

# **SUSTAINABLE CATALYTIC PROCESSES**

EDITED BY BASUDEB SAHA, MAOHONG FAN, AND JIANJI WANG



# ***Sustainable Catalytic Processes***

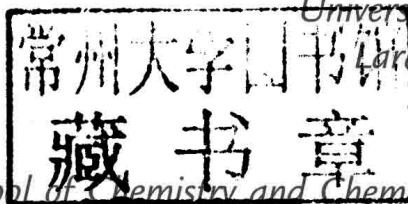
**Edited By**

**Basudeb Saha**

*Department of Chemistry, Purdue University,  
West Lafayette, Indiana, USA;  
Laboratory of Catalysis, Department of Chemistry,  
University of Delhi, Delhi, India*

**Maohong Fan**

*Department of Chemical and Petroleum Engineering,  
University of Wyoming,  
Laramie, WY, USA*



**Jianji Wang**

*School of Chemistry and Chemical Engineering,  
Key Laboratory of Green Chemical Media and Reactions,  
Ministry of Education, Henan Normal University,  
Xinxiang, Henan, PR China*

**ELSEVIER**

AMSTERDAM • BOSTON • HEIDELBERG • LONDON • NEW YORK • OXFORD  
PARIS • SAN DIEGO • SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Elsevier

Radarweg 29, PO Box 211, 1000 AE Amsterdam, Netherlands  
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK  
225 Wyman Street, Waltham, MA 02451, USA

Copyright © 2015 Elsevier B.V. All rights reserved.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: [www.elsevier.com/permissions](http://www.elsevier.com/permissions).

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

### Notices

Knowledge and best practice in this field are constantly changing. As new research and experience, broaden our understanding, changes in research methods, professional practices, or medical treatment, may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating, and using any information, methods, compounds, or experiments described herein. In using such, information or methods they should be mindful of their own safety and the safety of others, including, parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume, any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas, contained in the material herein.

ISBN: 978-0-444-59567-6

### British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

### Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

For Information on all Elsevier publications  
visit our website at <http://store.elsevier.com/>



Working together  
to grow libraries in  
developing countries

[www.elsevier.com](http://www.elsevier.com) • [www.bookaid.org](http://www.bookaid.org)

Printed in the United Kingdom

# ***Sustainable Catalytic Processes***



# *List of Contributors*

**Ejaz Ahmad** Renewable Energy and Chemicals Laboratory, Department of Chemical Engineering, Indian Institute of Technology, Delhi, India

**Md Imteyaz Alam** Renewable Energy and Chemicals Laboratory, Department of Chemical Engineering, Indian Institute of Technology, Delhi, India

**Asim Bhaumik** Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata, West Bengal, India

**Saikat Dutta** Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan

**Maohong Fan** Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY, USA

**Shelaka Gupta** Renewable Energy and Chemicals Laboratory, Department of Chemical Engineering, Indian Institute of Technology, Delhi, India

**M. Ali Haider** Renewable Energy and Chemicals Laboratory, Department of Chemical Engineering, Indian Institute of Technology, Delhi, India

**Xin Huang** School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing, PR China; Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY, USA

**Lingjun Li** School of Chemistry and Chemical Engineering, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang, Henan, PR China

**Nabanita Pal** Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata, West Bengal, India; Surface Physics and Materials Science Division, Saha Institute of Nuclear Physics, Kolkata, West Bengal, India

**Basudeb Saha** Department of Chemistry, Purdue University, West Lafayette, Indiana, USA; Laboratory of Catalysis, Department of Chemistry, University of Delhi, Delhi, India

**A. Sakthivel** Department of Chemistry, Inorganic Materials and Catalysis Laboratory, University of Delhi (North Campus), Delhi, India

**A.K. Singh** Department of Chemistry, Inorganic Materials and Catalysis Laboratory, University of Delhi (North Campus), Delhi, India

