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"Mesoporous Zeolites: Preparation, Characterization and Applications"

Edited by Javier Garcia-Martinez (Universidad de Alicante, Spain) and Kunhao Li, (Rive Technology, USA), Wiley-VCH Verlag GmbH & Co KGaA, Germany, 2015, 574 pages, ISBN: 978-3-527-33574-9, £120.00, €162.00, US$215.00

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Introduction

"Mesoporous Zeolites" is a comprehensive book published by Wiley in 2015. The book describes mesoporous materials, their synthesis, characterisation and applications. In addition to mesoporous materials, several chapters of the book review nanoporous materials.

The book was edited by Professor Javier Garcia-Martinez of Universidad de Alicante, Spain, and Kunhao Li, Project Leader at Rive Technology, USA. The two have broad experience of zeolites and in particular mesoporous zeolites. It is the first in a series and aims to bring to light the fast emerging field of mesoporous materials and their applications. To expand on this, various examples are included which demonstrate that mesoporous materials eliminate diffusion limitations. The book successfully fulfils these aims.

It is composed of 16 chapters that can be divided into six general topics: accessing micropores; nanozeolites and nanomaterials; mesoporous aluminosilicates; hierarchical zeolites; characterisation of mesoporous or hierarchical zeolites; and industrial applications of mesoporous zeolites.

Accessing Micropores

This is mainly covered in Chapter 1 authored by Professor Joaquín Pérez-Pariente *et al.* of Instituto de Catálisis y Petroleoquímica, Spain. The chapter gives an overview of diffusional limitations experienced by reactants or products in and out of the zeolite micropores. The chapter covers how these limitations can be overcome by three different but complementary strategies. The first two strategies involve reduction of crystal size of already existing material and creating large pores (mesopores) or cracks in the existing crystal. This enables large bulky molecules to access the active sites. The last approach is synthesis of new zeolite materials containing mesopores. Strategies such as controlling nucleation and growth by use of carbon black, blocking agents, synthesis in presence of pore forming agents and post synthesis methods such as removal of specific tetrahedral atoms are also covered in this chapter.

Nanozeolites: Synthesis and Applications

In my view, this is one of the most interesting topics in this book. It is covered in detail in Chapters 2 and 3. Chapter 2 is by Professor Heloise de Oliveira Pastore *et al.* of Instituto de Química, Brazil, and Universidade Federal de São Carlos, Brazil, while Chapter 3 is by Professor Trong-On Do *et al.* of Laval University, Canada.

Chapter 2 covers fundamentals, advantages and disadvantages of micrometre and nanometre sized zeolites. In the chapter, the authors detail how changes in chemical composition influence particle size of zeolite A. Among the nanosized zeolites included in this chapter are FAU, EMT, LTA, BEA, pentasil and aluminophosphates/silicoaluminophosphates. A table of the effect of different synthesis conditions on crystal size, with references, is included in this chapter.

Chapter 3 is on progress and strategies in synthesis of nanozeolites. Among them are synthesis from clear solution where the ratio between the rate of nucleation and the rate of growth is controlled. To synthesise nanozeolites, high nucleation rates and stabilisation of nuclear entities is required. The former is dependent on temperature, alkalinity and ageing while the latter is mainly dependent on structure directing agents. Other strategies covered in Chapter 3 include use of growth inhibitor, confined space synthesis and use of organic media. Towards the end of the chapter, the authors cover some of the recent advances in nanozeolites including but not limited to cracking of gas oil.

Mesoporous Aluminosilicates

Chapter 4 discusses efforts put towards improvement of mesoporous aluminosilicates since the discovery of M41S by Mobil scientists (1, 2). A review of various strategies (such as wall thickening, aluminium incorporation, surface silylation and zeolite/mesoporous composite materials) used to improve the properties of mesoporous aluminosilicates, in particular acidity and hydrothermal stability, are detailed in this chapter by Yu Liu of Dow Chemical, USA. Examples of the application of zeolite/mesoporous materials in cracking large hydrocarbons such as *n*-dodecane and vacuum gas oil (VGO) are included.

