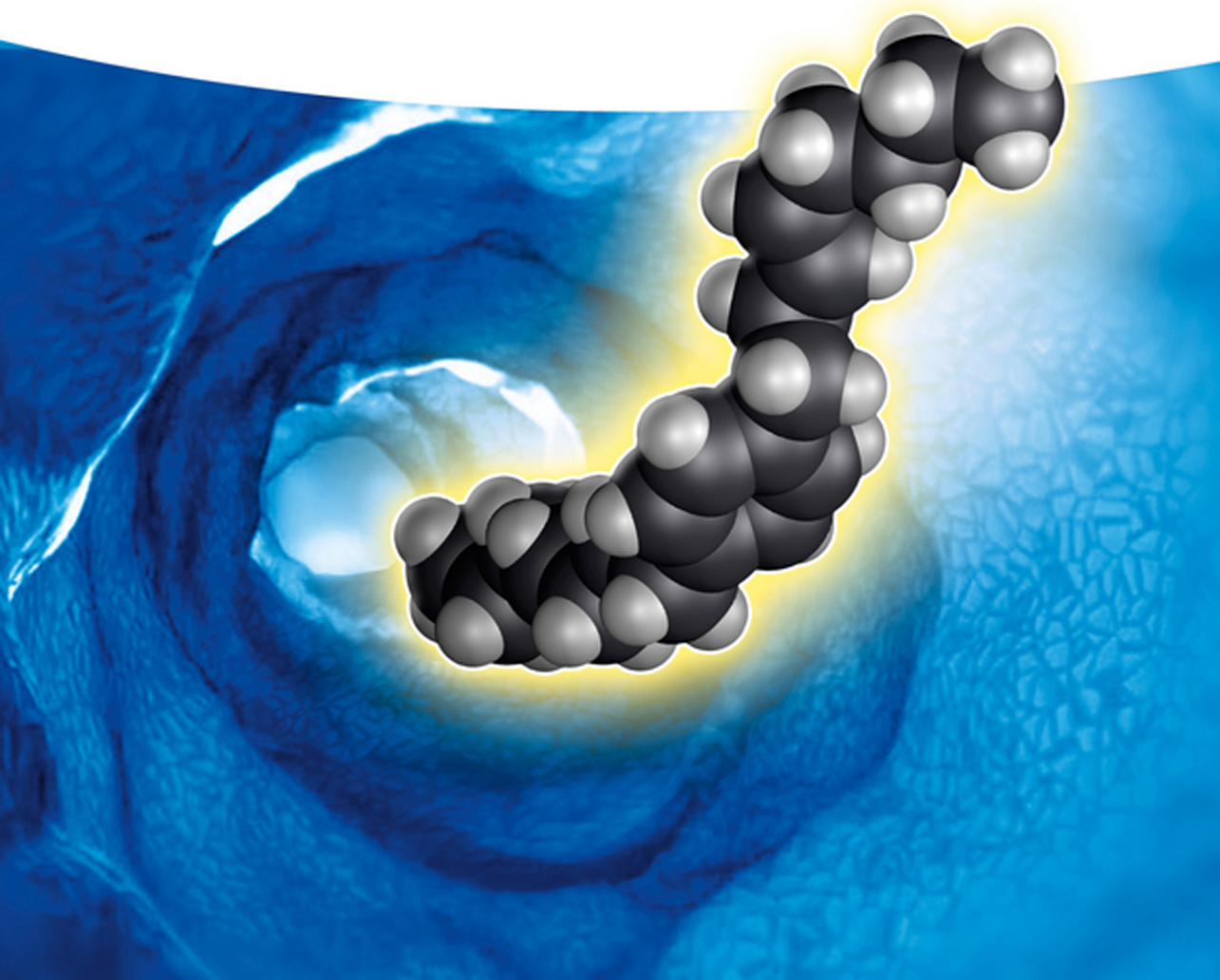


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Mesoporous Zeolites

Preparation, Characterization and Applications

With a Foreword by Mark E. Davis



Edited by
Javier García-Martínez
and Kunhao Li

Mesoporous Zeolites

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*Edited by Javier García-Martínez
and Kunhao Li*

