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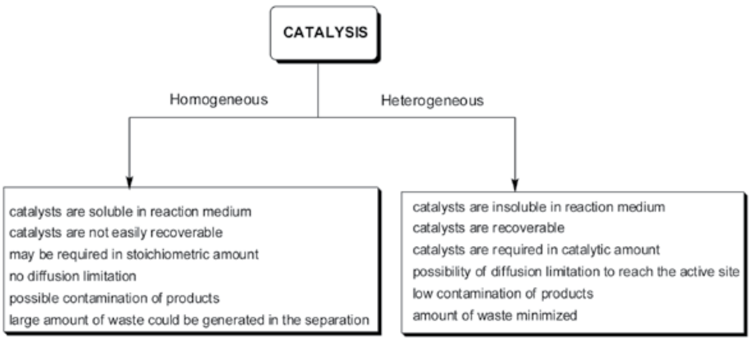
Metal-organic frameworks
as heterogeneous catalysts in liquid phase reactions: why are they so exceptional?

KEYWORDS: metal-organic frameworks, heterogeneous catalysis, coupling reactions, aerobic oxidation, reduction, Knoevenagel condensation

Abstract Metal-Organic Frameworks (MOFs) are crystalline porous materials consisting of metal ions or clusters of metal ions coordinated to rigid organic linkers to form one-, two-, or three-dimensional pore system. In the present Perspective, we discuss the interest of MOFs in heterogeneous catalysis that derive from unique features present in these materials related with high porosity, large surface area, high content of transition metals and the presence of coordinatively unsaturated sites. After presenting general properties of MOFs, different reaction types in which the use of MOFs can be advantageous with respect to current microporous catalysts are briefly reviewed making emphasis on aerobic oxidations, reductions, cross-coupling reactions and condensation of carbonyl groups. This article includes also a short section on our outlook for future developments in this field.

WHY METAL-ORGANIC FRAMEWORKS IN CATALYSIS?

The field of catalysis can be divided between homogeneous and heterogeneous catalysis (1). While homogeneous catalysis has many advantages, including a single type of active site, perfect knowledge and characterization of the molecules, complexes promoting the reaction and the mechanism is easier to rationalize and model, chemical industry generally prefers to use alternative heterogeneous catalysts. The use of heterogeneous catalysts allows continuous flow operation of a process and an easy separation of the catalyst from the reaction mixture, making possible its recovery and reuse.

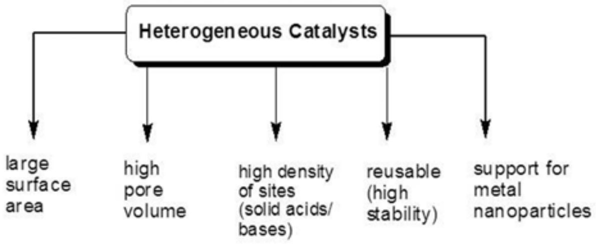


Scheme 1. Some of the general differences between homogeneous and heterogeneous catalysis.

Scheme 1 illustrates general differences between homogeneous and heterogeneous catalysis.

Heterogeneous catalysts are far more complex than the homogeneous one, because they are not molecules or complexes but rather complicated materials on which the active sites are generally distributed among different families with not exactly coincident surroundings or structures and, as consequence, they may exhibit different activity and even not exactly the same product selectivity. One concept that has emerged recently in heterogeneous catalysis is the "single-site solid catalysts" (2), meaning that in this type of solids all the active sites should be equal, as it happens in molecular catalysts. The existence of only one type of centre in the solid determines that all of them should promote the reaction at the same rate with the same selectivity (3). To develop single-site catalysts, crystalline materials in which there is a unit cell repeated in the structure are preferred over amorphous solids for which there is no a repeated building unit. In amorphous solids, different sites should be present. Crystallinity does not guarantee single-site solid catalysts unless the centre forms part of the unit cell and this only happens in a few crystalline materials.
Besides single site, other important parameters in heterogeneous catalysis are surface area and adsorption capacity. All the reaction processes in heterogeneous catalysis start with adsorption of

