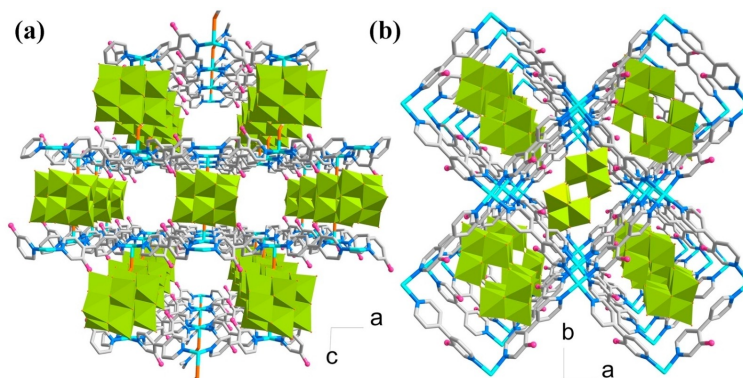


Figure 10. Structure of DT-NPY generated by the Cu-NPY framework and embedment of $[W_{10}O_{32}]^{4-}$ (a) and (b). Reproduced with permission from ref. [85] Copyright 2019 Elsevier.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Cyclohexane · KA oil · Metal organic frameworks · Oxidation · Porous solids

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