Zeolites and Catalysis

Synthesis, Reactions and Applications

Edited by
Jiří Čejka, Avelino Corma, and Stacey Zones

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The Editor

Prof. Dr. Jiří Čejka
Academy of Sciences of the Czech Republic
Heyrovský Institute of Physical Chemistry
Dokjškova
Dolejskova 3
182 23 Prague 8
Czech Republic

Prof. Dr. Avelino Corma
University Politecnica de Valencia
Institute de Tecnologia Quimica
Avenida de los Naranjos s/n
46022 Valencia
Spain

Prof. Dr. Stacey I. Zones
Chevron Texaco Energy Research
and Technology Company
100 Chevron Road
Richmond, CA 94802
USA

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Preface

One can safely say that the impact of zeolites in science and technology in the last 50 years has no precedents in the field of materials and catalysis. Although the first description of zeolites dates back up to 250 years ago, the last five decades experienced an incredible boom in zeolite research activities resulting in the successful synthesis of almost 200 different structural types of zeolites, numerous excellent scientific papers on the synthesis of zeolites, characterization of their properties, and applications of zeolites in adsorption and catalysis that have revolutionized the petrochemical industry. In addition, based on the knowledge of zeolites several other areas of porous materials have recently emerged including mesoporous materials, hierarchic systems, metal-organic frameworks (cationic-periodic polymers) and mesoporous organosilicas. All these materials have substantially increased the portfolio of novel porous materials possessing new interesting properties, but this topic is not covered in this book.

This book consists of two volumes. The first one is mostly concentrated on recent advances in the synthesis of zeolites and understanding of their properties while the second volume describes recent achievements in the application of zeolites mostly in catalysis.

More specifically, the first volume starts with a chapter by P. Cubillas and M.W. Anderson (Chapter 1) discussing mechanisms of the synthesis of zeolites and zeotypes, including nucleation and crystal growth, employing various microscopic techniques. This is followed by a chapter of K. Strohmaier (Chapter 2) providing a detailed survey on the synthesis of novel zeolites and different layered precursors incorporating different metal ions into the framework, and applying ever increasing number of structure-directing agents. A new approach to the synthesis of zeolites and other porous materials by ionothermal synthesis combining ionic liquids as the solvent together with the structure-directing agent is presented by R. Morris (Chapter 3). Zeolite synthesis can also be controlled by a simultaneous use of two different templates providing new tool for creative chemistry Nas discussed by the group of J. Pérez-Pariente (Chapter 4). Morphological control of zeolite crystals is one of the key issues to understand the mechanism of zeolite crystallization as well as to control the performance of zeolites in various applications as it is outlined by S.-E. Park and N. Jiang in Chapter 5. Introduction of other elements than silicon into the zeolite framework can be done not only via synthesis but also in the

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postsynthesis steps as highlighted for deboronation followed by realumination as described by C.Y. Chen and S.I. Zones (Chapter 6). P.A. Wright and G.M. Pearce show how the individual zeolite structures are built from basic secondary building units. The authors focus not only on general aspects of zeolite structures but also on the description of structures of zeolites determined very recently (Chapter 7).

Structural and textural characterization of zeolites starts in Chapter 8, written by E. Stavitski and B.M. Weckhuysen, providing good examples of application of vibrational spectroscopy under static conditions that can drive into *in situ* catalytic investigations. The group of K. de Jong (Chapter 9) makes an effort to evaluate different physicochemical methods used for textural characterization of zeolites. Gas physisorption, mercury porosimetry, electron microscopy (including 3D experiments), various NMR techniques up to *in situ* optical and fluorescence microscopy are discussed in detail. The location, coordination, and accessibility of framework aluminum are of key importance for acid-catalyzed reactions in zeolites and these issues are addressed by J.A. van Bokhoven and N. Danilina in Chapter 10. Theoretical background of zeolite reactivity employing different computational approaches and models is covered in Chapter 11 by E.A. Pidko and R.A. van Santen. S. Calero Diaz presents an overview of current developments in modeling of transport and accessibility in zeolites showing some recent models and simulation methods that are applied for systems of environmental and industrial interests (Chapter 12). The final chapter of the first volume is written by the group of F. Kapteijn (Chapter 13), in which diffusion in zeolites starting from basic models of diffusion up to the role of diffusion in adsorption and catalytic processes is discussed.

