

## CHAPTER 1

# *Introduction*

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## 1.1 Introduction

The last few decades have witnessed the unprecedented explosion of a new research field built around metal organic frameworks (MOFs). The first reports on metal organic frameworks (MOFs) or, more widely speaking, on coordination polymers date from the late 1950s<sup>1</sup> and early 1960s,<sup>2-6</sup> although it was not until the end of the last century when Robson and co-workers<sup>7,8</sup> followed by Kitagawa *et al.*,<sup>9,10</sup> Yaghi and coworkers,<sup>11</sup> and Ferey *et al.*<sup>12</sup> rediscovered and boosted the field. Metal organic frameworks are crystalline compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one- two-, or three-dimensional pore structures. The combination of organic and inorganic building blocks into highly ordered, crystalline structures offers an almost infinite number of combinations, enormous flexibility in pore size, shape and structure, and plenty opportunities for functionalization, grafting and encapsulation. These materials hold very high adsorption capacities, specific surface areas and pore volumes. Their porosity is much higher than that of their inorganic counterpart zeolites (up to 90%). In contrast to other nano-structured materials, many MOFs display a remarkable flexibility and respond to the presence of guests and external stimuli. Their

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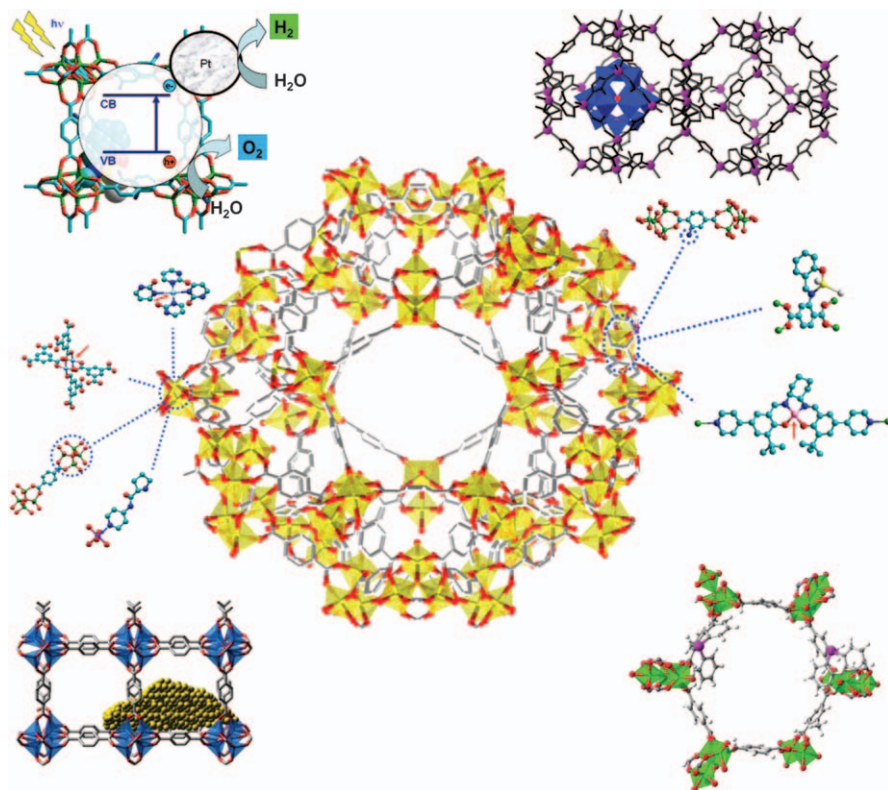
thermostability is sometimes unexpectedly high, reaching temperatures above 400 °C and their chemo-stability is acceptable in many cases.

Indeed MOFs are fascinating porous solids. The assembly of organic and inorganic struts allows, in theory, the facile tuning of properties, either by the chemical functionalization of the organic building units or by selection of the inorganic constituents. Even within such a relatively short time span, the field has rapidly evolved from an early stage, in which the main scope was the discovery of new structures, to a more mature stage in which dozens of applications are currently being explored. High adsorption capacities and easy tunability have crystallized in perspective applications in gas storage, separation and molecular sensing.<sup>13–17</sup> The possibility of synthesizing bio-compatible scaffolds infers a very promising future for medical applications.<sup>18,19</sup> Magnetic, semi-conductor and proton conducting MOFs will certainly find their way towards advanced applications in several research fields.<sup>20</sup> The easy compatibilization of MOFs with either organic or inorganic materials opens the door to advanced composites with applications varying from (opto)electronic devices to food packaging materials and membrane separation.<sup>21,22</sup> Last but not least, their tunable adsorption properties and pore size and topology, along with their intrinsic hybrid nature, all point at MOFs as very promising heterogeneous catalysts,<sup>23,24</sup> the topic of this book (see Figure 1.1 for a general picture).

