DEVELOPMENTS IN METAL ORGANIC FRAMEWORKS FOR UTILISATION IN CATALYSIS

Chemistry

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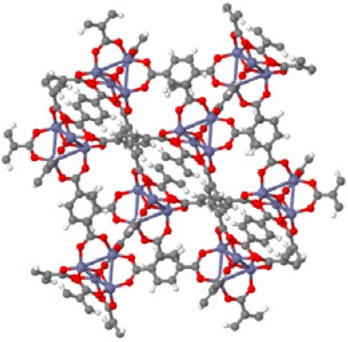
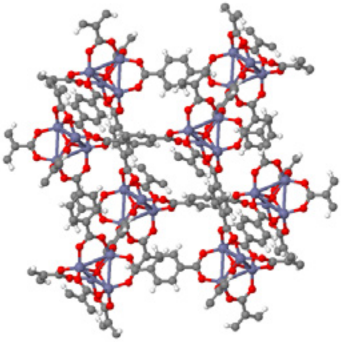
Metal organic frameworks (MOFs) are crystalline materials comprised of metal centres co-ordinately connected to each other by polydentate ligands. With the recent increase in research into MOFs the interesting properties of these materials become apparent. Most notable of these properties are the very high specific surface area and very high porosity. These two properties make MOFs interesting materials for catalysis. Developments on a number of methods have been made in making MOFs catalytically active. These have ranged from the use of catalytically active metal nanoparticles located in the pores of the material to the use of MOFs for the heterogenation of homogenous catalysts. It has been found however that the MOFs are sensitive to the conditions that they are place it (i.e. pH, temperature). This need for mild environments makes MOFs industrially non-comparable to robust nature of the common place zeolite catalyst. Therefore MOFs, for the moment at least, are constrained to small scale research in academic research laboratories until new MOFs can be developed that are resistant to these extreme conditions.

Introduction

Metal organic frameworks are crystalline compounds that are comprised of both organic molecules and inorganic atoms or clusters. The organic molecules are comprised of polydentate ligands that bridge between two or more metallic nodes. The metallic nodes are comprised of single transition metal atoms or clusters. Due to the large selection of the metallic nodes and polydentate ligands the properties of the MOFs can be easily adapted to suit the required properties. By interchanging the ligands and metal nodes the structure and properties of the MOF change. These changes can be drastic from just small changes to the molecular makeup of the MOF.

Some of the most notable features of MOFs are the extremely high porosity and high specific surface area of the molecular structures. The pores in the MOF are large in size and can be connected together to form tubular networks in the material. The pores can range in size from a few angstroms to several nanometres (Kuppler *et al.* 2009). This allows for very high selectivity of the size of molecules that can penetrate into the material and the ability to trap molecules within the structure upon formation of the MOF. The high specific surface area of the MOFs arises due to this highly porous network. This high specific surface area allows for large quantities of gases to bind to the surface of the material in a process known as physisorption as well as allowing access to a large number of catalytic sites within the crystalline structure. These properties make MOF ideal structures for materials used in catalysts, gas storage, drug delivery and molecular/ionic sieves, among many other useful applications (Kitagawa *et al.* 2004, Kuppler *et al.* 2009)





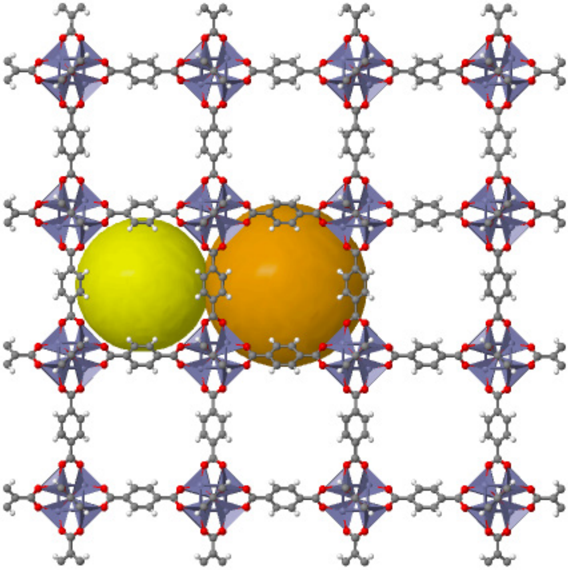


Figure 1: *MOF-5, a zinc – 1,4′-benzoic acid MOF. (a)Stereogram of unit cell (b) Pore size represented by spheres.*

