

ATLANTIS ADVANCES IN NANOTECHNOLOGY,  
MATERIAL SCIENCE AND ENERGY TECHNOLOGIES



Edited by Vincent Blay, Luis F. Bobadilla, Alejandro Cabrera-García

# Zeolites and Metal-Organic Frameworks

## From Lab to Industry

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## Zeolites and Metal-Organic Frameworks

**ATLANTIS ADVANCES IN NANOTECHNOLOGY, MATERIAL SCIENCE AND ENERGY TECHNOLOGIES**

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The aim of “Atlantis Advances in Nanotechnology, Material Science and Energy Technologies” is to publish high quality manuscripts giving an up-to date and clear view on topical scientific contents in nanotechnology, material sciences and energy technologies.

These three fields evolve rapidly and their understanding is essential with regard to contemporary science and as well as in the context of everyday life. Nanotechnology is a fast growing science and a technological field with applications in numerous areas such as materials, health, electronics, information processing, defence and security, catalysis, sensors, food, cosmetics and many more. The results of material sciences are the basis for any object around us, they are omnipresent in human life. Mastering materials and processes is therefore crucial. In particular, research on microscopic understanding is essential to develop models predicting the properties of new materials and structures. The final goal is to be able to predict macroscopic properties of materials from their microscopic properties. Finally, energy technologies enfold a complex area where each technological advance has to be weighed against economical, environmental, political and sociological constraints. Energy is closely linked to economic development and, more generally speaking, to everyday life.

As nanotechnology, materials science and energy technologies are closely interconnected, this series offers the reader both, highly specialized monographs as well as easy-to-grab overviews. Each publication focuses on one of the fields. At the same time, it is highly relevant to explore their interconnections and to include interdisciplinary approaches.

All book proposals submitted to this series are being reviewed by key experts before publication and each book focuses on a certain field putting it into perspective with its implications at the economic and societal level.

# Zeolites and Metal-Organic Frameworks

*From lab to industry*

*Edited by*

*Vincent Blay, Luis F. Bobadilla and Alejandro Cabrera García*

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# Prologue

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It is a pleasure for us to introduce this book *Zeolites and Metal-Organic Frameworks - From lab to industry*. The editors are distinguished alumni from the Instituto de Tecnología Química (ITQ), in Valencia, Spain. ITQ is a joint research centre founded in 1990 by the Spanish National Research Council (CSIC) and the Polytechnic University of Valencia (UPV). Catalysis by zeolites has been the most emblematic passion of ITQ, to which many other fields of research added over the years. ITQ has become an iconic research centre worldwide, embracing organic, inorganic, photo-, electro- and computational chemistry, materials science, pollution control, chemical engineering, and health care.

Our Center for Ordered Nanoporous Materials (CONS) was established at POSTECH, Pohang, Korea, in 2012. CONS is the National Creative Research Initiative Program supported by the National Research Foundation of Korea. Analogously to ITQ, CONS aims to become a leader in the field of ordered nanoporous materials science. The main objectives of CONS are to demonstrate new and innovative synthesis strategies and to create unique zeolite framework structures and/or compositions that could devise new processes and applications in environmentally sustainable catalysis and gas (mainly H<sub>2</sub> and CO<sub>2</sub>) separation.

As researchers, we strive to push forward the boundaries of scientific knowledge for the benefit of the society and, to this end, we must be aware of the need of extensive collaboration for progress and mutual enrichment. This book is one example, to which experienced and promising young researchers have equally contributed to bringing you their knowledge and findings acquired over the years.

The history of catalysis dates back to the dawn of civilization, when alcohol started to be produced by fermentation. It was not until 1835 that Berzelius initiated systematic studies of catalysts. These studies started to

be implemented as industrial processes mainly at the end of the 19<sup>th</sup> century. In the 1930s, Houdry developed the catalytic cracking of petroleum for Sun Oil and, in 1939, Chambers, Lewis and Gilliland, at MIT, worked out the basis of the fluid-bed reactor for the Catalytic Research Associates consortium (led by Standard Oil). In the 1950s, Milton and Breck discovered zeolites A, X and Y at Linde, Union Carbide. Zeolite A started to be used as an adsorbent, but it was not until the 1970s that Na-A zeolite was used in detergents, replacing phosphate builders, thanks to scientists at Henkel, and Procter and Gamble. In the 1960s, zeolite X revolutionized cracking in the petroleum industry at Mobil Oil. This work on zeolites definitely spurred the development of metal-organic frameworks, which took off in the mid-1990s after Kitagawa (Kyoto University) and Yaghi (University of California, Berkeley) observed permanent microporosity in metal-organic materials. Since those days, incredible progress has been made in both classes of materials. And their range of applications is being extended to undreamed-of levels, as this book manifests.

The proposal of a book targeting zeolites and metal-organic frameworks (MOFs) is interesting, as they share common features, which are also paralleled by remarkable differences. These are evidenced throughout the book. By addressing both materials in a synergic text, the reader will see opportunities for shifting and contributing to both fields of research, the commonalities and differences in terms of concepts, synthesis, characterization, properties, and applications.

In this sense, the book does a remarkable job. It is a book coordinated by, written by, and designed for young scholars and researchers, ranging from those in undergraduate and graduate university courses to PhDs and early-stage researchers. Moreover, the book provides an overview wide enough for most professionals to find it of interest and learn something new. It includes the participation of renowned experts and invited industry practitioners, ensuring rigor and a balance between new research, progress in the field, and a didactic approach that only experience bestows. By the end of the book, the readers will be excellently equipped to delve further into other important topics such as electrocatalysis, photocatalysis or sensing. The same applies to important characterization techniques, such as solid-state nuclear magnetic resonance or X-ray photoelectron spectroscopy, to name but a couple.