Mesoporous Zeolites

Preparation, Characterization and Applications

With a Foreword by Mark E. Davis

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The Editors

Prof. Dr. Javier García-Martínez
University of Alicante
Department of Inorganic Chemistry
Campus de San Vicente del Raspeig
03690 San Vicente del Raspeig
Alicante
Spain

Dr. Kunhao Li
Rive Technology, Inc.
1 Deerpark Drive, Suite A
Monmouth Junction
NJ 08852
United States

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Foreword

Mesoporous Zeolites: Preparation, Characterization and Applications provides a timely overview of an important, growing class of porous materials [1]. Mesoporous zeolites encompass solids that have both microporosity and mesoporosity. These hierarchically organized materials have mesoporosity that is connected to microporosity, and because of this feature can outperform purely microporous materials in certain applications. Contained within this monograph are 16 chapters that span the range of topics from preparation, detailed characterization, and examples of applications.

Hierarchically organized materials have existed for sometime; they were just not denoted as such. Much in the way that the term “nanotechnology” is now commonplace, “hierarchically organized materials” are also now becoming a prevalent notation for materials such as zeolites that contain mesoporosity. The use of this terminology has facilitated connections between mesoporous zeolites and other areas of science and technology such as biomineralization (where there are numerous examples of hierarchically organized materials) [2]. Thus, I am not implying that terminology of this type is bad, but rather, it is useful for organizing topics that may not have usually been associated with each other. In the past, materials that are now denoted as hierarchically organized microporous materials were prepared by steaming and acid leaching. For example, highly dealuminated zeolites that contain both mesopores and micropores have been commercialized for the synthesis of cumene (Dow/Kellogg process – 3DDM (three-dimensional dealuminated mordenite)) [3, 4]. With these types of materials, the size, shape, and number of mesopores are not controllable, and the compositions of the remaining microporous areas not readily manipulated. To overcome these limitations, there has been a plethora of new synthetic methods that lead to materials with varying amounts of control over the arrangements of the microporous and mesoporous areas contained within the material. Several chapters in this monograph nicely compare and contrast the numerous synthetic methodologies that have been reported for creating mesoporous zeolites with broad ranges of pore structures and solid material compositions.

The synthesis of mesoporous materials can be accomplished via numerous techniques that are outlined in the various chapters of this monograph. The

amazing numbers of materials that have emerged from these methodologies illustrate the creativity of the inventors in their designs to simultaneously control composition, structure, and textual properties. From a scientific point of view, these preparation methods will provide materials that will enable the investigation of structure–property relationships in a way that has not been available in the past. There is no doubt that much greater understanding of these structure–property relationships will lead to new concepts for applications.

The ability to create mesoporous zeolites with control over compositions and architectures with mesoporosity and microporosity opens new opportunities for structural and functional characterizations. Chapters within this monograph address this point. Also, these materials show complexity that extends the limits of some characterization methodologies. For example, how are the pore spaces defined? Measurement of surface area is a particular issue of concern. As pointed out in Chapter 11, the use of the BET equation for microporous materials is problematic. In fact, it is wrong. The original paper on the BET method provides the elegant derivation of the BET equation that has requirement of more than one layer of adsorbate in order for use [5]. Of course, this does not occur in zeolites. Therefore, the BET equation cannot be rigorously applied for zeolites (although the zeolite community has been wrongly doing this for decades). With mesoporous zeolites, the situation is even more complex. Thus, the preparation of highly ordered mesoporous zeolites could provide excellent models to develop correct methods for surface area measurements.

To date, the main thrust in the applications of these hierarchical materials is to take advantage of their textural properties, for example, to allow larger molecules to reach active sites and to provide enhanced transport properties into and out of the porous structures. This is only the beginning of what might be possible. I can imagine ways to tune the surface properties to take advantage of the two types of pores, for example, hydrophilic mesopores and hydrophobic micropores or vice versa. Thus, I believe that there are many avenues of exploration with these hierarchical materials that could lead to new applications that have not yet been investigated.

