

Metal-Organic Frameworks

Metal-organic frameworks, sometimes called porous coordination polymers, constitute a large and steadily expanding group of micro- and mesoporous materials. They combine inorganic parts (metal ions) with organic parts (linkers) to form crystalline three-dimensional structures with covalent bonds. At present, there are three main groups of crystalline nanoporous materials, namely zeolites, mesoporous molecular sieves, and now metal-organic frameworks (MOFs). From the chemical point of view, MOFs exhibit the greatest flexibility of structures and properties, as they benefit from the combination of organic and inorganic structural building units and from the possibility of modifications (both before and after the synthesis). As they bridge the gap between purely organic and inorganic materials, MOFs are exciting materials with a great potential for applications in adsorption, separation, drug delivery, biomedical applications, sensing, catalysis, etc. However, MOFs need to show improvements in stability and performance when compared with other nanoporous materials, particularly those that are already used in industrial applications.

This book edited by David Farrusseng is one of the very first attempts to evaluate the current state of the art in synthesis, structures, properties, and potential applications of MOFs. For this purpose, Farrusseng has brought together a number of excellent researchers from academia and industry, and their contributions cover practically all important areas of current MOFs research. The book starts with a brief introduction to MOFs, addressing the chemistry of porous materials, their chemical and textural properties, and the scope for preparing multifunctional frameworks. This is followed by a nice overview of post-synthetic procedures aimed at functionalizing MOFs following their preparation. Modification approaches include the coordination of various functionalities to unsaturated inorganic centers or to organic linkers. The key topics of this overview are chemical treatments of MOFs with various imines or amides, the potential of click chemistry, and the introduction of organometallic complexes.

The following chapters discuss the sorption properties of MOFs, with potential applications to separation and purification of gases, CO₂ capture, and hydrogen storage. In general, MOFs exhibit interesting adsorption properties on a laboratory scale, but to achieve real applications will also depend on other factors: production costs, environmental issues, long-term stability, shaping, product

formulation, recycling, etc. The separation of xylene isomers is an example of a challenging application, in which several MOF materials show promising properties compared with zeolites. Their high adsorption capacity and low adsorption enthalpy can favor some MOFs over zeolites, but poorer thermal and mechanical stability, as well as economic factors, could prevent large-scale applications.

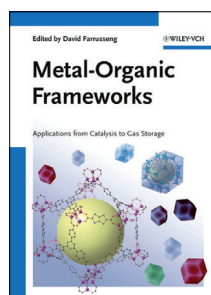
In recent years, there has been a rapid expansion in exploring the catalytic properties of MOFs for hundreds of different transformations of organic substrates. The fact that the book has only one chapter on the use of MOFs in catalysis might be seen as an underestimation of their potential in this area; although, the chapter discusses a wide variety of reactions in relation to the catalytic functionalities of MOFs. The chapter starts with unsaturated organometallic species and their role in catalysis, and deals with the activity of various organic functionalities, including amines and amides. In addition, the roles of intrinsic chirality and chiral organic functions are reviewed. Last but not least, MOFs can be used as matrices for encapsulation of catalytically active species. Polyoxometalates, metalloporphyrins, or metal nanoparticles embedded into the structure of MOFs are discussed as typical active species for a broad variety of acid-catalyzed, oxidation, hydrogenation, and C–C coupling reactions.

Probably the most exciting chapters are the two on biomedical applications and on imaging of MOFs. These areas seem to offer the greatest potential for realistic applications of MOFs, since in adsorption, separation, and catalysis there are many well-established competitors such as zeolites, activated carbons, etc. Applications to controlled drug release for precise dosing of pharmaceuticals or for the release of nitric oxide from NO-loaded MOFs to inhibit platelet aggregation in blood are discussed in detail. In that connection, the toxicity of some iron carboxylates has already been evaluated at the preclinical level.

Two chapters focus on MOFs that can be synthesized as thin films on different supports for sensing applications. Such MOF films are being evaluated for the detection of various ions, small molecules, oxygen, or even explosives.

As a logical conclusion, the final two chapters are centered on the synthesis and shaping of MOFs on the industrial scale, where the economic criteria are completely different from those on a laboratory scale. From the practical point of view, the shaping process that follows the synthesis is definitely critical for final applications.

As the editor explains in the preface, the purpose of this book is to form a critical assessment of the properties of MOFs in relation to process specifications and performance targets. There is no



Metal-Organic Frameworks
Applications from Catalysis to Gas Storage. Edited by David Farrusseng. Wiley-VCH, Weinheim, 2011. 392 pp., hardcover, € 119.00.—ISBN 978-3527328703

doubt that the book achieves that very well. Personally, however, I regret that there is no separate chapter on the structures of MOFs, as the most exciting properties of MOFs actually stem from the combination of their structural and chemical features. A table presenting the most important and structurally diverse MOFs with their textural properties would be more than welcome. In a similar way, when discussing adsorption or catalytic properties of MOFs, a few tables summarizing the applicability of MOFs in these areas would be very helpful for any reader.

This book is definitely a valuable addition to our steadily increasing knowledge of MOF materials. A broad readership of researchers, including

experienced ones as well as newcomers, will certainly benefit from this well-balanced book covering different topics on the chemistry and applications of metal-organic frameworks. I feel that, especially for students, this book can serve as a primary reference source during their first steps in learning about nanoporous materials in general, and metal-organic frameworks in particular.

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DOI: 10.1002/anie.201200812