**Jianji Wang** School of Chemistry and Chemical Engineering, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang, Henan, PR China

**Yonggang Wang** School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing, PR China

## ***List of Contributors***

---

**Fan Zhang** School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing, PR China; Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY, USA

**Anlian Zhu** School of Chemistry and Chemical Engineering, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang, Henan, PR China

# *Preface*

It was a fine spring day when my good friend Professor Maohong Fan and the co-editor of this book proposed me to edit a research-based book with Elsevier in the area of catalysis. The proposal was great, and I thought hard about a possible title for the book. Being a teacher and a researcher in the area of sustainable chemistry and catalysis with a reputed university and a former scientist of an international chemical company, I found a reference book summarizing contemporary research outcome in sustainable catalytic chemistry is important. So I agreed to edit this book with my co-editors, Professor Maohong Fan and Professor Jianji Wang, which can serve as a reference to researchers in industrial and academic settings to meet their growing interests in conducting research on the development of environmentally and economically viable chemical processes with catalyst participation.

During 2005–2015, there has been an increasing importance in the development of catalytic processes for the production of chemicals and fuels from nonconventional renewable sources to control rapid depletion of conventional fossil resources and prevent greenhouse gas emissions. Among several renewable sources, biomass has emerged as a preferred and sustainable resource for the production of chemical precursors, commodity and speciality chemicals and biofuels because of its abundancy and accessibility. However, deconstruction of biomass, especially second-generation lignocellulose, to access the constituents cellulose, hemicellulose and lignin for upgrading poses a significant challenge, which necessitates the utilization of heterogeneous catalytic substances of appropriate properties. Therefore, two chapters discussing various catalytic properties, preparation and characterization techniques and applications are included in this book. Further the utilization of these materials, along with several homogeneous catalytic substances for biomass deconstruction and upgradation of cellulose and hemicellulose into chemicals and biofuels, is summarized in two new chapters.

Another important component of biomass is lignin. Lignin is a natural biopolymer of important phenolic subunits and constitutes about 40% of carbon and energy values of biomass. While in 2005–2015, there has been significant attention given to the development of catalytic processes for the conversions of cellulose and hemicellulose, the valorization of lignin constituent phenolic monomers into high value chemicals for speciality applications such as ingredients for aroma, performance and agricultural products is important to improve the economic viability of biorefinery processes and to ensure the utilization

of complete carbon value of biomass. By keeping this in mind, one chapter is dedicated to the discussion of the catalytic processes for selective upgrading of lignin to the valuable products and the associated mechanistic insights.

An integrated biological and catalytic conversion process for upgrading the entire biomass into a variety of commodity and speciality chemicals is seen as a viable strategy for the production of diverse products. A limitation of this strategy is the deactivation of catalytic substances by biogenic impurities that are formed in the biological conversion step. Therefore, a chapter is presented discussing a detailed overview of the available knowledge on the mechanism leading to the deactivation of the catalyst surface by biogenic impurities. This will help in the better designing of catalysts and purification methods for the development of effective integrated processes for biomass conversions.

Coal gasification is an important process in the purview of sustainable catalytic processes. The efficiency of the coal gasification process in producing syngas with high carbon value and optimized carbon monoxide to hydrogen ratio is largely dependent on the effectiveness of catalysts. Therefore, a chapter is compiled on the latest development of catalysts for coal gasification processes. Besides discussing the benefits and reactivity of earth abundant and inexpensive alkali, alkaline earth and transition metals for the said process, the mechanisms and the recovery protocols of the aforementioned catalytic substances are presented with fundamental concepts and future outlook.

I am greatly thankful to my co-editors Professor Maohong Fan and Professor Jianji Wang for their valuable time in contributing and reviewing their chapters and helping me in designing appropriate chapter contents for the book. Their sincere support and courage are enormous.