The final chapter of this monograph is a nice overview of important issues when considering the commercialization of mesoporous zeolites. For those who strive to create materials for commercial application with greater control over topology and composition, one has to ask the question of whether the enhanced control over the properties provides sufficient enhancements in performance to justify the additional cost (greater synthetic control usually implies greater complexity in the synthesis and as such greater cost). The particular example of the mesostructured zeolite Y produced by Rive Technology, Inc., is illustrated in this final chapter to show how the right circumstances must be in play in order to have any chance of commercialization (this material is on the way of being commercially implemented; commercial FCC unit testing has already been accomplished).

In summary, this monograph provides the reader a very nice overview of the emerging field of mesoporous zeolites (and other hierarchical porous materials). It is a timely presentation that sets the stage for what might happen in this area of science and technology in the near future.

Mark E. Davis, November 2014

Pasadena, CA, USA

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Preface

Mesoporous Zeolites: An Emerging Technology in a Mature Field

Sometimes, a mature field has a renaissance due to a series of advances that catalyze the attention of research groups from around the world. This is the case of hierarchical zeolites. Although this is not a truly new field, it is experiencing an explosive growth due to a succession of exciting advances in the mature field of zeolites.

From catalysis to adsorption and from water treatment to animal feeding, applications of zeolites are both copious and valuable. Their crystalline structures, arranged in a variety of porous architectures, are a great example of what the ingenuity and hard work of many synthetic chemists are able to produce. The over 200 known zeolitic structures comprise pores in a variety of shapes (channels, cages, cavities, etc.) and sizes (typically below 1 nm). Zeolites are therefore microporous crystalline materials. For that reason, the title of this book might be viewed as a heresy, but in fact, introducing mesoporosity in zeolites is a long-standing goal in this mature field. Much effort in zeolite synthesis has been devoted to creating extra-large pore zeolites, with some producing beautiful, open structures. Different strategies, from the use of bulkier organic templates to the addition of germanium, have been productive in extending the range of zeolite micropore sizes.

While synthetic chemists continue to produce new, more open zeolite crystal structures, the field of hierarchical zeolites is emerging as a simple and effective alternative that overcomes the pore size limitation of current zeolites by creating materials with a combination of both zeolitic microporosity and additional larger mesoporosity. Different strategies have been developed to achieve this goal. All of them have their pros and cons, but more importantly all produce notably different materials, which in fact extends the number of mesoporous zeolites one can produce.

Some of these strategies involve the modification of synthesis conditions to produce known zeolite structures containing mesopores. These are the so-called bottom-up approaches. In some cases, the crystallization of zeolites is interrupted (for example, stopping the reaction before the zeolite is fully crystallized) or confined to produce nanosized zeolites. Although these materials are not hierarchical

in the sense that they do not have intracrystalline micro- and meso- or macropores, their very small size has a similar effect on reducing the diffusion path length and increasing the external surface area of zeolites. In other cases, either (or in some cases both) soft and hard templates are added during the zeolite synthesis. After zeolites are fully formed, these sacrificial templates are embedded inside their structure. The templates are subsequently removed, usually by calcination, producing a truly hierarchical zeolite. Here the seminal work done by Dr. Claus J. H. Jacobsen *et al.* of Haldor Topsøe Research Laboratories using carbon as a hard template to synthesize mesoporous zeolite single crystals in the year 2000 marked an important moment in the emerging field of *mesoporous zeolites*.

A different approach, with deep roots in the long history of zeolite manufacturing, is the posttreatment of conventional zeolites. Being well-known since the 1960s, the treatment of some zeolites, most notably zeolite Y, in steam significantly increases their hydrothermal stability and creates some mesoporosity, although not as interconnected as needed to significantly improve the diffusivity of certain bulky molecules. The posttreatment of zeolites both with bases and acids, mostly to remove silica or alumina, respectively, has been practiced for decades and widely used to tune the surface chemistry of zeolites and remove chemical "debris" from the crystal structure. Because of the higher content of silica than that of alumina in zeolites, the removal of the former with different bases, most commonly NaOH, produces intracrystalline mesoporosity in zeolites with Si/Al ranging from 20 to 50.

A landmark moment in the fabrication of mesoporous materials was the invention of MS41s mesostructured materials in Mobil Oil Company in the early 1990s. The potential of their large, uniform-sized mesopores for improving diffusion of large molecules raised a tremendous amount of interest in their use in industrial catalysis, such as fluid catalytic cracking. However, the weak acidity and poor hydrothermal stability associated with these amorphous materials, along with their high cost of synthesis, have limited their commercial application despite extensive effort to overcome these problems for the past two decades.

