

Characterization and Synthesis Catalytic Investigation of Metal-Organic Frameworks

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Abstract

The design and synthesis of catalysts for the chemical fixation of CO₂ is an area of current interest due to the increasing demand for fuel and the major contribution of CO₂ to global warming. An attractive approach to use CO₂ as a chemical feedstock is the coupling reaction of CO₂ and epoxides to form cyclic carbonates using catalyst. Metal-organic frameworks (MOFs) are promising candidates in heterogeneous catalysis because of their unique properties, including well-defined structures, large specific surface areas and tunable structural and functional features. One of the excellent strategies to construct MOFs with high density of catalytically active metal sites is to utilize metalloligands. In efforts to synthesize MOF-based catalysts for the chemical fixation of CO₂ and being inspired by highly active homogeneous metal-salen catalysts, this project involves the synthesis of salen type metalloligands and their assembly to MOFs.

Keywords: Synthesis, catalysts, Metal-organic frameworks, chemical,

Introduction

There is no doubt that catalysis is indispensable to mankind. Catalysis plays a key function in all biological reactions and is utilized in over 80% of all chemical industrial processes, which fulfills the societal needs, including food, clothes and fuel production. A catalyst is a chemical species that accelerates a chemical reaction, by offering an alternative and energetically more favorable pathway to the non-catalyzed reaction and is returned to its original state at the end of the reaction. Thereby, the use of catalysts enables processes to be carried out under more feasible reaction conditions, such as temperature and pressure that are attainable in industry. Yet, a catalyst only changes the kinetics of the reaction but not the thermodynamics, i.e. the overall change in free energy for a catalytic reaction equals that of the uncatalyzed reaction, this is because the catalyst accelerates forward and reverse reaction to the same extent. A characteristic of all good catalysts is the balance between bonding to reactants and separation from products. If the bonding is too weak the reactants cannot be readily activated, and if the bonding is too strong stable intermediates do form, both of which make the conversion of reactants to products unlikely. Three key parameters are often used to evaluate catalyst performance, i.e. activity, selectivity and stability.

Metal-organic frameworks

MOFs are a special group of coordination polymers that have been extensively investigated in recent years due to their unique properties and applications in various areas, including gas adsorption and separation, chemical sensing, magnetism

and catalysis. MOFs are solid materials with infinitely extended crystal structures, where cationic systems such as metal ions or clusters acting as nodes, are connected with polytopic organic ligands acting as linkers (Figure 1.1) These ligands are usually carboxylates or nitrogen donor moieties, which interact strongly with the metal centers (metal ions or clusters) via covalent or coordination bonds. Weaker intermolecular interactions, such as hydrogen bonds, van der Waals forces and π - π interactions, facilitate the formation of frameworks with well-defined structures and topologies. MOFs can be either two- or three-dimensional (2D, 3D) frameworks with structural flexibility and/or robustness, however, the establishment of permanent porosities is crucial for their function and provides these materials with high specific surface areas. One important feature of MOFs is that their structural aspects, including pore sizes, shapes and chemical properties, can be finely tuned by carefully selecting the metal building units, organic ligands and synthetic conditions.

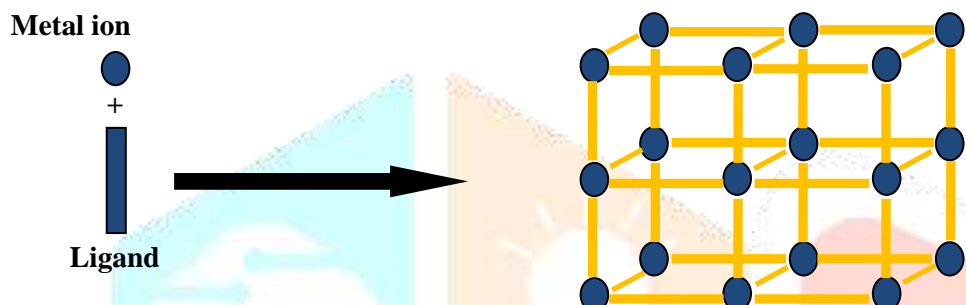


Figure 1.1 Schematic representation of a MOF

Designing MOFs for heterogeneous catalysis

Since 1994, when Fujita and coworkers demonstrated for the first time the catalytic activity of a MOF-based material, the 2D square network $[\text{Cd}(4,4'\text{-bpy})_2](\text{NO}_3)_2$, the design of MOFs for applications in heterogeneous catalysis has been growing rapidly. Because of the inorganic-organic hybrid nature of MOFs, MOF catalysts can be divided into two classes: (i) catalysis at the metal center where the metal ions/clusters are catalytically active and (ii) organic catalysts, where functional groups on the ligands induce the catalytic activity. In this project we are interested in MOFs with catalytically active metal centers. In these systems, the catalytically active metals can be incorporated directly as a part of the framework or modifying the linkers in the existing MOFs by introducing the catalyst (postsynthetic modification) as depicted in Figure 1.2.