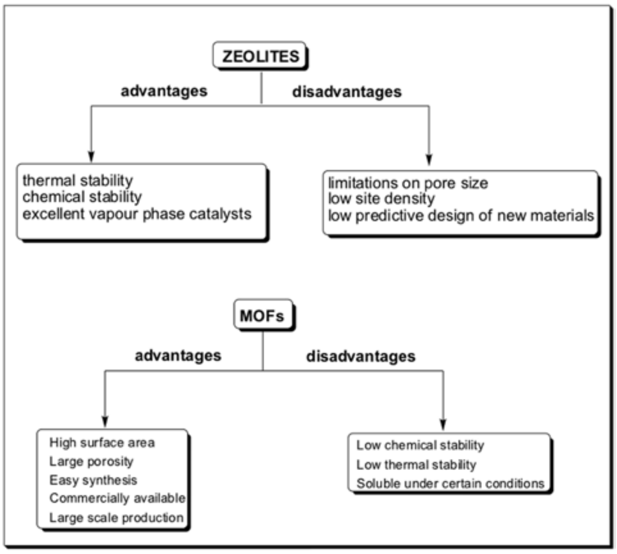
substrates and reagents on the active sites and finish with desorption of the reaction products, frequently being desorbed by substrates that should adsorb stronger starting a new cycle. In order to increase adsorption of substrates and reagents, one general strategy is to develop solid catalysts with high surface area. This large surface area values can be achieved by reducing the particle size of the catalyst in to the nanoscale, but also by using porous solids. In porous solids, mass transfer from exterior to the interior of the particle can take place through pores open to the external surface that allow access to the interior of the crystallite. Scheme 2 summarizes desirable properties of heterogeneous catalysts.
One example of crystalline and porous solids widely used in catalysis is zeolites that besides to be natural minerals can also be prepared in the laboratory by hydrothermal synthesis (4). Not surprisingly zeolites have become among the most important solid catalysts and most of the process in oil refining and a large variety of petrochemical transformations are based on the use of zeolites as selective acid/bifunctional catalysts (1). In this type of oil-related processes the reaction takes place in the gas phase. For other reactions taking place in the liquid phase and involving larger substrates, conventional zeolites are not so adequate catalysts due to diffusion limitations of large substrates and products inside zeolite micropores.



Scheme 2. Some wanted properties of heterogeneous catalysts.

While in oil refining and petrochemical, hydrocarbons may have relatively small size, other sectors in chemical industry, particularly the production of fine chemicals, require the transformation of molecules with high boiling point having several functional groups and large dimensions. These reactions have to be carried out in the liquid phase and the use of solvents. The limitation of zeolites in this case is the available pore size range that is typically about 1 nm or below. One attempt to overcome the limitations of zeolites was the use of mesoporous aluminosilicates such as MCM-41 (5, 6), but the catalytic performance of these mesoporous solids has been limited by its low structural stability and poor catalytic activity (7). Thus, neither micro- (zeolites) nor mesoporous (MCM-41 and SBA-15) silicates leave some limitations to be used as solid catalysts for liquid phase reactions. This gap could be filled by metal organic frameworks (MOFs) as heterogeneous catalysts. Scheme 3 illustrates the advantages-disadvantages of zeolites and MOFs as heterogeneous catalysts.

Since the initial reports on the synthesis of MOFs, also called as porous coordination polymers, there was a large interest in applying MOFs as heterogeneous catalysts (8-16), under conditions compatible with their stability, due to the high crystallinity, surface area, porosity and high metal content of these relatively novel materials. In the next section, we will describe briefly the structure and properties of MOFs that are relevant for the use of these solids as catalysts. We will also comment on the drawbacks and limitations that should be overcome in the future studies.

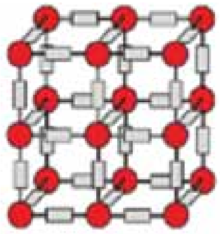


Scheme 3. Some of the advantages and disadvantages of zeolites and MOFs.