The second volume starts with a chapter of the group of J. Coronas concentrating on special applications of zeolites including green chemistry, hybrid materials, medicine, veterinary, optical- and electrical-based applications, multifunctional fabrics, and nanotechnology (Chapter 14). After that K.B. Yoon presents the opportunities to organize zeolite microcrystals into two- and three-dimensionally organized structures and the application of these organized entities in membranes, antibacterial functional fabrics, supramolecularly organized light-harvesting systems, and nonlinear optical films (Chapter 15).

The remaining chapters are exclusively devoted to the application of zeolites in catalysis. G. Bellussi opens this part with a broad overview of current industrial processes using zeolites as key components of the catalysts and further challenges in this area (Chapter 16). Generation, location, and characterization of catalytically active sites are discussed in depth by M. Hunger showing different aspects of shape selectivity and structural effect on the properties of active sites (Chapter 17). M. Rigutto (Chapter 18) stresses the importance of zeolites and the main reasons for their application in cracking and hydrocracking, the largest industrial processes employing zeolites as catalysts. Further, C. Perego and his coworkers focus on reforming and upgrading of diesel fractions, which with gasoline are by far the most important and valuable key fractions produced by petroleum refineries (Chapter 19). Transformation of aromatic compounds forms the heart of petrochemical processes with zeolites as key components of all catalysts. S. Al-Khattaf, M.A. Ali, and J. Čejka

highlight the most important recent achievements in application of zeolites in various alkylation, isomerization, disproportionation, and transalkylation reactions of aromatic hydrocarbons (Chapter 20). With decreasing supply of oil, natural gas obtains more and more importance. A. Martinez and his coauthors discuss in some detail different ways of methane upgrading into valuable fuels and chemicals (Chapter 21). Methanol, which can be obtained from natural gas, could be one of the strategic raw materials in future. Novel processes transforming methanol into olefins or gasoline are covered in Chapter 22 by M. Stöcker. Incorporation of catalytically active species into zeolite frameworks or channel systems for oxidation reactions is covered in Chapter 23 by T. Tatsumi. The main attention is devoted to Ti-silicates. G. Centi and S. Perathoner focus on increasing applicability of zeolites in environmental catalysis with a particular attention to conversion of nitrogen oxides (Chapter 24). K.L. Yeung and W. Han describe the emerging field of application of zeolites in fuel cells for clean energy generation. The authors show that zeolites can play an important role in hydrogen production, purification, conditioning, and storage (Chapter 25). The final chapter by the authors from the group of A. Corma presents possibilities of application of zeolite as catalysts in the synthesis of fine chemicals. The examples discussed include, for example, acylation, hydroxyalkylation, acetalization, isomerization, Diels–Alder, and Fischer glucosidation reactions.

Bringing together these excellent chapters describing the cutting edge of zeolite research and practice provides an optimistic view for the bright future of zeolites. The number of new synthesized zeolites is ever increasing and particularly novel extra-large pore zeolites or even chiral zeolitic materials will surely be applied in green catalytic processes enabling to transform bulkier substrates into desired products. In a similar way, application of zeolites in adsorption or separation is one of the most important applications of this type of materials saving particularly energy needed for more complex separation processes if zeolites were not available to do the job. Fast development of experimental techniques enables deeper insight into the structural and textural properties of zeolites, while particularly spectroscopical methods provide new exciting information about the accessibility of inner zeolite volumes and location and coordination of active sites. Catalysis is still the most promising area for application of zeolites, in which novel zeolitic catalysts with interesting shape-selective properties can enhance activities and selectivities not only in traditional areas such as petrochemistry but also in environmental protection, pollution control, green chemistry, and biomass conversion. Last but not least, novel approaches in the manipulation and modification of zeolites directed to fuel cells, light harvesting, membranes, and sensors clearly evidence a large potential of zeolites in these new areas of application. The only limitation in zeolite research is the lack of our imagination, which slows down our effort and attainment of new exciting achievements.

It was our great pleasure working with many friends and excellent researchers in the preparation of this book. We would like to thank sincerely all of them for their timely reviews on selected topics and the great effort to put the book together. We believe that this book on zeolites will be very helpful not only for experienced

researchers in this field but also students and newcomers will find it as a useful reference book.