Because of the extensive and fascinating work done using surfactants to template mesoporosity in amorphous solids, a long-standing goal in zeolite science and technology has been to adopt the surfactant-templating approach to create zeolites with well-controlled mesoporosity, in terms of both size and arrangement. The holy grail of zeolite S&T is to have a general, versatile, and robust way to impart controlled mesoporosity while maintaining the characteristic properties of zeolites, chiefly crystallinity, strong acidity, and hydrothermal stability. Despite the much effort, progress was limited, because the use of both structure directing agents (to produce a particular zeolite structure) and a surfactant (to impart mesoporosity) led to phase separation between the crystalline zeolite phase and an amorphous mesoporous material.

Recently, this long-standing goal of adopting the surfactant-templating approach to create zeolites with controlled mesoporosity has been achieved by a simple one-step process in which conventional zeolites are treated in a mild basic solution in the presence of a surfactant. The mesoporosity produced can

be tailored by using different surfactants and different conditions, in a similar manner as done in other surfactant-templated methods. The unique structure of these materials, with controlled mesoporosity and crystalline (zeolitic) pore walls, has been recently elucidated by the combination of high-res gas adsorption, electron tomography, and diffraction. More importantly, these materials show outstanding catalytic activity in diffusion-limited reactions, such as fluid catalytic cracking. This technology is now a commercial reality through Rive Technology and has been used in commercial refineries with excellent gasoline and diesel yields and reduced coke and light gas production.

Being aware of the relevance of this new field and motivated by the number of and significance of the scientific papers and patents published in this area, the editors of this book decided to co-organize an annual International Symposium on Mesoporous Zeolite (Indianapolis 2013, San Francisco 2014, Boston 2015) to present, discuss, and advance the field of mesoporous zeolites and its quick and successful adoption by the industry.

This book was born as a result of the first edition of this international symposium, and it is composed by 16 chapters written by some of the most active and leading experts in the field. We have tried to maintain a good balance between fundamental research, always important in a new field, and its implementation at commercial scale.

Chapter 1, by Prof. Joaquín Pérez-Pariente *et al* of Instituto de Catálisis y Petroleoquímica, gives an excellent survey of the general field and a comprehensive introduction to various strategies to improve accessibility to the intracrystalline voids of zeolites. Synthesis of large pore zeolites, reduction of zeolite crystal sizes to nanoscales, and different approaches to prepare mesoporous zeolites that constitute the main body of this book, are the three main directions of research to address the negative impact of the diffusion problem in zeolites. For those strategies mentioned in this chapter but not otherwise discussed in this book, for example, synthesis of large pore zeolites, interested readers should consult the corresponding references therein.

Chapter 2, by Prof. Heloise de O. Pastore *et al* of Instituto de Química and Universidade Federal de São Carlos, and Chapter 3, by Prof. Trong-On Do *et al* of Laval University, deal with progress in the field of zeolite nanocrystals (or nanozeolites). This is a field closely related to the main focus of this book on mesoporous zeolites. Zeolite nanocrystals and mesoporous zeolites reduce the diffusion path length into the micropore systems of zeolitic materials. Chapter 2 focuses more on the fundamentals, advantages, and challenges of different techniques in synthesis and characterization of zeolite nanocrystals, while Chapter 3 expands to important materials such as nanoporous zeolitic composites (mesoporous materials reinforced with nanozeolites) and their applications.

Chapter 4, by Dr. Yu Liu of The Dow Chemical Company, gives a nice review of different techniques that improved the stability and catalytic activity of mesostructured aluminosilicates and their potential in catalytic applications, with a focus on the efforts by Prof. Thomas J. Pinnavaia's group at Michigan State University. Some of these methods achieved strong acidity very close to that of zeolites, although

the lack of high-angle X-ray diffraction peaks caused some to argue that they are not crystalline zeolites. So, while some may not consider such materials as mesoporous zeolites, they represent the forefront of the push from amorphous mesostructured aluminosilicates toward the hydrothermal stability and activity necessary for industrial applications.