The structure of the MOF can be described as an infinite metal organic crystal (Hotskins *et al.* 1989) Depending on the structure of the organic struts used in the MOF (i.e. bond angles, denticity, length of ligand) and the metal nodes (coordination number, oxidation state) three different topologies can be made. These are one dimensional rods, two dimensional sheets and these are often stacked to create a three dimensional structure similar to graphite and 3D crystals. In catalysis, and therefore most pertinent to this review, the most commonly used structure is 3D crystals.

Initial research of MOFs was found to be slow due to poor methods of creating the structures. However recent developments have now made it possible to create the MOF with relative ease. The most commonly employed method today is the solvothermal process. This involves the addition of the ligands and metal slats to a boiling polar solvent. These reactions occur at relatively low temperatures (>300°C). Other recently developed methods include the use immiscible solvents and microwave solvothermal syntheses. Microwave solvothermal syntheses is an exciting new methods as it allows for control over a number of features, such as temperature and rate of crystallisation, during the reaction. Control over these features helps determine the particle size and macro-structure of the crystals and therefore the type and number of catalytic sites within the crystalline material (Kuppler *et al.* 2009).

Mechanisms for Catalytic Activity:

MOFs can act as catalysts through a number of methods. These range from the unique binding nature between the supporting ligands and the metallic nodes to the heterogenation of homo catalysts. In this section the different methods will be discussed and as will their potential areas of application:

1. Metal Nodes as Catalytic Centres:

As the name suggest in these types of catalysts the metal node itself acts as a catalyst in the reaction. There are two main methods in which the metal node can act as a catalyst.

Unsaturated metal node:

The structure of this kind of MOF is based on the three-unit building approach, the units being the inorganic node, the structural bridging ligands and labile ligands. During the activation step of the catalytic process these labile ligands detach from the metal centre leaving open a vacant coordination site and this causes a change in the number of electrons on the metal centre. (Chiu *et al.* 1999). This allows for the metal node to be catalytically active in oxidation addition/reductive elimination catalytic cycles and the unfilled orbitals on the metal can act as strong Lewis acids and accept an electron pair. This method of activating the metallic node by the removal of labile ligands is similar to that of transition metal homogenous catalysts.

These vacant coordination sites, and therefore unfilled orbitals, have a strong affinity for electrons and hence behave as strong Lewis acids. This allows the vacant coordination sites to catalyse reactions that can be catalysed by Lewis acids. Henschel *et al.* (2008) demonstrated the presence of these active sites in the MOF as during their study of MIL-101 the metal node was observed to be the active site in the reaction of cyanosilylation. This was attributed to the presence of Cr(III) sites in the MOF. By comparing two MOFs - one that contained Cr(II) and another that contained Cr(III) - it was found that the MOF that contained Cr(III) had higher activity in the catalysis of the reaction. This can be contributed to the fact that Cr(III) is much stronger Lewis acid than that of Cu(II). This is due to the higher oxidation state of Cr(III) than Cr(II). With less electrons and more positive charge Cr(III) will more readily accept electrons than Cr(II) and hence has a higher reactivity. This increase in reactivity by the stronger Lewis acid indicates that it is the metal centre that is acting as the catalytic site in the MOF.