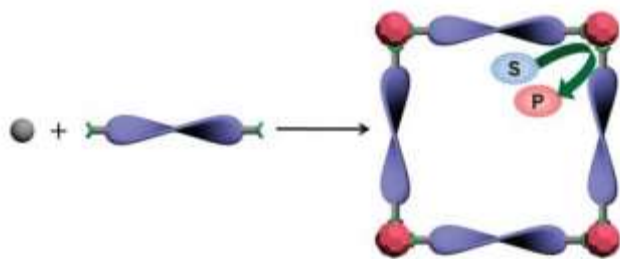


Figure 1.3 a. MOF-based metal node catalyst, direct incorporation

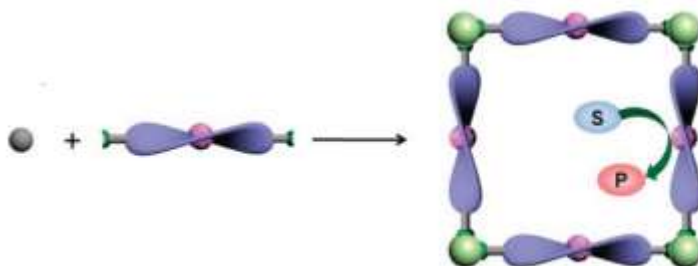


Figure 1.3 b MOF-based privileged metal catalyst, direct incorporation

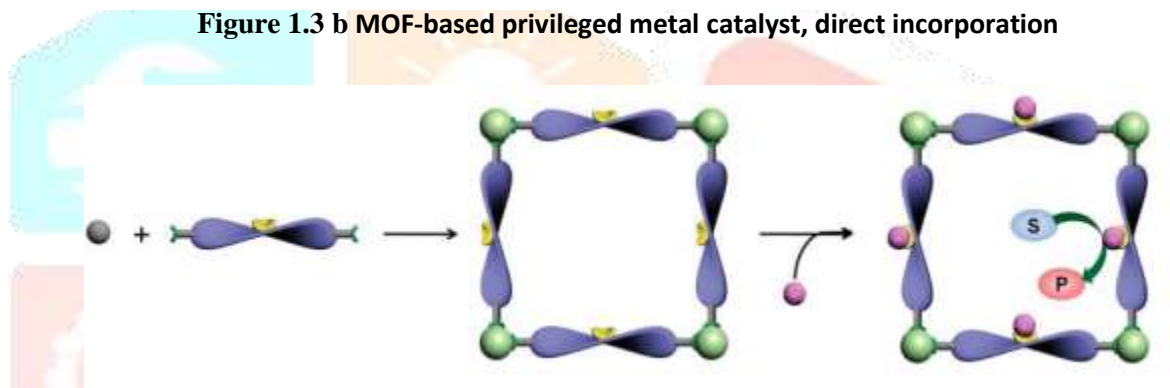


Figure 1.3 b MOF-based privileged metal catalyst, postsynthetic modification. Spheres represent metal ions/clusters and blue connecting units represent the organic ligands. The green arrow emphasizes the catalytic site in the framework (S = substrate, P = product).

An alternative approach to incorporate catalytically active metal sites into MOFs is by utilizing metalloligands. Metalloligands are molecular complexes that contain two or more Lewis basic sites that are able to coordinate with other metal ions. Ideally, a metalloligand contains two types of coordination sites, i.e. primary and secondary. The secondary groups react with catalytically active metal centers, producing the sites where interactions with guest molecules take place. The primary groups (generally carboxylates or pyridine derivatives) facilitate the formation of MOFs by coordinating to a second metal center. These compounds offer several advantages: (i) highly ordered architectures with high density of single catalytic sites, (ii) induce structural rigidity resulting in stable frameworks, (iii) tunable topology and surface functionality; by changing the nature of metal ions and organic linkers, and (iv) assembly of catalytically active homogeneous metal complexes into heterogeneous networks. Although, various metalloligands have been reported, the most common types are based on porphyrin and Schiff base complexes.