STRUCTURE OF MOFs AND THEIR PROPERTIES

MOFs are crystalline porous materials whose structure is constituted by nodes of metal ions or clusters of few metal ions that are held in place by rigid bi/multipodal organic linkers (17, 18). Scheme 4 illustrates the general structure of MOFs constituted by metal nodes (as red spheres) and rigid organic linkers (as rectangles). For example, the most commonly used MIL-101(Cr) (19) material consists of two types of zeotypic mesopores with free diameters of around 2.9 and 3.4 nm, accessible through two microporous windows of ca.1.2 and 1.6 nm. Furthermore, it has a high BET surface area of 4100 m^2/g and numerous potential unsaturated chromium sites (up to 3 mmol g^{-1}). Indeed, trimeric chromium(III) octahedral clusters of MIL-101(Cr) possess terminal hydroxyl groups or solvent molecules which can be removed from the coordination sphere of the metal by vacuum treatment. Thus, this activation process can lead to the formation of coordinatively unsaturated sites (20) (CUS) that will act as Lewis acid sites in the structure. On the other hand, UiO-66 obtained from the clusters of cationic $Zr_6O_4(OH)_4$ nodes and BDC (BDC: 1,4-benzenedicarboxylate) can survive without damaging the crystallinity in boiling water for prolonged periods of time (21). It has been possible to synthesise MOFs of virtually any transition metal, including those that are relevant in catalysis. Due to their composition, the metal content of MOFs is relatively large, particularly in comparison with the sometimes minute proportions of transition metals that can be incorporated in zeolites and other aluminosilicates. With respect to the organic linker, typical compounds are aromatic polycarboxylates or imidazolates that interact with the metal ion through strong Coulombic interactions and coordinative metal-ligand bonds. Thus, the two main characteristics that differentiate MOFs from other related materials are porosity and crystallinity.

The synthesis of new, robust MOFs has been a continuous trend topic in materials science and one of the main

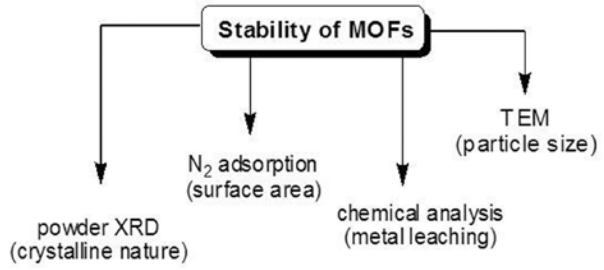


Scheme 4. General simplified model of a MOF strcuture.

outcomes of this research is that there is a large capability to predict the crystal structure of a given MOF knowing the coordination geometry around the metal nodes and the structure of the organic linkers that defines the directionality in the location of nodes. In this way, maintaining the same constitutive metal and changing the ligands by others with the same directionality, but different dimensions, should afford isostructural MOFs, where the pore size should enlarge and the framework density decrease as the size of the linker increases. This large flexibility in the design and preparation of MOFs and the high predictive capability for potential new structures is specific of this type of materials. Particularly in zeolites there is no direct relationship between the structure of quaternary ammonium ion used as template in the synthesis of the zeolite and the resulting pore geometry. Typical synthetic procedures consist in the solvatothermal crystallisation of mixtures of a soluble salt of the metal ion and the organic linker in appropriate proportions in the presence of amines as base. Dimethyl and diethyl formamides are among of the preferred solvents due to the high solubility of the precursors in these aprotic polar solvents. The synthetic protocols are highly reproducible.

Derived from the way in which the lattice is built (see Scheme 4), MOFs are among the solids with the lowest framework density (lowest mass in the volume of the unit cell), this leading to very high specific surface areas. Typical specific surface area of MOFs are over 1000 m^2/g, the current record being above 5000 m^2/g. These specific surface area value of MOFs is about one order of magnitude larger than that of large pore zeolites (the surface area of zeolites Y and Beta is in the range of 300-400 m^2/g). Similar situation occurs with pore size, when comparing MOFs and zeolites (15). While in conventional zeolites the largest pore size of typical structures is less than 1 nm and it has become difficult to overcome this value, in MOFs the pore size can be expanded into the mesopore range going easily to values of few nms. Even extra large pore MOFs can be designed and prepared, although these types of MOFs have to be handled cautiously to avoid the collapse of structure and, consequently their interest in catalysis is limited due to their lack of stability. Nevertheless, the possibility to design offers a wide range of MOFs with large surface area, high porosity and high metal content. These characteristics make MOFs extremely suited for their use as single site heterogeneous catalysts. Scheme 3 summarizes some differences between MOFs and zeolites as solid catalysts.