Horike *et al.* (2008) demonstrated that the majority of the catalytic activity by the MOF occurs in the tubular channels of MOFs. This allows selective catalysis to be exploited. On their study of a $Mn_3[(Mn_4Cl)_3(BTT)_8(CH3OH)_{10}]$ MOF it was found the MOF to could catalyse the cyanosilylation of aromatic aldehydes. The structure of the MOF was found to contain pores of 10Å. Upon using a variety of sizes for the substrates it was discovered that the highest conversion rates occurred with the smaller sized substrates. This preference for the smaller size substrates indicates that the majority of the catalytic activity occurs within the channels. This "sieve effect" can be used to selectively catalyse specific molecules in a solution.

Saturated metal node:

At these metal centres all coordination sites are occupied. In order for these metal nodes to act as a catalyst there must be a change in the coordination number around the metal centre. This change in coordination causes the formation of vacant sites. In this case however, the ligand that disassociates from the metal is one of the structural ligands. Due to the limited movement of the structural ligand, it remains close to the metal node.

One example of this type of catalysis is done by Llabres & Xamena *et al.* (2007). They created a palladium based MOF which was found to have similar catalytic properties to that of other palladium homogenous catalysts. The MOF was found to be an effective catalyst for Suzuki cross-coupling reactions and aerobic oxidation reactions. For the Suzuki cross-coupling reaction it was found that 85% conversion was achieved with a ~99% enantiomeric excess.

It was discovered that this catalytic activity is due to the change in oxidation state of palladium from Pd(II)-Pd(0). This change in oxidation state causes a change in the molecular geometry around the palladium metal centre. This change in geometry causes the crystal structure around the metal centre to break down with the dissociation of a structural ligand. The structural ligand has limited movement as it is still bound to other parts of the framework and so it is highly favourable for the structural ligand to re-bond to the metal node upon the metal node returning to its original structure. Some imperfections may occur upon returning to the original coordinated structure - structural ligands may not bind correctly, reactants may not disassociate and free the coordination sites. These potential defects will lead to the breakdown of the crystalline structure. Without this crystalline structure and the re-formation of the catalytically active metal node the catalyst will eventually fail. If the breakdown of the structure is total the catalyst may dissolve into solution.

2. Ligand Struts as Catalysts:

The polydentate bridging ligands within the MOF -also known as ligand struts - may also play a role in the catalytic activity of the MOF. The first method of ligand struts having a contribution to catalytic activity was to employ the use of homogenous catalysts as the ligand struts. The homogenous catalysts were modified to be able to act as the supports in a MOF.

Research done by Cho *et al.* (2006) was done on a manganese MOF. The MOF was designed to have similar catalytic activity to the catalyst used in the Katsuki–Jacobsen epoxidation reaction. The nature of the Katsuki–Jacobsen raection catalyst made it straightforward to convert the catalyst to a viable ligand strut. This was done by using two different ligand struts in the MOF, 4,4′-bipehnyldicarboxilate and salen. One notable difference between the Kastuki-Jacobsen catalyst and the catalytic ligand strut is the use of pyridine instead of 4-tetrabutyl-benzene in the complex. This allowed the catalyst to act as a structural ligand within the MOF (Kastuki 1995, Palucki *et al.* 1998). It was found that the reaction rate for the MOF catalyst was only slightly slower than that of the original Katsuki-Jacobsen catalyst variation of the catalyst. By comparing the two catalysts it was shown that incorporating catalytic activity into the ligand strut is a viable method for MOF in use as catalysts, the benefits of which will be discussed later.