I am also equally indebted to all of my outstanding colleagues and friends who authored the chapters in this book and gave their time to thoroughly review the chapters. This book will remain incomplete without the continuous support and help of the people of Elsevier. My sincere appreciation goes to Dr Kostas Marinakis — Senior Acquisition Editor, Sarah Jane Watson — Editorial Project Manager, Paul Prasad Chandramohan — Senior Project Manager and Tharangini Sakthivel — Contracts Coordinator with Global Rights Department for their help throughout the publication process as well as overseeing proof composition and corrections.

With my co-editors, I hope this book will become an ideal reference to students, scientists, academicians and industrialists of all areas of chemistry, especially sustainable, catalysis and environmental chemistry. I apologize in advance for any unforeseen errors in the composition, and would appreciate your sharing such mistakes along with any advice for the future editions.

**Editor: Basudeb Saha**  
**Co-editors: Maohong Fan and Jianji Wang**



# Contents

<b>List of Contributors .....</b>	<b>ix</b>
-----------------------------------	-----------

<b>Preface .....</b>	<b>xi</b>
----------------------	-----------

<b>Chapter 1: Role of Meso/Microporous Molecular Sieve Composite Materials on Various Catalytic Transformations .....</b>	<b>1</b>
---	----------

*A. Sakthivel, A.K. Singh*

1. Introduction .....	1
2. Zeolite and Zeolite-Like Molecular Sieves.....	2
3. Mesoporous Molecular Sieves .....	4
4. Progress in Mesoporous Molecular Sieves Assembled from Microporous Precursors .....	6
5. Meso/Microaluminosilicate Composite Materials as Potential Catalysts .....	8
6. Titanium-Based Meso/Microcomposite as Sustainable Catalysts .....	13
7. Meso/Microcomposite of Aluminophosphate-Based Materials as Potential Catalysts .....	14
8. Summary .....	18
Acknowledgements.....	18
References.....	18

<b>Chapter 2: Functionalized Mesoporous Materials as Sustainable Catalyst in Liquid Phase Catalytic Transformations.....</b>	<b>23</b>
--	-----------

*Nabanita Pal, Asim Bhaumik*

1. Introduction .....	23
2. Synthesis and Types of Functionalized Mesoporous Materials .....	25
3. Different Organic Transformations over Functionalized Mesoporous Catalysts .....	28
3.1 Acid–Base Catalysed Reactions on Functionalized Mesoporous Materials .....	29
3.2 Redox Reactions Catalysed by Functionalized Mesoporous Materials .....	36
3.3 Different Coupling Reactions over Functionalized Mesoporous Materials .....	43
3.4 Polymerization Reactions .....	52
3.5 Role of Functionalization over Ordered Mesoporous Silicas .....	52
4. Summary .....	54
List of Abbreviations.....	54
References.....	54

**Chapter 3: Sustainable Catalysis Systems Based on Ionic Liquids ..... 61**

*Jianji Wang, Anlian Zhu, Lingjun Li*

1. Introduction .....	61
2. Physical Properties of Ionic Liquids and Their Potentials in Sustainable Catalysis .....	62
2.1 Liquid Range.....	62
2.2 Density and Viscosity .....	64
2.3 Polarity .....	64
3. The Utilization of Ionic Liquids in Sustainable Catalysis Procedures .....	65
3.1 The Utilization of Ionic Liquids in Transition Metal Catalysis Reactions .....	66
3.2 Enzymatic Reactions in Ionic Liquids .....	70
3.3 The Dissolution and Conversion of Biomass in Ionic Liquids .....	74
3.4 The Transformation of CO <sub>2</sub> to Cyclocarbonates Using Ionic Liquids .....	80
3.5 The Utilization of Functionalized Ionic Liquids in Sustainable Catalysis .....	83
4. Outlook and Summary .....	88
References.....	89