One of the major limitations of MOFs for their use as solid catalysts is low framework stability in some cases . However, as the synthesis of these materials has progressed considerably, several easy-to-make, widely available MOFs have been prepared by now that can stand hydrothermal treatments for long times and even the contact with strong acids or bases. Examples of these robust MOFs include UiO-66 and MIL-101(Cr), but also some ZIF structures in where the ligands are not carboxylates but imidazolates and the interaction is metal-nitrogen, rather than metal-oxygen as in most common MOFs. It should be commented that stability has always to be a major concern while using MOFs in catalysis and any study in this area has to address satisfactorily this issue by characterizing the MOF samples after extensive use as catalyst, determining the crystallinity loss, variation in the surface area and even changes in the morphology and dimensions in the crystallites. Also, the liquid phase after catalysis has to be submitted to chemical analysis to prove or disprove the occurrence of leaching of metal ions to the solution. Scheme 5 summarizes some of common tests to evaluate the stability of MOFs as heterogeneous catalysts.



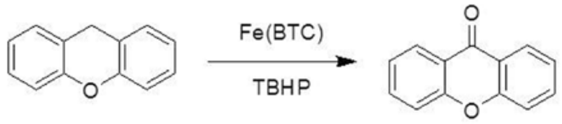
Scheme 5. Some common techniques needed to evaluate stability of MOFs when used as catalysts.

It is clear that framework stability is always related with the nature of reagents, products, solvent and reaction conditions. Therefore, there is a wide range of substrates, reagents, solvents and conditions that could be compatible with the stability of certain MOFs, such as MOF-5 and Cu3(BTC)2, (BTC: 1,3,5-benzenetricarboxylate) that would be, however, unstable under other conditions or in the presence of more aggressive reagents, such as amines or thiols (13). The field of MOFs as heterogeneous catalysts has been developing intensively since the last decade (8, 13). In the following sections, we will comment on selected reaction types trying to convey a general overview of the wide applicability of MOFs as heterogeneous catalysts for different general reaction types. The reader is also directed to comprehensive reviews in this area for a deep coverage of the existing literature (8, 9, 13, 16).

OXIDATION REACTIONS

Transition metals have a general catalytic activity in promoting many different types of oxidation reactions of organic compounds (22). At industrial scale, catalysts based on Co, Mn, Cr, V and Cu are currently used for a large variety of oxidations of aliphatic hydrocarbons, allylic and benzylic positions, alcohols and amines. In some cases, these transition metals are used as acetate or carboxylate salts. Therefore, it is not surprising that due to their large transition metal content, MOFs can also be suitable as heterogeneous catalysts for this reaction type.

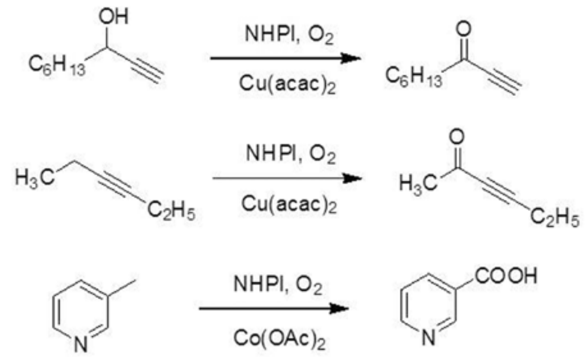
The selection of oxidizing reagent is a key point particularly for new processes to be developed. A crucial issue in this reaction type is sustainability, environmental benignity and reduction of wastes (particularly toxic metals), avoiding the generation of by-products formed stoichiometrically during the oxidation. Convenient oxidizing reagents are hydrogen peroxide or organic hydroperoxides, since the by-products of these reagents are water or the corresponding alcohols that can be recycled. There are several examples in the literature in where organic hydroperoxides have been used as oxidants in oxidation reactions (23). We have found that commercial Fe(BTC) is a suitable solid catalyst for the oxidation of benzylic positions of aromatic hydrocarbons (xanthene) (24) by *t*-butylhydroperoxide (TBHP) (Scheme 6). In this process, this MOF can be reused without much decrease in its activity.