According to the classical definition, a catalyst is a substance that increases the rate of a reaction towards equilibrium without being appreciably consumed. The word “catalysis” stems from Greek: “κατα” means “down” and “λυσισ” means “loosening”. The eastern approach to catalysis is different. The Chinese characters for catalyst refer to a marriage broker, emphasizing the fact that a catalyst brings together two different “species” resulting in a mechanism of production.<sup>25</sup> By using a satisfactory catalyst the desired reactions proceed with a higher rate and selectivity at relatively mild conditions.

It is convenient to distinguish between heterogeneous and homogeneous catalysis. In the former case the catalyst and reactants are present in different phases, whereas in the latter case we are dealing with a single-phase system, usually a solution. Strictly speaking heterogeneous catalysis is not limited to solid catalysts. For instance, a system consisting of a liquid phase catalyst dispersed in a continuous liquid phase is heterogeneous. However, in practice only in the case of solid catalysts the term “heterogeneous catalysis” is used. How important is catalysis in practice? In the production of bulk chemicals catalysis is visibly present in nearly all plants. In the same lines, the role of catalysis is crucial in environmental protection, especially in emission control. In contrast, in the production of fine chemicals and pharmaceuticals, catalysis is developing at a slower pace, mostly due to the lack of efficient catalysts and to the high added value of the products.

With the discovery and explosion of MOFs, it was only a matter of time until the first catalytic applications were explored.<sup>23</sup> First reports mostly consisted of demonstrating that a certain MOF contained the necessary catalytic centers to catalyze a given reaction. In many cases, the performance of the material was poor and many concerns existed regarding the stability of the materials under



**Figure 1.1** Metal organic frameworks offer a great number of possibilities for catalysis engineers: from semiconductor based photo-catalysis, to the encapsulation of different moieties and nanoparticles and from single site metal catalysis to the fine tuning of the organic moieties, either following pre or post-synthetic modifications.

reaction conditions. The current challenge is to develop truly efficient and selective catalytic processes using MOFs, ideally exploiting the versatility of these materials. In this sense, catalysis by MOFs is at this moment a *hot topic* in research, with new catalytic applications being continuously described, including new materials and new reactions. Indeed, it would not be overly controversial to state that we have already passed from poor “proof-of-concept” solids to highly active catalysts, in some cases with performances comparable to (or even surpassing) state-of-the-art catalysts.

Because the field is reaching now a stage of maturity, we strongly believe that this is the perfect timing to publish, to the best of our knowledge, the first book fully devoted to MOF catalysis. We would like to stress that this book does not intend to be just a literature review of the main advances in MOF catalysis until 2012 but a lasting reference book with a didactic spirit, where results and synthetic strategies are thoroughly discussed rather than simply highlighted.

The book contains outstanding contributions from some of the main players in the field of MOF catalysis. In its second part, after Llabrés i Xamena *et al.* introduce the different strategies for the inclusion of catalytically active sites in MOFs (Chapter 7), Dirk de Vos and colleagues explain in detail the possibilities of MOF metal nodes as catalytic sites along with synthetic strategies to enhance activity and selectivity (Chapter 8). In Chapter 9 Joseph T. Hupp and co-workers challenge the reader with the almost infinite possibilities of catalysis at the organic linker. Gascon and co-workers explore in Chapter 10 the utilization of the MOF porosity to host slightly bigger catalytic species. Finally, Wenbin Lin *et al.*, in Chapter 11, thoroughly investigate the limits of MOFs in asymmetric catalysis, probably one of the most promising catalytic applications together with photocatalysis, as rationally explained by Hermenegildo García and Belén Ferrer in Chapter 12. Since this is a rapidly developing research field, already outstanding catalytic reports on “brother” materials, the so-called Covalent Organic Frameworks (COFs) have been published during the last few years. In Chapter 13, Regina Palkovits, pioneer in the catalytic application of these materials, discusses the advantages and limitations of COFs.

As in the 21st Century catalysis is not a black-box anymore, characterization, rational design by synthesis, adsorptive properties and mechanistic insight are as important as the catalytic cycle itself. Indeed the development of structure–activity relationships in catalysis is the dream of every scientist involved in this field and the key towards rational design of new catalyst generations. For this reason, in the first part of the book, MOF synthesis and post-synthesis strategies are thoroughly discussed by Norbert Stock and Andrew D. Barrows, in Chapters 2 and 3 respectively. Carlo Lamberti, Silvia Bordiga and co-workers teach the reader on the most advanced spectroscopic and diffraction techniques for the characterization and structural determination of MOFs in Chapters 4 and 5. Last but not least, Evgeny Pidko and Emiel J. M. Hensen gather computation chemistry and MOF catalysis in Chapter 6.

The book finishes with a last Chapter where we not only speculate about future directions but also emphasize some of the main barriers that MOFs need to overcome to finally reach industrial catalytic applications.

We want to warmly acknowledge all the authors for their excellent contributions and the editorial team at RSC for their efforts on behalf of this book. We hope that this book will be valuable to the catalysis community both in industry and academia and especially to undergraduate students. We can only wish the reader as much joy as we had when editing this book.

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