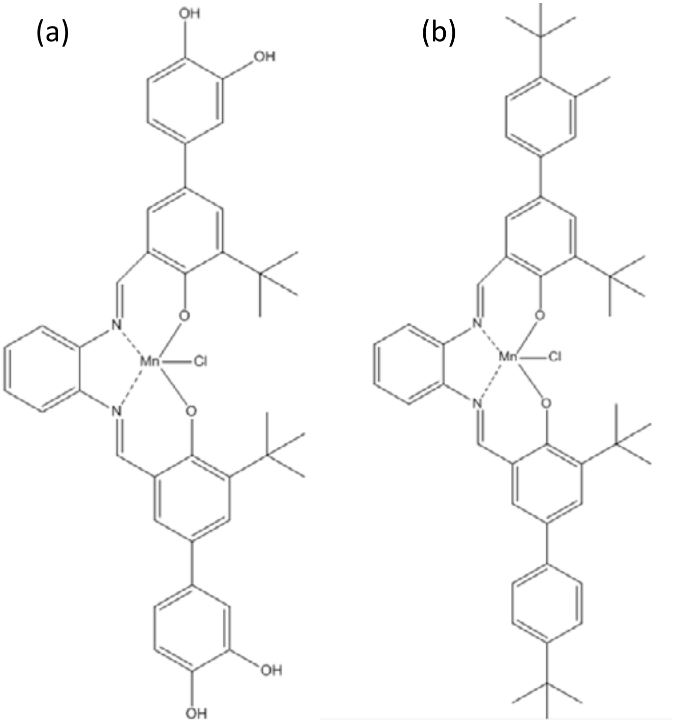
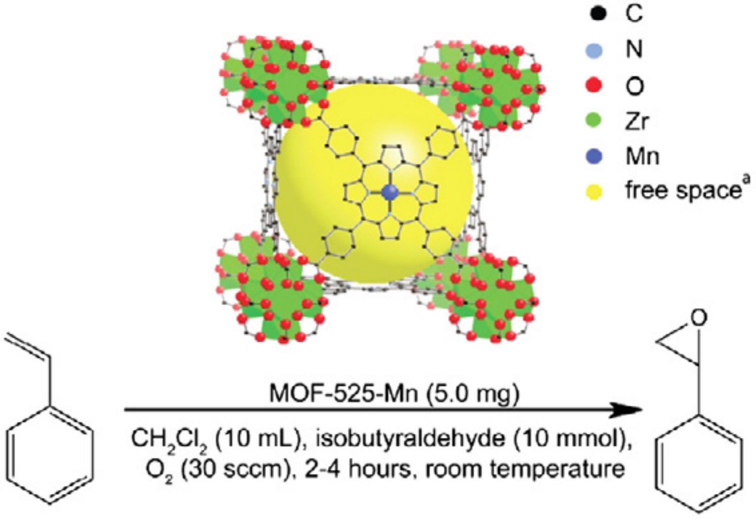


Figure 2: *(a) Mn containing ligand. (b) Katsuki-Jacobsen catalyst.*

A secondary metal containing organic ligand that has seen a great deal of research is the metaloporphyrin ligands. The porphyrins can be easily converted into ligand struts within a MOF. The key area in catalysis for metaloporphyrins - a free porphyrin with a metal centre, is in the oxidation of alkenes to epoxides. The metaloporphyrins are used as homogenous catalysts, however this method however may cause a number of problems. The catalysts may react intermolecularly which would deactivate the catalyst, or the porphyrins may not be soluble in the solvent. These along with the similar problems associated with homogenous catalysts make a heterogeneous variant more favourable (Nakagaki *et al.* 2013). These problems were found to be mitigated by placing the metaloporphyrin in a MOF. By placing the metaloporphyrins within a MOF the metaloporphyrins are fixed in position with regular spacing. This eliminates the intermolecular interaction between the metaloporphyrins that cause the formation of the deactivated catalyst as well as allowing the metaloporphyrin to be fully solvent accessible.

Work was done by Brown *et al.* (2015) to place manganese porphyrins within a zirconium MOF. It was found that there was minimal deactivation of the catalyst while the activity of the catalyst remained high. The reactions were performed on small alkenes as this would allow the molecules to fit within the pores of the material and therefore have full access to the activation site of the manganese porphyrin.