**Chapter 4: Catalysis for the Production of Sustainable Chemicals and Fuels from Biomass ..... 99**

*Md Imteyaz Alam, Basudeb Saha*

1. Introduction .....	99
2. Biomass and Biomass Compositions .....	99
3. Strategy for Biomass Conversion .....	100
4. Biomass to Value-Added Chemicals .....	101
5. 5-Hydroxymethyl Furfural .....	102
5.1 Aspects of HMF Synthesis .....	103
5.2 By-products in HMF Production .....	105
6. Catalyst for Biomass Conversion .....	105
7. Significance of 5-Hydroxymethyl Furfural as a Platform Chemical .....	107
7.1 Oxidation of HMF to FDCA .....	107
7.2 Oxidation of HMF to DFF .....	107
7.3 HMF to LA .....	107
8. Second-Generation Biofuels from Biomass .....	108
8.1 Cellulosic Ethanol .....	109
8.2 5-Ethoxymethyl Furfural .....	110
8.3 2,5-Dimethylfuran .....	111
8.4 Long Chain Hydrocarbons.....	114
9. Summary .....	120
References.....	120

**Chapter 5: Lignin Deconstruction: Chemical and Biological Approaches..... 125***Saikat Dutta*

1. Introduction .....	125
2. Lignin Valorization Techniques .....	128
2.1 Chemical Techniques .....	128
3. Enzymatic Techniques .....	138
4. Carbonization .....	144
4.1 Carbon Fibres .....	145
5. Summary and Outlook .....	151
References .....	153

**Chapter 6: Integrated Bio- and Chemocatalytic Processing for Biorenewable Chemicals and Fuels..... 157***Md Imteyaz Alam, Shelaka Gupta, Ejaz Ahmad, M. Ali Haider*

1. Introduction .....	157
2. Biocatalytic Transformation to Platform Molecules .....	159
3. Challenges Related to the Nature of Biogenic Impurities .....	165
4. Strategies for Catalytic Transformation of Platform Molecules .....	168
5. Conclusions .....	174
References .....	174

**Chapter 7: Catalytic Coal Gasification..... 179***Xin Huang, Fan Zhang, Maohong Fan, Yonggang Wang*

1. Introduction .....	179
2. Catalysts for Coal Gasification .....	181
2.1 Alkali Metal Compounds .....	181
2.2 Alkaline Earth Metal Compounds .....	185
2.3 Transition Metal Compounds .....	189
2.4 Composite Catalysts .....	191
2.5 Invalidation and Recovery of Catalyst .....	194
3. Conclusion and Outlook .....	196
References .....	196

