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Introduction

“The Chemistry of Metal-Organic Frameworks: Synthesis, Characterization, and Applications” aims to provide a complete reference book to researchers within the metal-organic frameworks (MOFs) field, covering a range of topics including topology networks, applications and characterisation techniques. MOFs are materials which contain metal ion centres and organic bridging ligands and are often, but not always, porous. Over the past 15 years the field has proliferated a huge number of publications with over 10,000 MOF structures published. More recently the literature has moved towards testing MOFs for a range of applications and considering how materials are formed and scaled-up. The book reflects this change with several chapters detailing possible applications as well as the fundamental chemistry of the materials. The book is split into several different parts with the two largest sections devoted to the metal nodes and linkers along with the resulting functionality. It is noteworthy that the appendix contains the names of companies commercially supplying MOFs along with datasheets for the seven most stable materials, which is useful but could have been extended to include a wider range of materials.

Network Topology

The first scientific chapter of the book authored by Frank Hoffmann and Michael Fröba (University of Hamburg, Germany) is dedicated to network topology. The majority of MOF papers now published contain topological considerations in terms of the periodic networks so it is appropriate to discuss some of the fundamentals associated with nets and topologies within the book. Topological descriptions make use of a range of different symbols which are used to characterise the aspects of the topology and these symbols are explored in detail with examples which can be related to the MOF field. The chapter is useful to MOF chemists interested in predicting the properties of certain structures as well as designing MOFs with a set of desired properties. The authors also encourage the community to publish MOF structures in the augmented version (-a) (Figure 1) for two reasons:
aesthetics and that visually this representation appeals to the chemist’s instinct of designing structures using different types of polyhedral.

Part I: MOF Chemistry of Metallic Clusters and Other Nodes

This part of the book consists of seven different chapters and centres around the chemistry of metal nodes within MOF structures. Most of the chapters focus on a specific group of metals, for example alkaline earth metals (Chapter 4 by Debasis Banerjee et al. (Rutgers University, USA)) or lanthanide group metals (Chapter 9 by Klaus Müller-Buschbaum (Universität Würzburg, Germany)). There is no set chapter format within the book and as a result the information within each chapter varies. Generally however they contain a good summary of known MOFs and their interesting properties.

The first chapter of Part I by Alexander Schoedel and Omar Yaghi (University of California, Berkeley, USA) details the reticular chemistry of MOFs based on zinc and copper secondary building units (SBUs). The diversity and number of zinc- and copper-based MOFs that are reported is in part due to the versatility found in the SBUs of the metal centres. A useful table summarising the most common zinc- and copper-based SBUs along with associated MOFs and references can be found at the end of the chapter.

Chapter 6 by Mathieu Bosch, Shuai Yuan and Hong-Cai Zhou (Texas A&M University, USA) examines the use of Group 4 metals (titanium, zirconium and hafnium) in MOF synthesis. Materials based on these metal centres have been widely studied by the community and are generally more stable than MOFs based on other metals. The focus of the chapter is the zirconium-based MOF UiO series of materials, their modulated synthesis and material stability. The effect of missing linker defects and post-synthetic linker exchange are also discussed and the large variety of accessible zirconium-based MOFs is in evidence. The chapter also details zirconium porphyrinic MOFs and the different types of connectivity observed in these structures, as is exemplified in Figure 2.

Chapter 8 by Elisa Barea, L. Marleny Rodríguez-Albelo and Jorge Navarro (Universidad de Granada, Spain) focuses on using platinum group metals (pgms) in MOF synthesis. This is of interest as these materials are rare and MOFs which contain pgms tend to incorporate them as metallic nanoparticles within the pores not as the metal nodes themselves. The chapter describes single metal node MOFs, metallooligand based mixed metal MOFs, paddle-wheel metal cluster based MOFs and the subsequent properties of these materials.

Part II: Functional Linkers

This section concentrates on organic linkers and the functionality that can be introduced into MOFs by using different organic molecules. Due to the huge diversity in this area each chapter covers a different topic of interest. Chapter 10 by Hiroyasu Furukawa and Xixi Sun (University of California, Berkeley) explains the use of extended linkers to form ultra-high surface area MOFs. The chapter contains a table of linkers used in MOF synthesis. The resulting MOF formula, name and
Using MOFs as catalysts is of particular interest. With the wide range of metals and linkers that can be incorporated into MOFs there is the potential to design materials as catalysts for specific transformations. Chapter 12 by Alexandre Legrand, Jérôme Canivet and David Farrusseng (University Lyon 1, France) focuses on this subject and gives a broad overview of the topic and materials. Different routes for designing MOF catalysts are also discussed. Specific examples are given along with methods to accurately and reliably characterise such materials.