Two closely related approaches to mesoporous zeolites are included in this book, Chapter 5 by Prof. David P. Serrano *et al* of Instituto IMDEA Energía and Universidad Rey Juan Carlos and Chapter 6 by Prof. Feng-Shou Xiao *et al* of Zhejiang University, to represent the many recent developments in “soft-templated” “bottom-up” approaches. Chapter 5 reviews the main synthesis strategies based on the use of different types of organosilanes for the preparation of mesoporous zeolites and their potential in various catalytic applications. Chapter 6 mainly describes progress made by using polymers as mesopore templates. Adding organosilanes or polymers into zeolite synthesis mixtures perturbs zeolite crystallization. Space occupied by the occluded soft templates constitutes mesopores after removal of the organic moiety by calcination. As described in detail in this chapter, the nature of templates and the Si (and Al) sources used, as well as reaction conditions, have strong effects on the characteristics of the resulting mesoporous zeolites, including mesopore location and size, crystal morphology, crystallinity, and so on.

Chapter 7, by Prof. Wei Fan *et al* of University of Massachusetts Amherst, focuses on another major “bottom-up” approach that involves the use of hard templates such as carbon. Zeolite crystallization in the confined space within carbon matrices was originally developed as a way to prepare zeolite nanocrystals. Crystallization techniques such as steam-assisted crystallization (SAC) and vapor phase transport (VPT), coupled with careful control of the architecture of the carbon templates, have led to the preparation of many mesoporous zeolites with different morphology and features, for example, zeolites with ordered mesopores through the use of 3DOM (three-dimensionally ordered macroporous) carbon as templates.

Pioneered by Prof. Masahiko Matsukata *et al.* and followed by continued efforts by Prof. Javier Pérez-Ramírez and many others, desilication of zeolites to form mesoporous zeolites has become a main “top-down” approach because of its simplicity and low cost. In Chapter 8, progress in this field is reviewed and different views on the mechanism and nature of the materials are presented. Some relevant examples of the positive effects of desilication on the catalytic performance of zeolites modified by using the postsynthetic method are also presented and discussed in this contribution.

Chapter 9, by Prof. Irina I. Ivanova *et al* of Moscow State University, describes the “top-down” approach, referred to as “surfactant-templated zeolite recrystallization,” under development in her laboratory. This approach involves a two-step treatment of already synthesized zeolite crystals: first treating zeolites in strong bases such as NaOH to depolymerize the structure and form defects (and under certain conditions also desilicated mesoporosity) in the remaining zeolite crystals and followed by treating the reaction mixture with cationic surfactants under

hydrothermal conditions and adjusted pH for extended period of time to induce the formation of amorphous aluminosilicates mesostructures similar to MCM-41. In spite of the composite nature of the product, it shows improved hydrothermal stability and acidity superior to amorphous aluminosilicates and superior catalytic performance in various types of model compound catalytic testing compared to conventional zeolites.

Chapter 10, by Prof. Javier García-Martínez *et al* of Universidad de Alicante and Rive Technology, Inc, describes the development and commercialization of the first mesostructured zeolite in large-scale industrial catalysis; fluid catalytic cracking (FCC). The approach incorporates treatment of already synthesized zeolites with cationic surfactants in basic media. Convincing characterization results showed that uniformly sized mesopores are created within the zeolite crystals possibly through a crystal rearrangement mechanism (or pseudomorphic transformation as suggested by some authors). There was no sign of formation of additional amorphous mesoporous phases. It was also shown that the size of the intracrystalline mesopores can be tuned by using surfactants of different sizes. The mesoporous zeolites prepared by this approach showed strong acidity and excellent hydrothermal stability. Laboratory testing and refinery operation confirmed significant improvement of the performance of FCC catalysts made from the mesoporous zeolites, which are attributed to improved diffusion through the intracrystalline mesopores. In addition, research in using mesoporous zeolites for industrial separation is also discussed.