**Index..... 201**

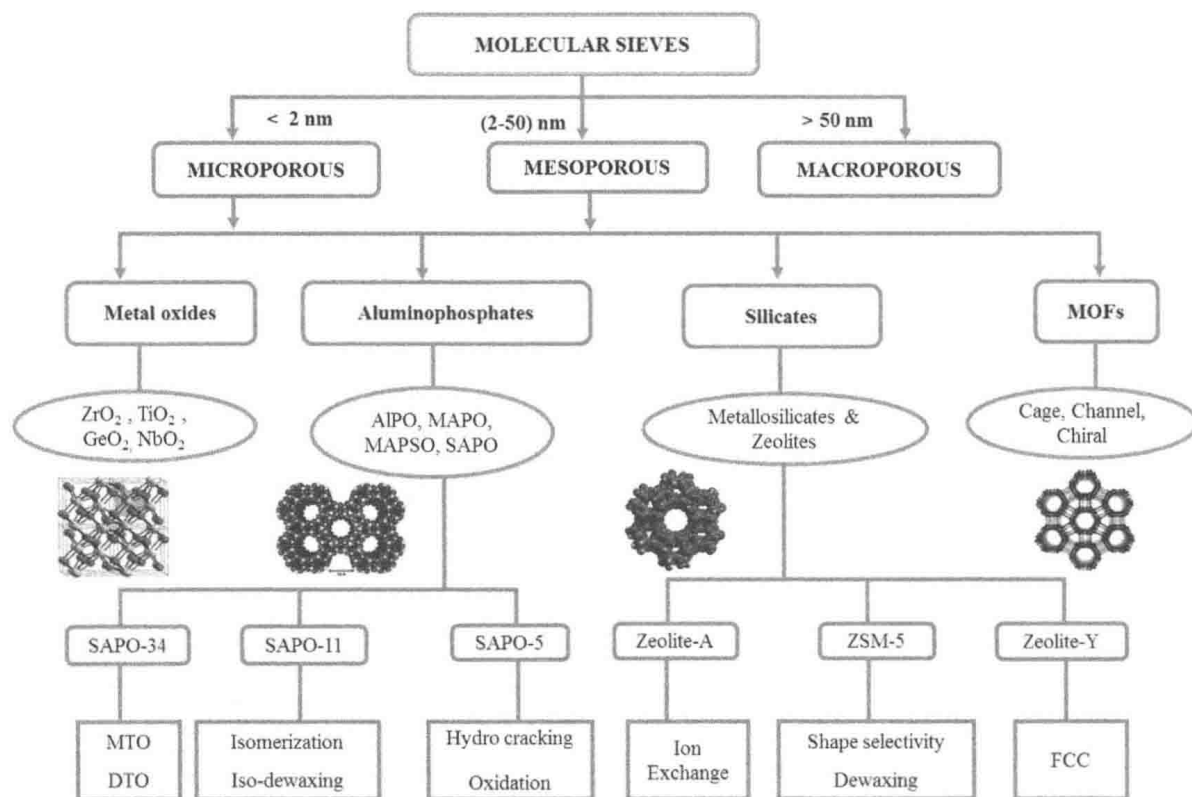
# ***Role of Meso/Microporous Molecular Sieve Composite Materials on Various Catalytic Transformations***

**A. Sakthivel, A.K. Singh**

*Department of Chemistry, Inorganic Materials and Catalysis Laboratory, University of Delhi (North Campus), Delhi, India*

## **1. Introduction**

The development of inorganic materials possessing a framework structure with channels, voids, cavities and appropriate pore dimensional accesses (voids) is a prime area of materials sciences owing to their sorption, catalytic and molecular sieve properties [1]. In this regard, the synthesis and design of open framework molecular sieves, with tailored pore size and controllable framework topology, have attracted great interest among materials researchers. Notably, the field of heterogeneous catalysis has witnessed the major application of such engineered materials in petrochemical and fine chemical processes, specifically for adsorption and support [2,3]. The basic criteria that enable their extensive application are the inherent porosity and high surface area. The International Union of Pure and Applied Chemistry has classified these porous materials into three classes based on pore size: microporous ( $d < 2$  nm), mesoporous ( $2 \text{ nm} < d < 50$  nm) and macroporous ( $d > 50$  nm) [4]. In scientific applications, it is more precise to use the term 'molecular sieves' in place of porous materials. These materials possess selective sieving/adsorption properties at the molecular level owing to their exclusive shape, size and molecular polarity [5]. A material is considered a molecular sieve when it can selectively separate particular molecules or components from a mixture based on shape and size. The term molecular sieve was coined by McBain to explain the sieving properties of certain microporous charcoal and natural zeolites [5]. Scheme 1 summarizes the classification of molecular sieves, different types of molecular sieves materials and their importance in various applications.



Scheme 1

Various types of molecular sieve classifications and their important applications.

