

A Research on the Characterization and Catalytic Investigation of Metal-Organic Frameworks

***Dr. Anita Prashant**

Abstract

Given the rising need for fuel and the significant role that CO₂ plays in global warming, there is currently interest in the design and synthesis of catalysts for the chemical fixation of CO₂. The coupling reaction of CO₂ with epoxides to create cyclic carbonates using a catalyst is an appealing method of exploiting CO₂ as a chemical feedstock. The distinct characteristics of metal-organic frameworks (MOFs), such as their high specific surface areas, well-defined structures, and adjustable structural and functional aspects, make them attractive options for heterogeneous catalysis. Using metalloligands is one of the best ways to create MOFs with a high density of catalytically active metal sites. Motivated by extremely active homogeneous metal-salen catalysts, this study aims to create MOF-based catalysts for the chemical fixation of CO₂ by synthesizing salen type metalloligands and assembling them into MOFs.

Keywords: Catalysts Synthesis, Chemical, Metal-Organic Frameworks

Introduction

Without a doubt, catalysis is essential to humankind. All biological reactions depend on catalysis, which is also used in more than 80% of chemical industrial operations that produce food, clothing, and fuel, among other necessities for society. By providing a different and energetically more advantageous route to the non-catalyzed process, a catalyst is a chemical species that speeds up a chemical reaction and returns to its initial state at the conclusion of the reaction. As a result, the employment of catalysts makes it possible to conduct operations at more practical reaction conditions, such pressure and temperature, that are achievable in industry. However, since a catalyst speeds both forward and reverse reactions equally, it only modifies the kinetics of the reaction and not the thermodynamics; in other words, the total change in free energy for a catalytic reaction is equal to that of the uncatalyzed process. The harmony between reactant bonding and product separation is a feature of all effective catalysts. It is unlikely that reactants will convert to products if the bonding is too strong because stable intermediates will emerge and reactants cannot be easily activated. Catalyst performance is often assessed using three essential parameters: stability, selectivity, and activity.

Frameworks of metals and organics

MOFs are a unique class of coordination polymers that have been the subject of much research recently because of their unusual qualities and uses in a number of fields, including as chemical sensing, gas adsorption and separation, magnetism, and catalysis. MOFs are solid materials with indefinitely extended crystal structures that are joined by polytopic organic ligands that function as

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linkers and cationic systems like metal ions or clusters that serve as nodes (Figure 1.1). These ligands, which are often carboxylates or nitrogen donor moieties, have strong covalent or coordination bond interactions with the metal centers (metal ions or clusters). Van der Waals forces, hydrogen bonds, and π - π interactions are examples of weaker intermolecular interactions that make it easier to create frameworks with distinct topologies and architectures. The formation of persistent porosities is essential to the operation of MOFs, which may be two- or three-dimensional (2D, 3D) frameworks with structural flexibility and/or resilience. This gives these materials large specific surface areas. By carefully choosing the metal building blocks, organic ligands, and synthesis conditions, MOFs' structural characteristics—such as pore sizes, shapes, and chemical properties—can be precisely adjusted.

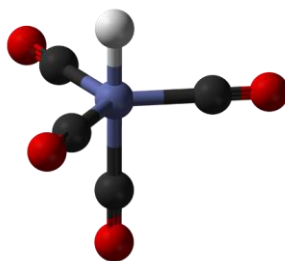


Figure 1: Schematic representation of a MOF

Designing MOFs for heterogeneous catalysis

Designing MOFs for use in heterogeneous catalysis has been accelerating since 1994, when Fujita and colleagues first showed the catalytic activity of a MOF-based material, the 2D square network $[\text{Cd}(4,4'\text{-bpy})_2](\text{NO}_3)_2$. MOF catalysts may be classified into two kinds due to their inorganic-organic hybrid nature: (i) catalysis at the metal center, where the metal ions or clusters are catalytically active, and (ii) organic catalysts, where the catalytic activity is induced by functional groups on the ligands. MOFs with metal cores that are catalytically active are of interest to us in our endeavor. The catalytically active metals in these systems may be added straight to the framework or modified by adding the catalyst (postsynthetic modification) to the linkers in the already-existing MOFs.