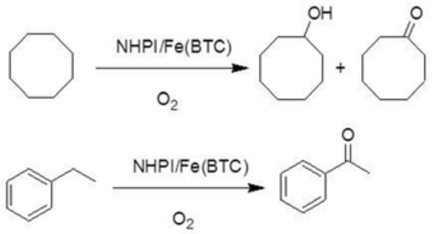
Scheme 6. Oxidation of xanthene to xanthone by TBHP catalyzed by Fe(BTC).

Besides organic hydroperoxides and hydrogen peroxide, the use of molecular oxygen as terminal oxidant is of considerable interest due to its cost-effectiveness. However, oxygen as reagent is extremely unselective since it can attack not only the substrate, but also the primary oxidation products, giving rise to a large number of compounds arising from consecutive oxidations. This lack of selectivity makes aerobic oxidations in general uninteresting due to complexity of the reaction mixture. One possibility is to achieve selectivity in the reaction products by means of a catalyst. We have found that commercial Fe(BTC) or $Cu_3(BTC)_2$ are not able to activate molecular oxygen for the oxidation of hydrocarbons or alcohols. However, we were inspired by the works of Ishii on the use of N-hydroxyphthalimide (NHPI) and other organic co-catalysts that upon coordination with transition metal ions can promote oxidations of a large variety of organic functional groups (25) (Scheme 7). Accordingly, we adsorbed NHPI on the internal voids of MOFs and used the resulting NHPI/MOF system as catalyst for aerobic oxidation of hydrocarbons. In this way, by using NHPI incorporated in commercial Fe(BTC), the aerobic oxidation of benzylic hydrocarbons and cyclooctane can be performed in the absence of solvent (26). High conversions with selectivities above 90% can be achieved for oxidation of ethylbenzene and cycloalkanes (Scheme 8). The key point to achieve product selectivity compared to homogeneous solution is to perform the reaction in a confined reaction cavity (MOF pores) of the adequate polarity to prefer adsorption of apolar hydrocarbon substrate with respect to the more polar primary products. In this way, the high concentration of substrate in the reaction cavity and desorption of the products can lead to high selectivities to the target ol/one mixture compared to the homogeneous phase, where indiscriminate oxidation takes place.

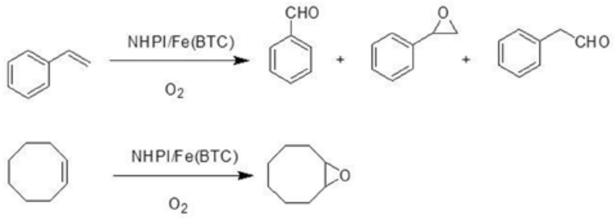
The same NHPI/Fe(BTC) system is also able to promote the aerobic oxidation of styrene and cyclooctene (Scheme 9). In the case of styrene, a remarkable change in the selectivity as a function of conversion was observed (27). Understanding the origin of this change in selectivity is important because it can give hints about possible ways to improve selectivity towards the most desirable product, styrene epoxide. Oxidation of alkenes to the corresponding epoxides is a process of large industrial importance since many epoxides are produced in large quantities and epoxides are base chemicals for the preparation of a large variety of polymers and commodities (28). Thus, it was observed that in the aerobic oxidation of styrene promoted by NHPI/Fe(BTC) the initial product with very high selectivity is benzaldehyde coming from the oxidative degradation of C=C double bond. As the concentration of benzaldehyde increases, styrene oxide starts to appear, growing in percentage to reach 50% selectivity at high styrene conversion. Controls in which aerobic styrene oxidation was performed in the presence of benzaldehyde added on purpose since the initial time do not exhibit any induction period for the appearance of styrene oxide. All these catalytic data point out that styrene oxide formation involves really as reagent or co-catalyst, an oxidized form of benzaldehyde. In contrast, under the same conditions NHPI/Fe(BTC) promotes the aerobic epoxidation of cyclooctene with very high selectivity towards the epoxide. Comparison with homogeneous metal salts show that the initial activity of soluble salts is similar as that of MOF, but dissolved metal ions deactivate quickly due to formation of the corresponding metal oxides. In contrast, the crystal framework of MOF maintains stable the metal ions avoiding their aggregation and collapse. This clearly shows the superior performance of MOF respect to homogeneous metal salts.