## 2. Zeolite and Zeolite-Like Molecular Sieves

Zeolite and zeolite-like molecular sieves are one of the most important framework molecular sieve materials extensively used as catalysts and adsorbents in several petroleum and fine chemical processes [6–9]. Their elemental composition can be regulated by the introduction of heteroatoms (B, Ti, V, Cr, Fe, Co, Ga, etc.) either in the framework or extra-framework and subsequently alter the active sites of materials. By definition, zeolites are aluminosilicates framework materials that is based on a three-dimensional network of  $(\text{SiO}_4)^{4-}$  and  $(\text{AlO}_4)^{5-}$  tetrahedra [5,10–13]. The extended arrangements of connected primary tetrahedra may be defined as secondary building units (SBU), such as single four rings, six rings and more complex units like double four rings and double six rings, etc., which are further linked to form a structural sub unit (SSU) (Figure 1) [5,10,14].

Aluminophosphate molecular sieves are another class of porous crystalline inorganic solid materials that are formed from alternating  $\text{AlO}_4^{5-}$  and  $\text{PO}_4^{3-}$  tetrahedra, which were first synthesized by Wilson and co-workers [15,16]. This was the first family of framework oxide molecular sieves, which is free from silicate. Their general formula can be expressed as  $[(\text{AlO}_2)_x(\text{PO}_2)_x] \cdot y \text{H}_2\text{O}$ , indicating that, contrary to most of the zeolites, aluminophosphate molecular sieves are ordered with an Al/P ratio that is always unity.



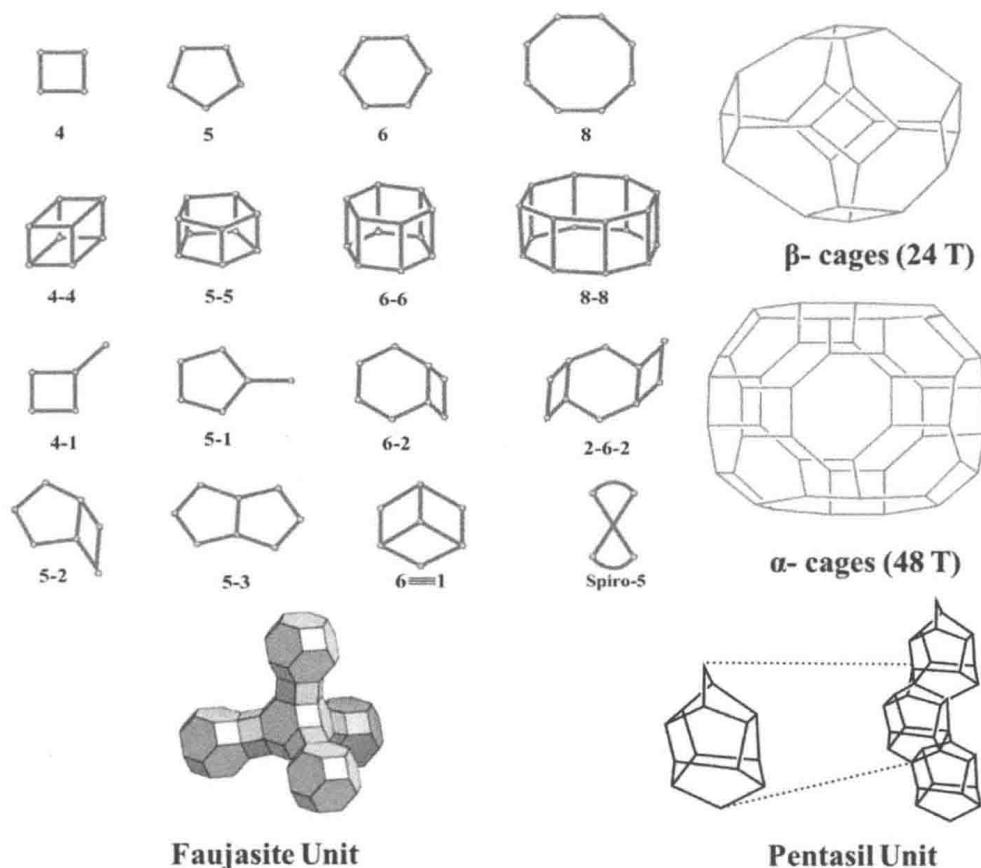


Figure 1

Secondary building unit and structural sub units of zeolite molecular sieves [5].