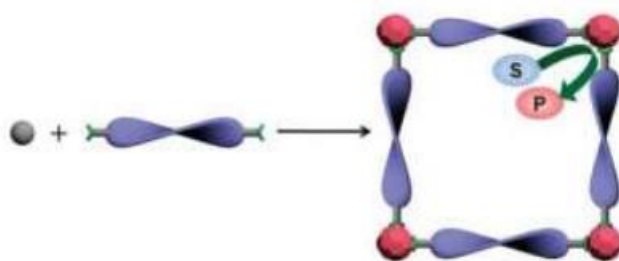


Figure 1.2 a. MOF-based metal node catalyst, direct incorporation

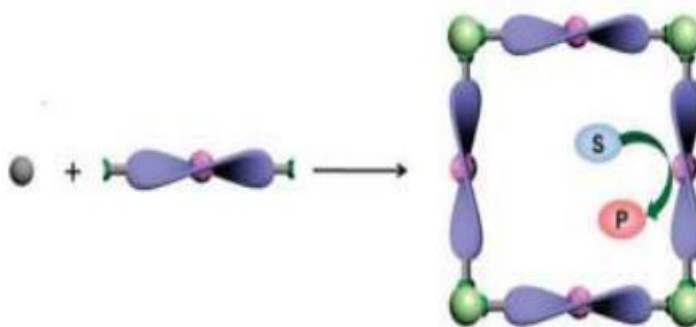


Figure 1.2 b MOF-based privileged metal catalyst, direct incorporation

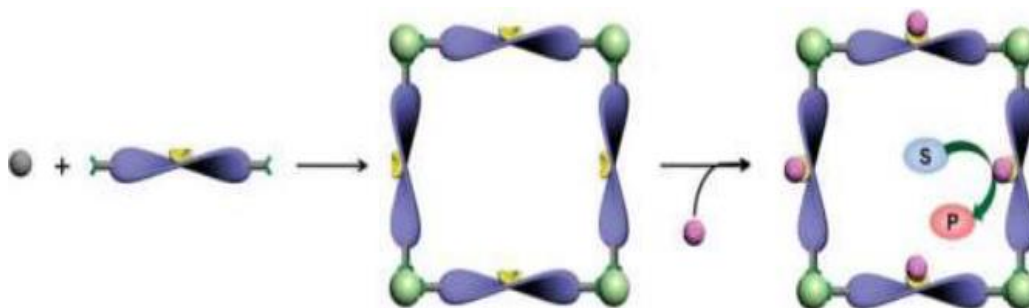


Figure 1.2 C Spheres represent metal ions/clusters and blue connecting units represent the organic ligands.

The green arrow emphasizes the catalytic site in the framework (S = substrate, P = product).

Using metalloligands is an alternate method of adding catalytically active metal sites to MOFs. Molecular complexes having two or more Lewis basic sites that may interact with other metal ions are known as metalloligands. A metalloligand should ideally have both primary and secondary coordination sites. The locations where interactions with guest molecules occur are created when the secondary groups react with catalytically active metal centers. By coupling to a second metal center, the main groups—typically carboxylates or pyridine derivatives—help MOFs develop. By altering the composition of metal ions and organic linkers, these compounds provide a number of benefits, including (i) highly ordered architectures with a high density of single catalytic sites, (ii) structural rigidity that results in stable frameworks, (iii) tunable topology and surface functionality, and (iv) the assembly of catalytically active homogeneous metal complexes into heterogeneous networks. The most prevalent kinds of metalloligands are based on porphyrin and Schiff base complexes, despite the fact that many other kinds have been documented.

Due to its significant role in global warming and the growing demand for fuel and other energy

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sources worldwide, chemical fixation of CO₂ has drawn a lot of interest in recent decades. It is very desirable to employ CO₂ as a chemical feedstock as it is a widely accessible, affordable, harmless, and renewable carbon supply. Nevertheless, CO₂ has strong thermodynamic stability, and it may be difficult to convert it into more appealing compounds. Numerous methods for using CO₂ as a source of energy and materials have been documented to date; some of them have actually been used in industrial settings. CO₂ may be reduced both photochemically and electrochemically to produce CO, methane, methanol, and formic acid. The cycloaddition reaction of CO₂ to epoxides to produce cyclic carbonates and/or polycarbonates is an alternate and appealing strategy that has attracted a lot of attention lately. With their low toxicity and wide range of industrial uses as solvents, diluents, and coalescing agents, cyclic carbonates are important products. Additionally, polycarbonates are widely utilized in the medical, optical, and electronics industries.

Numerous catalytic systems, including homogenous metallocene complexes, inorganic ammonium salts, and very poisonous phosgene, have been created for the synthesis of cyclic carbonates. Metal oxides and titanosilicates are two examples of heterogeneous catalysts that have been used, although they often need high temperatures and/or pressures and have poor reaction yields. Therefore, the development of effective heterogeneous catalysts for the coupling reaction of CO₂ with epoxides is urgently needed. MOFs are appealing options because of their huge specific surface area, persistent porosity, and strong affinity for CO₂. The cycloaddition of CO₂ to epoxides is often catalyzed by acid, and MOFs may readily include the acidic catalytic sites. Furthermore, it is anticipated that the highly ordered 3D arrays of catalytic sites in MOFs would provide product selectivities that are on par with those of homogeneous catalysts. These chemicals' crystalline structure also makes it simple to separate them from reaction mixes and repurpose them.