Other chapters in this section detail linkers which can be used to introduce chirality (Chapter 13 by Christel Kutzscher et al. (Technische Universität Dresden)) or optical functionality (Chapter 15 by Mark Allendorf, Kirsty Leong and Ryan Zarkesh (Sandia National Laboratories, USA)) into MOF materials. Chapter 14 by Gang Xu et al. (Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, P.R. China) describes how designing organic linkers can be used to produce electron-conducting MOFs. Overall the focus of the chapters in Part II is on properties of the materials and how these could be used in specific applications.

Part III: Special MOF Classes and Morphology

Design of MOFs

This is the smallest section of the book and contains some interesting examples of nanoparticle MOFs (Chapter 16 by Michael Beetz, Andreas Zimpel and Stefan Wuttke (University of Munich, Germany)) and surface MOFs (Chapter 17 by Lars Heinke et al. (Karlsruhe Institute of Technology, Germany)). The challenges associated with these two sets of materials are discussed whilst also noting their advantages over the bulk materials. Of particular interest from an industrial point of view is Chapter 18 by U-Hwang Lee (Research Center for Nanocatalysts, Korea Research Institute of Chemical Technology, Korea) et al. on granulation and shaping of MOFs. To date the literature contains very little information on this, so a chapter dedicated to the subject is promising. Different techniques (granulation, extrusion, pressing) are discussed along with their impact on the MOF. The performance of a shaped MOF is highly dependent on how it has been shaped and will be determined by its application. Ensuring that the MOF structure remains intact is important as is retaining surface area so for this reason there is a compromise.
between these parameters and the mechanical strength and stability of the shaped body. This chapter is a nice introduction to the shaping of MOFs and the important aspects researchers need to consider when producing shaped MOFs.

Part IV: Progress in Advanced Characterisation of MOFs

This part of the book features characterisation techniques used to investigate MOF materials beyond the standard single crystal determination and X-ray diffraction measurements. Chapter 25 by Guillaume Maurin (CNRS UM ENSCM Université Montpellier, France) covers the role of molecular simulations within the field and is particularly timely given the developments that have occurred recently with software developed to both generate potential MOFs and screen materials for interesting adsorption properties.

Chapter 26 by Olesia Halbherr (Ruhr-University Bochum, Germany) and Roland Fischer (Technical University Munich) details defects and disorder in MOF structures. This is a very current topic within the field, as how defects affect the stability and performance of MOFs is of great interest at the moment. This chapter includes different types of defects within MOFs, ways to characterise them and finishes with a couple of examples. It is a good summary of the current understanding of defects.

The most interesting chapter within this section however deals with adsorption methodology (Chapter 19 by Irena Senkovska (Technische Universität Dresden) et al.). The reliable characterisation of porosity and surface area within MOFs is essential to any MOF researcher. The authors cover everything from sample preparation, choice of adsorbive and the theory behind the Brunauer, Emmett and Teller (BET) equation. It is an important and necessary chapter which details methodology for the reproducible determination of surface area and porosity within MOFs.

Conclusion

The scope of the book is ambitious and provides a comprehensive summary of the current field. It provides both a high level overview of the subject and detailed examples of the materials and their applications. For the reader however there is a lack of structure to the book, each chapter has a different author and there is not a consistent chapter format. As a result, some chapters focus on fundamental chemistry and material design while others are more concerned with applications and material performance. This disparity is the main flaw with the book, however there is a comprehensive list of references for follow up reading should a more detailed view be sought. As a whole the book is a good introduction for early stage researchers and a useful reference book for more established researchers within the MOF field.

Reference


The Reviewer

Sheena Hindocha joined Johnson Matthey in 2014 after completing her PhD at Imperial College London, UK. She now works as a Senior Scientist at Johnson Matthey Technology Centre in Sonning Common, UK, where she researches metal-organic frameworks for a range of different applications.