Scheme 7. Transition metal catalyzed oxidation of functional groups requiring the presence of NHPI as co-catalyst.



Scheme 8. Aerobic oxidation of cyclooctane and ethylbenzene catalyzed by NHPI/Fe(BTC).

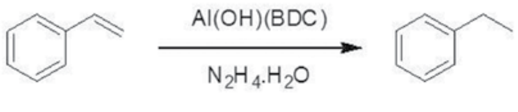


Scheme 9. Aerobic oxidation of cyclooctene and styrene catalyzed by NHPI/Fe(BTC).

REDUCTION REACTIONS

Hydrogenation of C-C multiple bonds are the most widely used type of reduction in organic synthesis (29). Besides hydrogen gas, one alternative to perform this reaction that can be more convenient experimentally for small or medium scale hydrogenations is the use of some reagent that can evolve hydrogen under reaction conditions. One of these reagents is hydrazine that is soluble in water as well as in organic solvents and, when protonated as hydrochloride, is relatively stable and convenient as reducing agent (29). The use of hydrazine instead of hydrogen avoids performing the hydrogenation reaction in closed reactors under high pressure and also minimizes the hazards associated to the use of hydrogen gas. Another advantage of the use of hydrazine is that no noble metals are required in the composition of the catalyst.

We have found that Al(OH)(BDC) with the structure of MIL-53(Al) is a convenient catalyst for hydrogenation of styrene to ethylbenzene by hydrazine (Scheme 10) (30). The catalytic activity of MIL-53(Al) for the process is better than that of other commercial MOFs. The activity of MIL-53(Al) was unexpected and it raises the issue about the need or not of having CUS around the metal ions in order a MOF to act as catalyst. Catalytic activity in MOFs generally derives from metal ions having free coordination positions. Accordingly, MIL-53(Al) should be inactive since its structure is constituted by Al^{3+} ions coordinated octahedrally through two carboxylate groups of BDC without CUS. However, the possibility that defects in the crystal structure with a fraction of Al^{3+} being not totally saturated could introduce catalytic activity in the material has to be considered. Accordingly, it is very likely that MIL-53(Al) is acting as catalyst due to the presence of defects in the crystal structure. In addition, these defects could be created under the reaction conditions, since some reagents can compete with the linker to coordinate with the metal. The presence of defects has been recognized as very important in catalysis for other porous solids such as zeolites where it is known that a significant fraction of Al^{3+} present in their composition does not occupy framework positions, but it is forming oligo- or polymeric oxyhydroxyaluminates. These extraframework Al can play an important role in catalysis since they introduce Lewis acidity in the material. It should be, however, commented that in comparison with zeolites, MOFs are considerably more crystalline, although on the other hand, the coordinative metal-ligand bonds are less robust due to their relatively low strength and are prone to undergo reversible changes.



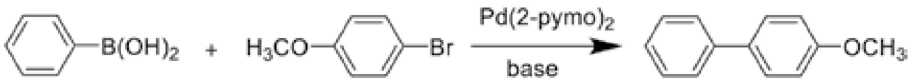
Scheme 10. Reduction of styrene to ethylbenzene catalyzed by Al(OH)(BDC).

Besides hydrazine as hydrogen source, hydrogenations of multiple bonds can be catalyzed by MOFs containing metal nanoparticles embedded inside MOFs pores as active sites (13). In these processes, MOF is really acting as inert support providing large surface area to the active nanoparticle. The role of MOF should be control the metal nanoparticle size distribution to small dimensions and avoid growth of these nanoparticles during the course of the reaction by aggregation of the nanoparticles.

C-C COUPLING REACTIONS

Formation of C-C bonds catalyzed by Pd complexes have become a powerful reaction in the toolbox of organic synthesis due to the high yields that can be achieved, mild reaction conditions, wide scope and compatibility with many different functional groups (31, 32). One of the most obvious possibilities is to use the metal nodes as active sites for the cross-coupling reaction and this strategy requires the synthesis of a Pd-MOFs. In this way, $Pd(2\text{-pymo})_2$ (2-pymo: 2-pyrimidinolate) can promote the Suzuki-coupling between 4-methoxybromobenzene and phenylboronic acid (Scheme 11) (33).