Jiří Čejka — Prague
Avelino Corma Canos — Valencia
Stacey I. Zones — Richmond
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List of Contributors

Sulaiman Al-Khattaf
King Fahd University of
Petroleum & Minerals (KFUPM)
Chemical Engineering
Department
Research Institute
Dhahran
Saudi Arabia

Mohammad Ashraf Ali
King Fahd University of
Petroleum & Minerals (KFUPM)
Center of Excellence in Refining
& Petrochemicals
Research Institute Dhahran
Saudi Arabia

Giuseppe Bellussi
Enitecnologie
San Donato Milanese
Research Centre
Refining & Marketing Division
Research & Technological
Development
Via F. Maritano 26
20097 San Donato Milanese (MI)
Italy

Vincenzo Calemma
Eni S.p.A.
Refining & Marketing Division
20097 San Donato Milanese (MI)
Italy

Angela Carati
Enitecnologie
San Donato Milanese
Research Centre
Refining & Marketing Division
Research & Technological
Development
Via F. Maritano 26
20097 San Donato Milanese (MI)
Italy

Clara Casado
Universidad de Zaragoza
Chemical and Environmental
Engineering
Department and Nanoscience
Institute of Aragón
María de Luna 3
50018 Zaragoza
Spain

Jiří Čejka
Academy of Sciences of the Czech
Republic
Heyrovský Institute of Physical
Chemistry Dokjškova
Dolejskova 3
182 23 Prague 8
Czech Republic

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Gabriele Centi
Universita di Messina
Dip. Di Chimica Industriale ed
Ingegneria dei Materiali
Salita Sperone 31
98166 Messina
Italy

Maria J. Climent
Universidad Politécnica
de Valencia
Instituto de Tecnología Química
UPV-CSIC
Avda. de los Naranjos s/n
46022 Valencia
Spain

Avelino Corma
University Politecnica de Valencia
Institute de Tecnologia Quimica
Avenida de los Naranjos s/n
46022 Valencia
Spain

Joaquín Coronas
Universidad de Zaragoza
Chemical and Environmental
Engineering Department and
Nanoscience Institute of Aragón
María de Luna 3
50018 Zaragoza
Spain

Andrés García-Trenco
UPV-CSIC
Instituto de Tecnología Química
Avenida de los Naranjos s/n
46022 Valencia
Spain

Wei Han
The Hong Kong University of
Science and Technology
Department of Chemical and
Biomolecular Engineering
Clear Water Bay Kowloon
Hong Kong
PR China

Michael Hunger
University of Stuttgart
Institute of Chemical Technology
70550 Stuttgart
Germany

Sara Iborra
Universidad Politécnica
de Valencia
Instituto de Tecnología Química
UPV-CSIC
Avda. de los Naranjos s/n
46022 Valencia
Spain

Agustín Martínez
UPV-CSIC
Instituto de Tecnología Química
Avenida de los Naranjos s/n
46022 Valencia
Spain

Roberto Millini
Enitecnologie
San Donato Milanese
Research Centre
Refining & Marketing Division
Research & Technological
Development
Via F. Maritano 26
20097 San Donato Milanese (MI)
Italy

Carlo Perego
Eni S.p.A.
Istituto Eni Donegani
Via Fauser 4
28100 Novara
Italy

Ernest Peris
UPV-CSIC
Instituto de Tecnología Química
Avenida de los Naranjos s/n
46022 Valencia
Spain

Siglinda Perathoner
Universita di Messina
Dip. Di Chimica Industriale ed
Ingegneria dei Materiali
Salita Sperone 31
98166 Messina
Italy

Paolo Pollesel
Eni S.p.A.
Refining & Marketing Division
20097 San Donato Milanese (MI)
Italy

Gonzalo Prieto
UPV-CSIC
Instituto de Tecnología Química
Avenida de los Naranjos s/n
46022 Valencia
Spain

Marcello Rigutto
Shell Technology Centre
Amsterdam
Grasweg 31
1031 HW Amsterdam
The Netherlands

Víctor Sebastián
Universidad de Zaragoza
Chemical and Environmental
Engineering Department and
Nanoscience Institute of Aragón
María de Luna 3
50018 Zaragoza
Spain

Michael Stöcker
SINTEF Materials and Chemistry
Department of Hydrocarbon
Process Chemistry
P.O. Box 124 Blindern
0314 Oslo
Norway

Takashi Tatsumi
Tokyo Institute of Technology
Chemical Resources Laboratory
Division of Catalytic Chemistry
4259-R1-9 Nagatsuta-cho
Midori-ku
Yokohama 226–8503
Japan

King Lun Yeung
The Hong Kong University of
Science and Technology
Department of Chemical and
Biomolecular Engineering
Clear Water Bay Kowloon
Hong Kong
PR China

Kyung Byung Yoon
Sogang University
Department of Chemistry
Center for Microcrystal Assembly
Seoul 121–742
Korea