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Introduction

Stefan Kaskel

In 2002, Ferdi Schüth asked me to write a review chapter on metal–organic frameworks (MOFs) for the handbook of porous solids. Most of the MOFs known at that time would easily fit in one chapter of a book, and even some materials with relatively low porosity could be discussed. What a tremendous progress after a little more than one decade! By 2016 one could fill an encyclopedia with MOF structures alone. Significant progress has not only led to the discovery of materials with record surface areas exceeding that of traditional adsorbents. Major hurdles such as poor hydrothermal stability of the early MOFs have been overcome due to the development of highly stable aluminum and zirconium MOFs. Nowadays more than 10 000 MOFs are known, and MOF databases of hypothetical and real MOFs are being developed for managing the enormous amounts of data. They also give access to search more easily for desired properties, and MOFs with their tailorable pore size and functionality seem to be ideal for the computational design of novel functional materials. In that sense, MOFs are certainly a prototypical "materials genome" test case, as relation between structure and function is readily computed.

Due to the enormous number of MOF structures published today, often the question is asked: Do we need new MOFs? The answer is a question of imagination and creativity! The most exciting research nowadays addresses challenges imagining properties not foreseen 10 years ago. A good example is electronics. For device integration, a key target is the development of electron-conducting MOFs with specific response combining porosity and semiconducting behavior. The latter will enable sensor integration for various control operations. But also ion conductivity is important for fuel cell membranes and other physical properties become relevant, thus fostering the search for ever new materials with enhanced or customized performance.

MOFs have also contributed significantly to the fundamental understanding in the field of porous materials, adsorption phenomena, separation technology, and catalysis. Especially flexibility (switchability) of some MOF materials is a unique feature not observed in other porous solids.

Innovation cycles in materials science may take 20 years or even longer. In the case of polyacrylonitrile (PAN)-based carbon fibers, after their discovery

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in the early 1960s in Japan, it took several innovation cycles, and only today's huge demand in energy savings resulting from the use of lightweight composites changed the scene to a situation where carbon fibre (CF) composites are ubiquitous in airplanes and enter even the car manufacturing sector.

As for any new material, prices are high at an early discovery stage due to the economy of scale. However, such high prices inhibit innovation severely since industry will not consider their use as long as they are not cost competitive. In general the limited availability of even kilogram MOF amounts is an innovation blocker because prototype demonstration requires often a few kilogram material. In this context, start-ups and research institutes offering MOFs for demonstration purposes play a key role. Currently there are already a few sources available offering kilogram MOF samples such as MOF Technologies, metal-organic-frameworks.eu, and ImmondoTech, while some smaller companies offer development services (MOFapps, NuMat, framergy). The biggest company involved in MOF commercialization from early on is BASF. Several larger companies in the United States and Japan have considered MOF commercialization but seem to be waiting how the market develops and for the early patents to run out. For larger-scale production regulatory issues such as REACH, EPA-regulations, toxic substances control act (TSCA), ASEAN regulations, and so on, need to be addressed, an issue that seems impossible to be handled by small and medium sized enterprises (SMEs).

Roadmaps can help to identify promising development targets, and expert workshops are a useful instrument to match technology push with market needs by bringing experts from research institutes and industry together. The outcome of such an expert workshop held late 2013 was published early 2015 as a Roadmap by DECHEMA (Roadmap MOF). However, industrial application targets are changing from year to year.

The chemistry of MOFs as the underlying technological basis has now reached a mature standard, and the book may serve as a basic reference describing the most important compositions, technologies, analysis techniques, and basic properties.

The aim of this book was to organize MOF compounds according to their main components: (i) clusters (or better multinuclear complexes) and (ii) linker systems. Following a more general structural view of networks and their topologies, PART I largely follows the organization of metals in the periodic table, without aiming at a classification since chemical similarity within the periodic table generates fluent passage between certain groups nor aiming for an exhaustive description of all known structures or metals used.

Essential functions in MOFs are generated nowadays by specific functional groups in the linkers, as outlined in PART II. This is not only relevant to achieve the highest degree of porosity by rigid and extended linker design but becomes especially important when it comes to optical or electronic functionality such as fluorescence or charge transport. But also catalysis and separation profit from the modular integration of enantioselective or other functional groups introducing a high degree of selectivity.

Since shaping of MOFs into granules, monoliths, and nanostructures is a prerequisite for any application, PART III addresses those topics specifically. While the chapter on nanoparticles is mostly addressing modern medicinal targets, the chapters on shaping on a macroscale and thin films mostly address technical applications such as heat storage and electronic integration.

The progress in specific characterization methods for MOFs outlined in PART IV is impressive, illuminating long-range structural features, local structural features, reactivity of open sites, and the importance of defect chemistry. Especially the development of *in situ* monitoring techniques in combination with spectroscopies and diffraction gives deep insight into flexibility phenomena and crystallization mechanisms, emphasizing that crystallization is a much more complex phenomenon, and more needs to be understood to achieve a truly rational design of MOFs and other networks. The importance of theoretical modeling and prediction is also pointed out in a chapter by Maurin included in this section.

The appendix contains brief descriptions of a few MOFs that are commercially available, since they are either relatively easy to upscale and/or highly stable chemically. The information summarized shall be a basis for industrial users who are interested to test MOFs in applications as a first choice testing set. This somewhat arbitrary selection is based on the editor experience. Further information is available on request.

We hope the book will be a good starting point for readers as an introduction into MOF chemistry and for experts as a standard reference book.