Hierarchical Zeolites

Hierarchical zeolites contain both micropores and mesopores. Various strategies of creating hierarchical zeolites are discussed in Chapters 5–9 and Chapter 14. Chapter 5 by Professor David P. Serrano *et al.* of Instituto IMDEA Energía, Spain, focuses on strategies of synthesising hierarchical zeolites using organosilanes. In this chapter, different types of organosilanes (simple organosilanes, silylated polymers and amphiphile organosilanes) and their effects are discussed.

Perturbation of zeolite crystallisation by addition of polymers or organosilanes is described in Chapter 6 by Professor Feng-Shou Xiao *et al.* of Zhejiang University, China. The chapter details how sources of silicon and aluminium, reaction conditions and type of template influence the size and location of mesopores, crystal morphology and crystallinity.

Chapter 7 by Zhuopeng Wang *et al.* of University of Massachusetts Amherst, USA, primarily focuses on synthesis of hierarchical zeolites in a confined space mainly using carbon as the hard template. Crystallisation techniques such as vapour phase transport (VPT) and steam assisted crystallisation (SAC) are also covered in this chapter. A summary of representative framework types synthesised using the confined space method is presented in table form.

While Chapter 7 is on the ‘bottom-up’ strategy, Chapter 8 by Masaru Ogura *et al.*, University of Tokyo, Japan, focuses on ‘top-down’. The chapter also reviews different opinions on the ‘top-down’ mechanism. The main treatment method covered in this chapter is desilication, where the effects of alkali concentration, temperature and duration of treatment are critical to the type of mesopores formed. Although other zeolite types are covered, the main focus is on ZSM-5. In addition to synthetic approaches, the catalytic performances of various desilicated materials are presented. **Figure 1** shows scanning electron microscopy (SEM) of mesoporous mordenite zeolite obtained by de-ironation through heat treatment.

Chapter 9 is by Professor Irina Ivanova *et al.* of Moscow State University, Russia. Chapter 9 is very similar to Chapter 8 in that it focuses on the ‘top-down’ method, except that after desilication, it covers an extra step of zeolite recrystallisation and the role played by surfactants. The composite product shows improved

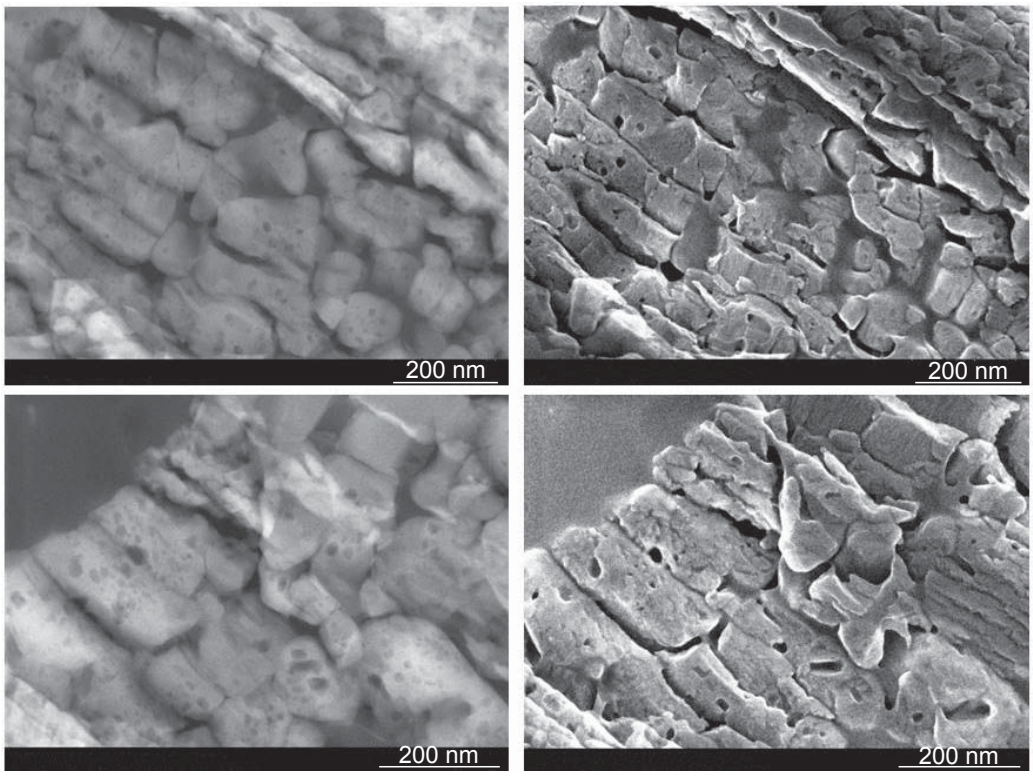


Fig. 1. Dark field SEM images of mesoporous mordenite zeolite obtained through de-ironation

hydrothermal stability and catalytic activity compared to the mesoporous aluminosilicates.