As in any other emerging field, the discovery of new materials poses significant challenges regarding their proper characterization. Chapter 11, by Dr. Matthias Thommes *et al.* of Quantachrome Instruments, presents the fundamentals as well as recent advances in both theoretical and experimental gas adsorption for the characterization of textural properties of mesoporous zeolites, including pore size, pore volume, surface area, pore connectivity, and so on. Chapter 12, by Prof. Jörg Kärger *et al.* of Universität Leipzig, discusses the fundamentals of diffusion and different techniques of diffusion measurement, with focus on pulsed field gradient nuclear magnetic resonance (PFG-NMR), for measuring mass transport in hierarchical pore systems. Chapter 13, by Prof. Xiaodong Zou *et al.* of Stockholm University, describes the basic principles of electron microscopy, including scanning electron microscopy (SEM), transmission electron microscopy and high-resolution transmission electron microscopy (TEM and HRTEM), conventional and three-dimensional rotation electron diffraction (ED and RED), and electron tomography (ET) and their use in revealing the complex framework and pore structures of zeolites and mesoporous zeolites. Chapter 14, by Prof. Jerzy Datka *et al.* of Jagiellonian University examines different techniques used for measuring the Brønsted and Lewis acid properties of zeolites and how preparation methods, particularly desilication, leads to changes in acid properties that impact the catalytic performance of mesoporous zeolites.

Chapter 15, by Prof. Kostas S. Triantafyllidis *et al* of Aristotle University of Thessaloniki and Chemical Process and Energy Resources Institute (CPERI), discusses the opportunities and challenges of using mesoporous zeolites in various

processes, such as catalytic fast pyrolysis (CFP), catalytic cracking, hydroprocessing, methanol to hydrocarbons (MTH), for producing biomass-derived fuels and chemicals.

Lastly, this book concludes with Chapter 16 by Dr. Roberto Millini of Eni S.p.A. on the industrial perspectives for mesoporous zeolites. Currently, the majority of research in the field of mesoporous zeolites remain in academia, with the exception of the surfactant-templated zeolite mesostructuring technology described in

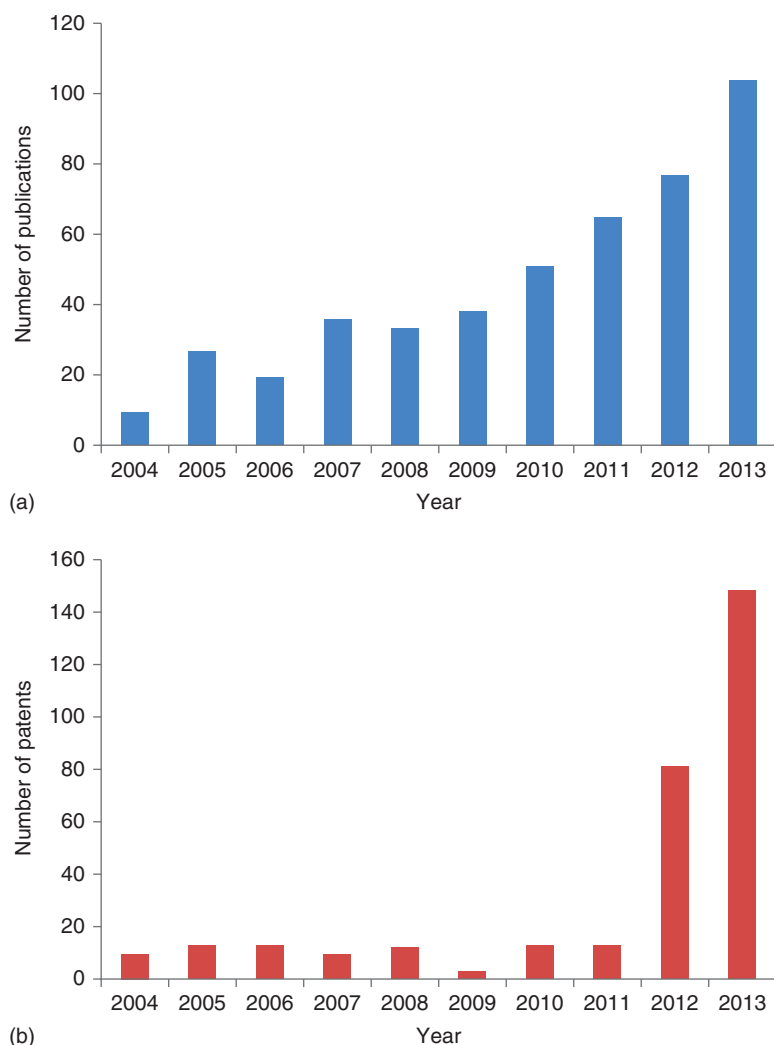


Figure 1 Total number of scientific articles a) and patents b) on mesoporous zeolites published during the past decade. In 2013, the number of patents on this topic already

exceeded the number of papers published, which shows the interest of the industry in these new materials. Source: ScienceDirect and GooglePatents.