[a] Free space in the pore is illustrated by a yellow sphere that contacts the van der Waals radii of the framework atoms

Figure 3: *Epoxation of Phenylethene using MOF-525-Mn and molecular oxygen (Brown et al. 2015)*

Non-Metal containing Ligands:
These ligands may have functional groups that do not bind to the metal nodes. Similar to the MOFs mentioned before organic variants of these catalysts also benefit from the large number of catalytic sites within the material. While research has been done in this area, the methods of which the ligands may act as catalysts are limited when compared other methods. This is due to the requirements for a molecule to act as a ligand strut. Organic catalysts tend to be bulky in nature and will therefore occupy a large fraction of the internal volume that would be otherwise occupied the reactants and solvent. These limitations reduce the number of viable active sites that may be used in MOF by reducing the accessibility to the catalytic site. There is, however, documented work done by organic catalysts in MOF. The most notable work is done by Kitagawa *et al.* with the development with ligands that contain free amide groups. These act as stable bases for the Knoevengal condensation reaction.

The amide groups of 1,3,5-benzenetricarboxylic acid tris-N-(4-pyridyl)amide (4-BTPDA), when part of a MOF with cadmium, catalysed the reaction between benzaldehyde and malonodinitrile. It is interesting to note that in this case the homogenous version of the catalyst did not catalyse the reaction. This was due to hydrogen bonding that occurs intermolecularly between the 4-BTPDA molecules. This was one of the first instances where a molecule was unreactive in its free form but once contained with a MOF acted as an efficient catalyst (Kumar *et al.* 2004)

3. MOFs as Supports for Catalysts.

MOFs, with their crystalline nature and high surface area, make excellent materials as supports for a wide range of secondary catalyst. This method of placing a catalyst in or onto the surface of a MOF is known as a “host-guest” network. When a homogenous catalyst is placed in a MOF it can described as the heterogenation of a homogenous catalyst. It is important to note however that this is different than the aforementioned use of a metal containing ligand as a structural component of the MOF. In this case the catalyst is located in the pores and tubular channels of the MOF.

Similar to the work done by Brown *et al.* on the use of metaloporphyrins in MOFs Alkordi *et al.* (2008) worked on the use of encapsulated metaloporphyrins as catalysts. The metaloporphyrins were encapsulated in the pores of a MOF of the formula $[In_{48}(HImDC)_{96}]$. The pores in this MOF were large enough to house both the metal porphyrin and the reacting compound while the gaps within the surrounding structure that encapsulates the pores, were small enough for the metaloporphyrins to remain within the pores. Through the use of charged porphyrins and electrostatic techniques during the syntheses of the MOF it was possible to increase the porphyrin content of the MOF beyond 60%. By using a post-synthetic modification technique of adding the metal ion to the porphyrin after the formation of the MOF, it was possible to create a large variety of metal porphyrins from the same MOF. These metal porphyrins were found to be effective catalysts for the oxidation of alkanes, similar to that of the use as porphyrins as the ligand struts.

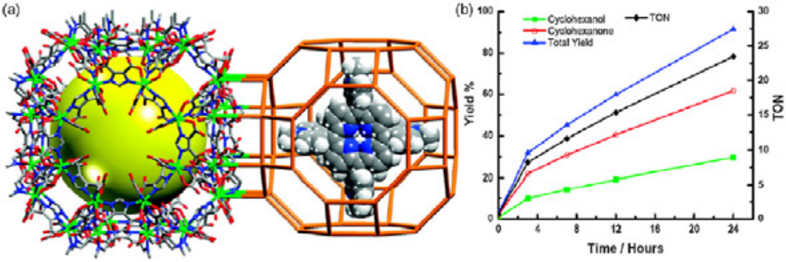


Figure 4: *(a) Crystal structure of rho-ZMOF (left) and schematic presentation of [H2TMPyP]4+ porphyrin ring enclosed in rho-ZMOF R-cage (right, drawn to scale). (b) Cyclohexane catalytic oxidation using Mn-RTMPyP as a catalyst at 65 ◦C (Alkordi et al. 2008)*

A similar method was used for the heterogenation of a cationic homogenous catalysts. Developed by Genna *et al.* (2013) the technique involves the cationic exchange of guest molecules in the framework of the MOF. The MOF was comprised of an anionic framework with stabilizing cations located in pores in the MOF. Upon addition of the cationic catalyst to a solution containing the host MOF a partial cationic exchange of the cationic catalysts and the indigenous cations occurred. It was found that up to 34% mol exchange occurred in the MOF (Genna *et al.* 2013)