While Chapters 5–9 cover the generation of hierarchical zeolites mainly by desilication, Chapter 14 by Professor Jerzy Datka *et al.* of Jagiellonian University, Poland, explores both desilication and dealumination. It also investigates the nature of the formed acidity including various techniques used for measuring acidity.

Characterisation of Mesoporous and Hierarchical Zeolites

Discovery of new materials poses significant challenges with regard to proper characterisation. Characterisation and the challenges associated with mesoporous zeolites are covered in Chapters 11, 12 and 13.

Recent advances in characterisation of mesoporous zeolites by gas adsorption are covered in Chapter 11 by Matthias Thommes *et al.* of Quantachrome Instruments, USA. In this chapter the choice of adsorptive and the adsorption mechanism are discussed along with data analysis to determine surface area, pore size distribution and porosity. In the summary section, the authors consent that pore size analysis of zeolites and hierarchically structured micro-meso porous materials is a challenge.

Fundamentals of diffusion and diffusion measurements (micro, macro, macro/meso, macro/micro, meso/meso, and meso/micro) including pulsed field gradient nuclear magnetic resonance (PFG-NMR) are explored in Chapter 12 by Professor Jörg Kärger *et al.* of Universität Leipzig, Germany.

Principles and use of techniques such as SEM, high-resolution transmission electron microscopy (HR-TEM) and transmission electron microscopy (TEM), rotation electron diffraction and electron tomography in analysis of complex structures such as zeolites is discussed in Chapter 13 by Professor Xiadong Zou *et al.* of Stockholm University, Sweden. An example of the use of electron tomography to quantify mesopores and platinum nanoparticles in mesoporous zeolite Y is included in this chapter.

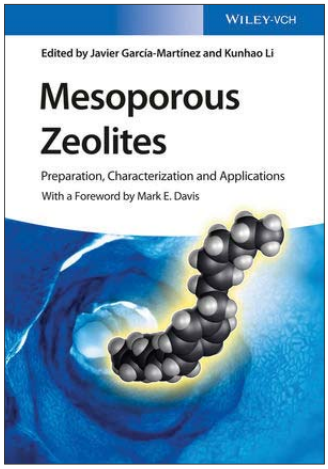
Industrial Application of Mesoporous Zeolites

Similarly to Chapter 9, Chapter 10 by Professor Javier Garcia-Martinez *et al.* of Universidad de Alicante, Spain, demonstrates how mesopores can be tuned by using surfactants of different size. The chapter also includes details on the commercialisation of the first mesoporous zeolites in a fluid catalytic cracking unit by Rive Technology. The use of mesoporous zeolites for biomass conversion to fuels and chemicals is reviewed by Professor Kostas S. Triantafyllidis *et al.* of University of Thessaloniki, Greece, and Chemical Process and Energy Resources Institute (CPERI), Greece, in Chapter 15. Areas covered in this chapter include the use of mesoporous zeolites in catalytic fast pyrolysis of lignocellulosic biomass, cracking of vegetable oils, methanol to hydrocarbons, methanol to dimethyl ether, methanol to gasoline, methanol to olefins and hydroprocessing of biomass derived feeds.

To conclude is Chapter 16 by Roberto Milini of Eni SpA, Italy, on industrial perspectives for mesoporous zeolites.

Summary

This book is interesting and very informative. It broadly covers all areas of mesoporous materials: synthesis, characterisation and application. The book is meant for someone with knowledge of zeolites and microporous materials. In my view, one of the areas not fully addressed in this book is the enormous cost associated with the templating agents and potential loss of materials during desilication or dealumination. A review on what is been done to reduce the costs is also missing.



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The Reviewer

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