Chapter 10. Much of the R&D work has been undertaken by Rive Technology, Inc., a start-up company established in 2006 specifically aiming to bring the mesoporous zeolite technology into petroleum refining and petrochemical industries. On its road from discovery to commercialization, many technological, economic, environmental, safety, and health hurdles had to be overcome to achieve its current status as the first commercialized mesoporous zeolite technology in FCC applications.

The emerging field of hierarchical zeolites in general and mesoporous zeolites in particular is growing very rapidly thanks to the original contributions of many groups. This book aims at providing a comprehensive (although no way complete) and up-to-date perspective on this exciting field, which is going through a renaissance because of the new ways porosity can be introduced into zeolites. Nowadays scientific journals and conferences dealing with zeolites, catalysts, or porous materials extensively cover the advances in hierarchical zeolites. However, and despite their relative novelty, these materials are not just a hot research topic. Already in 2013 the number of patents exceeded the number of papers in the field (Figure 1). Although the system used to obtain the number of articles and patents was different, the trend is clear evidence of the interest of industry in this new class of materials.

As we are organizing the third International Symposium on Mesoporous Zeolites, which will be held in August in Boston during the ACS Fall Meeting, we feel that it is time to have a single monograph devoted to the different synthetic strategies, characterization tools, and application opportunities of mesoporous zeolites. We want to thank all the authors who put time aside from their busy agendas to write the different chapters that make this monograph. Their effort and expertise have made it possible to produce the first book specifically devoted to the emerging field of hierarchical zeolites, which provides a glimpse of the myriad of opportunities that they offer. We hope that it will help to inspire new and valuable discoveries and bring excitement and new opportunities to the field of zeolites and related materials.

*Javier Garcia Martinez and
Kunhao Li*
Rive Technology, Princeton
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List of Contributors

Teresa Álvaro-Muñoz

Institute of Catalysis and
Petrochemistry (ICP-CSIC)
Molecular Sieves Group
C/Marie Curie, 2
Cantoblanco
28049 Madrid
Spain

Michael Beaver

Rive Technology, Inc.
1 Deer Park Drive
Monmouth Junction
NJ 08852
USA

Giuseppe Bellussi

Eni S.p.A
San Donato Milanese Research
Centre
Refining & Marketing Division
Via F. Maritano 26
20097 San Donato Milanese
Italy

Dilson Cardoso

Catalysis Laboratory
Chemical Engineering
Department
Federal University of São Carlos
São Carlos
SP 13565-905
Brazil

Katie A. Cychosz

Quantachrome Instruments
1900 Corporate Drive
Boynton Beach
FL 33426
USA

Jerzy Datka

Jagiellonian University
Faculty of Chemistry
Ingardena 3 Street
30-060 Kraków
Poland

Trong-On Do

Laval University
Faculty of Science and
Engineering
Department of Chemical
Engineering
1065, avenue de la Médecine
Québec G1V 0A8
Canada

Dirk Enke

Universität Leipzig
Abteilung Grenzflächenphysik
Linnéstr. 5
04103 Leipzig
Germany

José M. Escola

Rey Juan Carlos University
ESCET, Chemical and
Environmental Engineering
Group
c/Tulipán s/n
28933 Móstoles
Madrid
Spain

Wei Fan

University of Massachusetts
Department of Chemical
Engineering
686 North Pleasant Street
159 Goessman Lab
Amherst
MA 01003
USA

Javier García-Martínez

Rive Technology, Inc.
1 Deer Park Drive
Monmouth Junction
NJ 08852
USA

and

University of Alicante
Inorganic Chemistry
Department
Campus de San Vicente
03690 Alicante
Spain

Roger Gläser

Universität Leipzig
Abteilung Grenzflächenphysik
Linnéstr. 5
04103 Leipzig
Germany