In the past decades, chemical fixation of CO₂ has received much attention as a result of the increasing demand for fuel and other energy sources all around the globe, as well as its major contribution to the global warming. Because CO₂ is readily available, nontoxic, inexpensive and a renewable carbon resource, it is highly desirable to utilize CO₂ as a chemical feedstock. However, CO₂ displays high thermodynamic stability and its transformation to more desirable products is a challenging task. To date, various methodologies in utilizing CO₂ as a source of materials and energy have been reported, some of which have already been exploited in industrial applications. This includes the photo- and electrochemical reduction of CO₂ to CO, methane, methanol and formic acid. An alternative and attractive approach, which has recently gained significant interest, is the cycloaddition reaction of CO₂ to epoxides to yield cyclic carbonates and/or polycarbonates. Cyclic carbonates are valuable products, displaying low toxicity and have broad industrial applications, such as solvents, diluents and coalescing agents. Furthermore, polycarbonates have been immensely used in electronics, optical media and medical industry.

Many catalytic systems have been developed for cyclic carbonate formation, such as the usage of highly toxic phosgene, inorganic ammonium salts and homogeneous metallocene complexes. Although several types of heterogeneous catalysts have also been employed (metal oxides and titanosilicates), these materials generally require high temperatures and/or pressures and also suffer from low reaction yields. Thus, there is a pressing need to develop efficient heterogeneous catalysts for the coupling reaction of CO₂ with epoxides. MOFs are attractive candidates due to their high affinity for CO₂, permanent porosity and large specific surface area. The cycloaddition of CO₂ to epoxides is generally acid catalyzed and the acidic catalytic sites can be easily incorporated in MOFs. Moreover, the highly organized 3D arrays of catalytic sites in MOFs are envisioned to result in product selectivities that are comparable to homogeneous catalysts. The crystalline nature of these compounds also allows for easy separation from reaction mixtures and their reuse.



Figure 1.4 Cycloaddition of CO₂ to epoxides to form cyclic carbonates, general reaction. R = alkyl/aryl group

Synthesis of MOFs

For all the attempted synthesis of MOFs, only metalloligand 7aI was utilized as the ligand component because of its ease of preparation, compared to the other metalloligands. As a first trial for the formation of crystalline frameworks, 7aI was dissolved in ethanol to give 2.5% (w/v) solutions and layered with 6 mM aqueous solutions of four different metal salts, namely Ca(NO₃)₂·4H₂O, CaCl₂·2H₂O, Cu(NO₃)₂·3H₂O and Zn(NO₃)₂·6H₂O, respectively. In all cases an orange gel-like precipitate formed after the mixtures were allowed to stand at room temperature for several days. These observations apparently indicated that water was not a proper solvent for this task.

Experiment	7aI (mmol)	Metal salt	Temperature (°C)	Reaction time (h)	Observation
1	0.03	LaCl ₃ ·7H ₂ O	80	1	No precipitate
2	0.03	Zn(NO ₃) ₂ ·6H ₂ O	100	12	No precipitate
3	0.03	Cu(NO ₃) ₂ ·3H ₂ O	100	18	Reddish orange crystalline solid

Table 1.1 Attempted synthesis of MOFs, constructed from 7aI and different metal salts in 3 mL of DMF upon heating

As emphasized in Table 1.1, crystalline material was observed when 7aI was treated with the Cu(II) metal salt under the previously described reaction conditions. In contrast, no precipitate was observed when La(III) and Zn(II) metal precursors were utilized under similar conditions. Additionally, light orange flakes were observed floating in the Cu(II)-metalloligand solution. These crystals were insoluble in methanol and slightly soluble in DMF, indicating that a coordination polymer was formed. Unfortunately, the crystals were not single, rather forming fibrous networks. Still, these findings suggested that Cu(II) metal ions were ideal candidates for the preparation of MOFs with metalloligand 7aI. Thus, we have chosen Cu(NO₃)₂·3H₂O as the secondary metal component.

Conclusion

A series of carboxylic acid functionalized metalloligands with Cr(III), Cu(II) and Co(III) metal centers were successfully prepared. The incorporation of Cr(III) to 5a proceeded well, but alternative synthetic procedures are envisioned to increase the reaction yield with the latter two metals. To the best of our knowledge these are the first salen type metalloligands with primary functional groups arranged on the diamine backbone. The construction of MOFs from the Cr(III) metalloligand 7aI turned out to be more difficult compared to numerous reported frameworks with salen metalloligands with modified aryl backbone. Although, room temperature synthesis was unsuccessful due to the high solubility of the tert-butyl substituted ligand, high temperature methods including solvothermal synthesis gave promising results, using Cu(II) as a secondary metal component. The formation of coordination polymers was concluded by solubility test, but we were not able to get the structural determination of these compounds because we could not isolate X-ray quality single crystals.

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