

175

Structure and Bonding

Series Editor:

D.M.P. Mingos, Oxford, United Kingdom

Editorial Board:

X. Duan, Beijing, China

L.H. Gade, Heidelberg, Germany

Y. Lu, Urbana, IL, USA

F. Neese, Mülheim an der Ruhr, Germany

J. Pérez-Pariente, Madrid, Spain

S. Schneider, Göttingen, Germany

D. Stalke, Göttingen, Germany

Aims and Scope

Structure and Bonding is a publication which uniquely bridges the journal and book format. Organized into topical volumes, the series publishes in depth and critical reviews on all topics concerning structure and bonding. With over 50 years of history, the series has developed from covering theoretical methods for simple molecules to more complex systems.

Topics addressed in the series now include the design and engineering of molecular solids such as molecular machines, surfaces, two dimensional materials, metal clusters and supramolecular species based either on complementary hydrogen bonding networks or metal coordination centers in metal-organic framework materials (MOFs). Also of interest is the study of reaction coordinates of organometallic transformations and catalytic processes, and the electronic properties of metal ions involved in important biochemical enzymatic reactions.

Volumes on physical and spectroscopic techniques used to provide insights into structural and bonding problems, as well as experimental studies associated with the development of bonding models, reactivity pathways and rates of chemical processes are also relevant for the series.

Structure and Bonding is able to contribute to the challenges of communicating the enormous amount of data now produced in contemporary research by producing volumes which summarize important developments in selected areas of current interest and provide the conceptual framework necessary to use and interpret mega-databases.

We welcome proposals for volumes in the series within the scope mentioned above. Structure and Bonding offers our authors and readers:

- OnlineFirst publication. Each chapter is published online as it is finished, ahead of the print volume
- Wide dissemination. The chapters and the volume will be available on our platform SpringerLink, one of the largest collections of scholarly content in the world. SpringerLink attracts more than 50 million users at 15.000 institutions worldwide.
- Easy manuscript preparation. Authors do not have to spend their valuable time on the layout of their contribution. Springer will take care of all the layout related issues and will provide support throughout the complete process.

More information about this series at <http://www.springer.com/series/430>

Luis Gómez-Hortigüela

Editor

Insights into the Chemistry of Organic Structure-Directing Agents in the Synthesis of Zeolitic Materials

With contributions by

B. Bernardo-Maestro · M.Á. Cambor · P.A. Cox ·
L. Gómez-Hortigüela · L.B. McCusker · M. Moliner ·
C. Paris · F. Rey · J. Simancas · S. Smeets · A. Turrina ·
A.E. Watts · P.A. Wright

 Springer

Editor

Luis Gómez-Hortigüela
Instituto de Catálisis y Petroleoquímica - CSIC
Madrid, Spain

ISSN 0081-5993

ISSN 1616-8550 (electronic)

Structure and Bonding

ISBN 978-3-319-74288-5

ISBN 978-3-319-74289-2 (eBook)

<https://doi.org/10.1007/978-3-319-74289-2>

Library of Congress Control Number: 2018935595

© Springer International Publishing AG, part of Springer Nature 2018

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Printed on acid-free paper

This Springer imprint is published by the registered company Springer International Publishing AG part of Springer Nature.

The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

Since their first use, the addition of organic species (usually organic cations) to the synthesis gels of zeolite materials has triggered the most important revolution in the preparation and discovery of new zeolitic materials with unprecedented properties. These organic species drive the crystallization pathway toward a particular zeolite framework type with specific chemical properties, and hence they are referred to as organic structure-directing agents. During the crystallization process, these organic agents organize the inorganic units into a particular geometry from which viable nuclei of the host-guest system will be produced, which will promote the crystallization of a certain zeolitic material. The use of organic structure-directing agents has enabled the discovery of a large number of new zeolite topologies, with very different pore shapes and sizes; in addition, they have made accessible particular chemical compositions of zeolite networks. Both of these factors have greatly amplified the number of applications of this important class of materials in different sectors of the chemical industry.