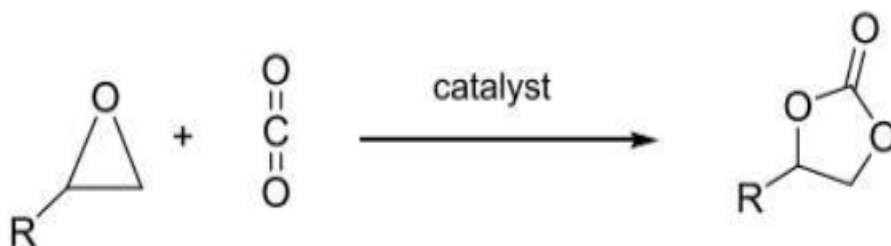


Figure 1.3 Cycloaddition of CO₂ to epoxides to form cyclic carbonates, general reaction. R = alkyl/aryl group

MOF Synthesis

Due to its simplicity of manufacture in comparison to the other metalloligands, only metalloligand 7aI was used as the ligand component for all attempted MOF synthesis. 7aI was dissolved in ethanol to create 2.5% (w/v) solutions as a preliminary test for the development of crystalline frameworks. These were then layered with 6 mM aqueous solutions of four distinct metal salts: Ca(NO₃)₂·4H₂O, CaCl₂·2H₂O, Cu(NO₃)₂·3H₂O, and Zn(NO₃)₂·6H₂O, in that order. After the combinations were left to remain at room temperature for a few days, an orange gel-like precipitate developed in each instance. Water was not a suitable solvent for this purpose, based on these findings.

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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

When 7aI was treated with the Cu (II) metal salt under the previously mentioned reaction conditions, crystalline material was seen, as highlighted in Table 1.1. On the other hand, when La(III) and Zn(II) metal precursors were used in comparable circumstances, no precipitate was seen. Light orange flakes were also seen floating in the solution of Cu (II)-metalloligand. A coordination polymer was generated, as shown by the crystals' modest solubility in DMF and insoluble nature in methanol. Regretfully, the crystals formed fibrous networks rather than being solitary. Nevertheless, these results showed that Cu (II) metal ions were the best options for using metalloligand 7aI to construct MOFs.

Therefore, Cu (NO₃)₂·3H₂O has been selected as the secondary metal component.

Conclusion

It was effectively possible to create a number of carboxylic acid functionalized metalloligands with Cr(III), Cu(II), and Co(III) metal centers. Although the addition of Cr(III) to 5a went well, other synthetic processes are planned to boost the reaction yield with the last two metals. As far as we are aware, they are the first metalloids of the Salen type that have major functional groups positioned on the diamine backbone. Compared to several previously published frameworks using salen metalloligands with modified aryl backbones, the formation of MOFs from the Cr(III) metalloligand 7aI proved to be more challenging. Using Cu(II) as a secondary metal component, high temperature techniques such as solvothermal synthesis produced encouraging results, despite the fact that room temperature synthesis failed because of the high solubility of the tert-butyl substituted ligand. A solubility test was used to determine the formation of coordination polymers, but since we were unable to isolate single crystals of X-ray grade, we were unable to determine the structural makeup of these compounds.

***Department of Chemistry
BBD Govt. College
Chimanpura, Shahpura**

References

- [1] Chorkendorff, I.; Niemantsverdriet, J. W. Concepts of Modern Catalysis and Kinetics, 2nd ed. Wiley-VCH Verlag GmbH & Company, Weinheim, 2007.

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- [2] Baerns, M. Basic Principles in Applied Catalysis. Springer-Verlag, Berlin Heidelberg, 2004.
- [3] Ma, Z.; Zaera, F. In Encyclopedia of Inorganic Chemistry, 2nd ed. King, R. B., Ed. Heterogeneous Catalysis by Metals. John Wiley & Sons, 2006, pp. 1-17.
- [4] Nelson, D. L.; Cox, M. M. Lehninger Principles of Biochemistry, 5th ed. W. H. Freeman and Company, New York, 2008.
- [5] Farnetti, E.; Monte, R. D.; Kašpar, J. In Inorganic and Bio-Inorganic Chemistry, Vol. 2. Bertini, I., Ed. Homogeneous and Heterogeneous Catalysis. Eolss Publishers, Oxford, 2007, pp. 50-56.
- [6] Duca, G. Homogeneous Catalysis with Metal Complexes. Springer-Verlag, Berlin Heidelberg, 2012.
- [7] Fadhel, A. Z.; Pollet, P.; Liotta, C. L.; Eckert, C. A. Molecules. 2010, 15, 8400-8424.
- [8] Wang, Z.; Cohen, S. M. Chem. Soc. Rev. 2009, 38, 1315-1329.
- [9] Kleter, G.A., Harris, C., Stephenson, G., Unsworth, J. (2008) Comparison of herbicide regimes and the associated potential environmental effects on glyphosate-resistant crops versus what they replace in Europe. Pest Management Science 64:479-488. DOI: 10.1002/ps.1513
- [10] Senesi, N., Wilkinson, K.J. (eds.) (2008) Biophysical Chemistry of Fractal Structures and Processes in the Environment. IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, J. Buffle & H. Van Leeuwen (Eds), Vol. 11, John Wiley and Sons, New York, 340 pp. ISBN: 978-0-470-01474-5
- [11] Violante A.; Huang P.M.; Gadd G.M. (eds) (2008) Biophysico-Chemical Processes of Heavy Metals and Metalloids in Soil Environments. IUPAC Series on Biophysico-Chemical Processes in Environmental Systems, P.M.Huang & N. Senesi (Eds), Vol. 1, Wiley-Interscience, Hoboken, New Jersey, 658 pp. ISBN: 978-0-471-73778-0