Kinga Góra-Marek

Jagiellonian University
Faculty of Chemistry
Ingardena 3 Street
30-060 Kraków
Poland

Rémy Guillet-Nicolas

Quantachrome Instruments
1900 Corporate Drive
Boynton Beach
FL 33426
USA

Eleni F. Iliopoulou

Chemical Process and Energy
Resources Institute
(CPERI)/Centre for Research and
Technology Hellas (CERTH)
6th km Charilaou-Thermi Road
57001 Thermi-Thessaloniki
Greece

Irina I. Ivanova

M.V. Lomonosov
Moscow State University
Department of Chemistry
Leninskie Gory 1, bld. 3
119991 Moscow
Russia

and

A.V. Topchiev Institute of
Petrochemical Synthesis
Russian Academy of Sciences
Leninsky Prospect 29
119991 Moscow
Russia

Stamatia A. Karakoulia

Chemical Process and Energy
Resources Institute
(CPERI)/Centre for Research and
Technology Hellas (CERTH)
6th km Charilaou-Thermi Road
57001 Thermi-Thessaloniki
Greece

Jörg Kärger

Universität Leipzig
Abteilung Grenzflächenphysik
Linnéstr. 5
04103 Leipzig
Germany

Elena E. Knyazeva

M.V. Lomonosov, Moscow State
University
Department of Chemistry
Leninskie Gory 1, bld. 3
119991 Moscow
Russia

and

A.V. Topchiev Institute of
Petrochemical Synthesis
Russian Academy of Sciences
Leninsky Prospect 29
119991 Moscow
Russia

Angelos A. Lappas

Chemical Process and Energy
Resources Institute
(CPERI)/Centre for Research and
Technology Hellas (CERTH)
6th km Charilaou-Thermi Road
57001 Thermi-Thessaloniki
Greece

Kunhao Li

Rive Technology, Inc.
1 Deer Park Drive
Monmouth Junction
NJ 08852
USA

Yu Liu

Dow Chemical Company
Hydrocarbon R&D Department
2301N Brazosport BLVD
Freeport
TX 77541
USA

Angelina A. Maerle

M.V. Lomonosov Moscow State
University
Department of Chemistry
Leninskie Gory 1, bld. 3
119991 Moscow
Russia

Masahiko Matsukata

Waseda University
School of Science and
Engineering
Department of Applied
Chemistry
Okubo 3-4-1
Shinjuku-ku
Tokyo 169-8555
Japan

Xiangju Meng

Zhejiang University
Department of Chemistry
Institute of Catalysis
Tianmushan Road 148
Hangzhou 310028
China

Roberto Millini

Eni S.p.A
San Donato Milanese Research
Centre
Refining & Marketing Division
Via F. Maritano 26
20097 San Donato Milanese
Italy

Christos K. Nitsos

Aristotle University of
Thessaloniki
Laboratory of General and
Inorganic Chemical Technology
Department of Chemistry
University Campus
PO Box 116
54124 Thessaloniki
Greece

Masaru Ogura

The University of Tokyo
Institute of Industrial Science
Komaba 4-6-1
Meguro
Tokyo 153-8505
Japan

Heloise de Oliveira Pastore

Micro and Mesoporous
Molecular Sieves Group
Institute of Chemistry, University
of Campinas
270, Monteiro Lobato St.
Campinas
SP 13083-861
Brazil

Joaquín Pérez-Pariente

Institute of Catalysis and
Petrochemistry (ICP-CSIC)
Molecular Sieves Group
C/Marie Curie, 2
Cantoblanco
28049 Madrid
Spain

Patricia Pizarro

IMDEA Energy Institute
Avda Ramón de la Sagra, n° 3
28935 Móstoles
Spain

and

Rey Juan Carlos University
ESCET, Chemical and
Environmental Engineering
Group
c/Tulipán s/n
28933 Móstoles
Madrid
Spain

David P. Serrano

IMDEA Energy Institute
Avda Ramón de la Sagra, n° 3
28935 Móstoles
Spain

and

Rey Juan Carlos University
ESCET, Chemical and
Environmental Engineering
Group
c/Tulipán s/n
28933 Móstoles
Madrid
Spain