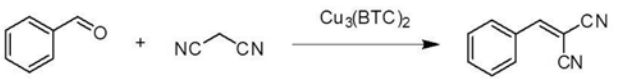
A second strategy is to use the organic linkers of the MOF as ligands to form a complex with Pd^{2+} ion that would be immobilized in the structure. This strategy has the advantage to mimic some highly active homogeneous Pd complexes for C-C cross-coupling reaction. In particular, nitrogen heterocyclic carbenes have been reported to bind strongly with Pd^{2+} ions forming complexes that have high activity in cross-coupling reactions (34). The target in this area should be to develop an extremely efficient and reusable solid catalyst that can compete favourably with homogeneous and heterogeneous Pd catalysts in the cross-coupling of highly demanding reagents. This goal has almost been achieved using MIL-101 as host to incorporate small Pd NPs (35). The high activity of Pd/MIL-101 can be demonstrated by the fact that this solid is able to promote cross-coupling using chlorobenzene as substrate and even chlorobenzenes having substituents in the ortho-position that makes the coupling unfavourable due to steric encumbrance. This MOF catalyst is among the most efficient solid catalysts ever reported.



Scheme 11. $Pd(2\text{-pymo})_2$ catalysed Suzuki-Miyaura coupling reaction.

CARBONYL GROUP CONDENSATION REACTIONS

One of the reaction types often used in the formation of C-C bonds in organic chemistry is condensation reactions in which nucleophilic α-positions of a carbonyl compound attacks other reactive carbonyl group of aldehydes, ketones or carboxylic esters (36). One of the favourite condensation reactions that has been widely used to rank the catalytic activity of Lewis acids has been the Knoevenagel condensation between an active methylene compound and an aldehyde (36). Knoevenagel condensation between benzaldehyde and malononitrile has been performed with zeolites and their activity has been compared with MOFs in the liquid phase (37). It was found that Cu3(BTC)2 and Fe(BTC) are more active and selective than zeolite β and porous titanosilicate TS-1 as catalysts for this condensation. The reason for this better performance of these MOFs is because acidity of zeolites can be too strong for this type of condensation reactions and generally promote secondary reactions that eventually result in lower selectivity due to the formation of byproducts that become entrapped inside the micropores and act as poisons. The optimal strength of MOFs minimizes these secondary process and increases selectivity towards the wanted conjugated product.



Scheme 12. Knoevenagel condensation between benzaldehyde and malononitrile catalyzed by Cu$_3$(BTC)$_2$.

SUMMARY AND FUTURE PROSPECTS

In spite of the large number of reports that have already appeared using MOFs as heterogeneous catalysts for liquid phase reactions, this area is clearly still in its infancy and it will be continuously growing in the next years. Since the synthesis of new MOFs with even higher stability, porosity and density in active sites continues to develop intensively, there will be a large interest in testing the catalytic performance of each of these new materials. MOFs having increasing degree in complexity by including a cocktail of various metals and various ligands (mixed-metals and mixed-ligands MOFs) or by incorporating within the voids actives sites will be prepared and they will improve the current performance in various reaction types.

Considering the flexibility in the design and synthesis of MOFs, these materials appear to be very promising for their application in tandem or cascade reactions. Process intensification is a constant target in chemical engineering and this can be achieved by combining two or more individual reactions in a single process. Tandem reactions require generally the presence of catalyst with more than one type of site and it appears that MOFs are very suited in this area, since they can offer several possibilities to locate different sites including nodes, organic linkers and voids. MOFs can adapted to the tandem reactions by design during the synthesis and by post-sysnthetic modification of the structure. As commented earlier, many chemical processes are carried out in continuous flow and are based on the use of a solid catalyst. Amorphous and crystalline metal oxides, supported metal nanoparticles, zeolites as acid or bifunctional catalysts are examples of successful solids currently used in the chemical industry. Therefore, the target in the field of MOFs as catalysts is to show that they can also compete favorably with other solids as industrial catalysts in reactions that lead to the production of fine chemicals. Development of an industrial process based on the use of MOF as catalyst will serve to prove that this type of crystalline solids can overcome their main limitations in terms of stability and durability. We have no doubt that in the near future some important chemical processes will make use of MOFs as catalysts.

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