Comparing the MOF encapsulating catalysts, ZJU-28-[Rh(dppe)(COD)]BF4, to the free homogenous catalysts it was found that the two catalysts had similar reactivity and turnover rates. It was found however, that the heterogeneous variant of the catalysed could be isolated and recycled four times before there was minimal loss in reactivity. The homogenous variant could only be used one additional time, this was was with only a further 200 addition turnovers by the catalyst. This was then followed by a total breakdown of the catalytic material (Genna *et al.* 2013).

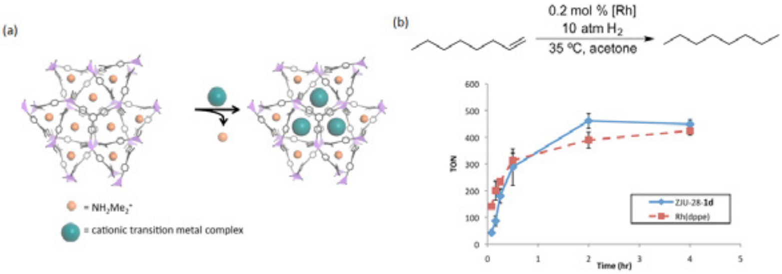


Figure 5: *(a) cationic exchange of transition metal complex with endogenous guest cation. Hydrogenation of 1-octene to n-octane in acetone catalysed by ZJU-28- [Rh(dppe)(COD)] BF4 (circles) and homogeneous 1d (squares). Conditions: 0.5 M 1-octene in acetone, 0.0013 mmol [Rh] (Genna et al. 2013)*

Methods for the deposition of a heterogeneous catalyst on to the surface of the MOF have also been developed. It was found that palladium could be deposited onto the surface of a zinc MOF via a metal-organic vapour deposition technique. Upon deposition of the palladium metal it was found that the surface are of the MOF drastically reduced from 2885m^2/g to 985m^2/g. Upon analysis of the catalytic activity for the catalyst, for the hydrogenation reaction, it was found to comparable to that of the industry standard of Pd/C catalyst. It is noted however, that this MOF system was unstable at room temperature (Sabo *et al.* 2007).

By using deposition techniques nanoclusters of pure metals can be impregnated into the pores of the MOF. This technique involves the absorption of vaporous organometallic compounds into the pores of the MOF. Once inside the pores of the MOF the precursor compounds breakdown to create pure metallic nanoparticles. By using this technique a number of different nanoparticles were formed within the MOF. A broad range of reactions have been attempted by using various nanoparticles, each of which have been found to useful for catalysing various reactions e.g. Ru-nanoparticles for the oxidation of benzyl alcohol to benzaldehyde (Hermes *et al.* 2005)

Conclusion

Developments in the use of MOFs for catalysis are still in their infancy with the majority of papers in this field having only been published in the past five years. The main area of research is for these materials to perform efficiently under more stringent conditions such as high temperature, acidic or basic conditions or under a range of pressures. Currently under such conditions the MOF breaks down due to a weak metal node to ligand strut bond, compared to that of a covalent bond. Improvements in these aspects will then allow MOF to be used in industrial applications. With all the advances in the past few years MOF still have yet to be able to compete with zeolite equivalent catalysts. It appears the key area of catalysis where MOF will play their role is in catalysis under mild conditions.

With the wide range of possible mechanisms for catalysis by MOFs, or MOF derivatives, it appears that MOF will be able to act as viable catalysts for a whole host of reactions. The main advantage of MOFs is their activity and mechanism being finely controllable by careful selection of metal nodes and ligand supports. The number of possible configurations of ligands and metal nodes makes the number of possible MOFs appears endless. The versatility of MOFs and their capacity to act as catalysts is has been an area of academic research for the past few years but due to the limitations described above MOFs are currently only feasible for small scale industrial application under mild conditions.

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