Traditionally, the main properties whereby researchers designed new organic structure-directing agents focused on their size, shape, and hydrophobicity (chapter “[Introduction to the Zeolite Structure-Directing Phenomenon by Organic Species: General Aspects](#)”). However, and due to the complexity of the crystallization process of zeolite materials, a deep knowledge of the chemical role played by these organic species was not available. As a consequence, research on the use of organic structure-directing agents was mainly based on a trial-and-error basis, carrying out systematic explorations of the structure-directing ability of different organic species and synthesizing new materials, but basing the research efforts only on empirical evidence and chemical intuition. Nevertheless, one of the major aims in this research field is the rational design of organic structure-directing agents for the synthesis of a targeted zeolite material. This, which was not possible just a few years ago, is starting to become accessible thanks to the great advancement of mainly two physico-chemical techniques that have greatly enhanced our knowledge of the organic structure-directing phenomenon: (1) diffraction techniques (chapter “[Location of Organic Structure-Directing Agents in Zeolites Using Diffraction](#)”).

Techniques”), which now allow to find the location of the organic species within zeolite frameworks, enabling the establishment of structural relationships between zeolite topologies and the geometrical properties of the organic structure-directing agents that drive their crystallization, and (2) molecular modeling techniques (chapter “**Molecular Modelling of Structure Direction Phenomena**”), which have allowed to understand, from a molecular level, the structure-directing mode of action of these organic species. In addition, and based in part on the knowledge gained through these techniques, in recent years new chemical concepts are emerging in structure-direction of zeolite frameworks by organic species. In this context, the spectrum of organic compounds, which was originally almost exclusively based on quaternary ammonium cations (based on nitrogen), has been notably amplified by the use of alternative organic cations based on phosphonium or sulfonium ions (chapter “**Beyond Nitrogen OSDAs**”), or by organometallic compounds (chapter “**Metal Complexes as Structure-Directing Agents for Zeolites and Related Microporous Materials**”), providing new structure-directing agents with novel chemical properties that can be transferred into zeolite materials. Not only the use of new types of organic compounds but also the appropriate use of intermolecular interactions that trigger a remarkable supramolecular chemistry during the structure-direction phenomenon has provided with new zeolitic materials (chapter “**Role of Supramolecular Chemistry During Templating Phenomenon in Zeolite Synthesis**”). The geometrical correspondence between organic structure-directing agents and zeolite frameworks has additionally enabled a strategy to tackle one of the greatest challenges in zeolite (and materials) science, the search for enantiopure chiral solids able to perform enantioselective operations (chapter “**Chiral Organic Structure-Directing Agents**”). All these aspects that will be covered in the different chapters of this book have notably enhanced our knowledge on the organic structure-directing phenomenon during the crystallization of zeolites, and have led to new complex materials with novel and sometimes unprecedented properties that have greatly expanded the range of applications of zeolites in different fields.

Madrid, Spain

Luis Gómez-Hortigüela

Contents

| | |
|---|------------|
| Introduction to the Zeolite Structure-Directing Phenomenon by Organic Species: General Aspects | 1 |
| Luis Gómez-Hortigüela and Miguel Á. Cambor | |
| Location of Organic Structure-Directing Agents in Zeolites Using Diffraction Techniques | 43 |
| Stef Smeets and Lynne B. McCusker | |
| Molecular Modelling of Structure Direction Phenomena | 75 |
| Alessandro Turrina and Paul A. Cox | |
| Beyond Nitrogen OSDAs | 103 |
| Fernando Rey and Jorge Simancas | |
| Role of Supramolecular Chemistry During Templating Phenomenon in Zeolite Synthesis | 139 |
| Cecilia Paris and Manuel Moliner | |
| Metal Complexes as Structure-Directing Agents for Zeolites and Related Microporous Materials | 179 |
| Abigail E. Watts, Alessandro Turrina, and Paul A. Wright | |
| Chiral Organic Structure-Directing Agents | 201 |
| Luis Gómez-Hortigüela and Beatriz Bernardo-Maestro | |
| Index | 245 |