In Chapter 1, Professors Valtchev and Mintova provide a knowledgeable introduction to zeolites and metal-organic frameworks – what they are, how they are classified, why they are so important –, as well as some other matters that are expanded on later in the book.

Chapter 2 overviews the different synthesis methods available for zeolites and metal-organic frameworks: from classical hydrothermal syntheses to non-conventional sono- or mechanochemical methods in the case of zeolites. An interesting account of the knowledge on the crystallization mechanism of zeolites is also provided, which is one of the most complex and fundamental questions open to discussion in this field. The chapter also provides a brief presentation of some standard characterization methods of porous materials for phase identification and textural analysis.

Characterization is a topic of great importance in porous materials, as it bridges the knowledge gap between the preparation of the material and its performance in the real application. We can correlate this performance (for instance, in catalysis, adsorption, drug delivery, etc.) with properties of the material and then alter or tune the synthesis protocols to affect the properties in the desired manner. Based largely on the experience of Professor Daturi's group in the last decades, Chapter 3 presents a general, infrared spectroscopy methodology to observe the potential active site directly or by adsorption of probe molecules, as well as several examples that illustrate the qualitative and quantitative analyses of the physicochemical vibrational properties of the entities on the surface of the material.

Having prepared and characterized the materials, the book moves on to present some relevant applications. Petroleum refining is the field which fostered the development of zeolites and the one in which they add the most value. Thus, Chapter 4 presents an industrial overview of the many oil & gas processes in which zeolites are involved. These include separation operations, fluid catalytic cracking, hydrocracking, isomerization, alkylation of benzene, dewaxing, etc. However, the stability of metal-organic frameworks prevents their consideration for many of these processes, although the expert authors from CEPESA also identify some promising niches for MOFs.

Chapter 5 presents how zeolites and MOFs could contribute to the biorefineries of tomorrow, which would use renewable biomass residues as feedstocks instead of fossil resources. Many of these transformations are carried out in aqueous media, therefore the stability of both zeolites and MOFs is involved. Nevertheless, some of these materials turn out remarkably suitable, and great progress has been achieved in the conversion of cellulose, hemicellulose and lignin polymers present in biomass over some zeolites and MOFs. The platform molecules resulting from the refining could then be used by the chemical industry in other processes.

As a counterpoint to the previous chapters, in Chapter 6 zeolites and MOFs do not act as catalysts themselves but they are used to host enzymes, which are sophisticated biocatalysts developed by nature, fine-tuned by

the biotechnologists and protein engineers. The advantages of heterogenization of catalysts into periodic structures also apply to biocatalysts. In this case, given the large molecular size of enzymes, the larger pores of MOFs are especially well suited. In addition to describing the immobilization of important enzymes such as lipases and laccases, the authors, one of the leading groups in this field, also discuss the characterization techniques involved.

In Chapter 7, the applications of MOFs and zeolites as adsorbents are addressed. In addition to the design of materials, other strategies to adjust their behaviour as adsorbents are presented, such as ion exchange, post-synthesis modification or, very promising for the case of MOFs, the presence of defects. An ample review of applications in both gas and liquid phases is presented, including research and uses as diverse as hydrogen storage, removal of heavy metal ions or radionuclides, and CO<sub>2</sub> capture, which evidence the possibilities for tailoring these materials to any objective.

Adsorption can be further improved by a suitable design of the material at the mesoscale. Membranes are a remarkable example of a technical presentation of zeolites and MOFs. Membranes hold promise to improve many industrial processes. For instance, separations could be carried out in a continuous steady operation and reactions could be performed without worrying about equilibrium limitations and/or with higher selectivity, as highly pure products would be withdrawn as they form. In Chapter 8, Prof. Matsukata and his group expand on these ideas and tell us how membranes are prepared, characterized and applied for separations, as well as the hard challenges in this field.

Adsorption and diffusion are key phenomena in porous materials. These are very suitable for study in computational chemistry experiments, and so are chemical reactions. Chapter 9 starts with the fundamentals of computational chemistry and the different methods available, which condition the level of exactness achievable and the computation time required. It teaches us how the computational models are designed and how the experiments are run and exploited by means of algorithms, concluding with the results of applications to current questions.

Chapter 10 presents the state of the art of biomedical applications of zeolites and especially MOFs, a young but promising field, which includes their use in drug delivery, contrast agents, in diagnosis and therapy, as well as multifunctional materials for combination therapy.

The application of heterogeneous catalysts in the fine chemical industry (pharmaceutical, cosmetic, phytosanitary, etc.) has been traditionally low. Their comparatively low production volumes allowed the generation

of high proportions of residues, which can no longer be tolerated in our current efforts for a sustainable industry. Nowadays, in addition to high product yields, chemo-, region- and stereoselectivity are the main goals in organic syntheses given the importance of avoiding by-products and additional purification steps. Thus, in Chapter 11 the applicability of zeolites and MOFs as catalysts for this industry is also demonstrated.

Lastly, in Chapter 12, Professor Falabella and his colleagues provide a commercially oriented, high-level overview of most applications of zeolites and MOFs, including adsorption, ion exchange, catalysis, composites and other devices. Importantly, they provide their knowledgeable forecast on the future of these materials in the coming years.

Overall, this book is a demonstration of liveliness in the world of ordered porous materials, in general, and of zeolites and MOFs, in particular, both showing ever-growing opportunities in traditional and in emerging fields of application. One can speculate whether our predecessors in the field would ever have dreamt of the extensive benefits that these materials have brought to the society. On the other hand, the book evidences, through all the contributors, that the next generations are going to be deserving successors to face the major scientific challenges of the decades ahead. They will bring greater benefits to the society through ordered porous materials that we cannot even dream of today.