Conventionally, zeolites and zeolite-like molecular sieve materials are synthesized under hydrothermal conditions using silicon and aluminium sources in the presence of alkali metal cations or organic amines/ammonium cations, which act as templates or structure-directing agents (SDAs). The primary Td units ( $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$ ) combine to form SBUs, which grow around the template of different framework structures. The properties of the resulting zeolite are influenced by several factors, including the composition and pH of the reaction mixture, crystallization temperature, duration of the reaction and choice of SDAs. Figure 2 represents the several stages involved in the synthesis of different zeolitic systems [17].

The intrinsic properties of these molecular sieves, namely strong acidity, large internal surface area, pore volume and unique framework topology facilitate as possible applications in catalysis and adsorption processes. Further, researchers have focused on developing new zeolitic materials with improved textural properties. The major drawback of zeolites is their inability to diffuse bulkier reactant molecules due to their small pore openings and channel size ( $<0.8$  nm) [18].

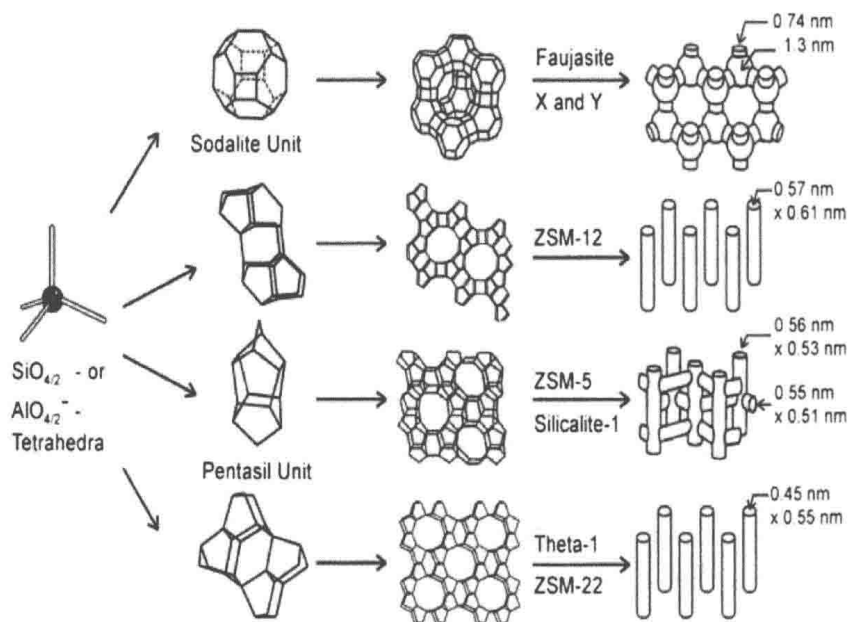


Figure 2

Structures of four selected zeolites (from top to bottom: (1) faujasite or zeolites X, Y; (2) zeolite ZSM-12; (3) zeolite ZSM-5 or silicalite-1; (4) zeolite Theta-1 or ZSM-22) and their micropore systems and dimensions. *Reproduced from Ref. [17].*

### 3. Mesoporous Molecular Sieves

The limitations of microporous zeolite were addressed, to some extent, in 1992, when researchers at Mobil synthesized M41S molecular sieves, the first family of mesoporous silicates with a larger pore size (1.5–10 nm) [19]. A liquid crystal templating (LCT) mechanism, in which surfactant media serve as the organizing agents, was used to assemble hexagonal, cubic and lamellar mesophases of MCM-41, MCM-48 and MCM-50, respectively (Figure 3). These materials possess a high surface area ( $>1000 \text{ m}^2/\text{g}$ ), and their pore size can be tailored by varying the reactant stoichiometry and nature of the

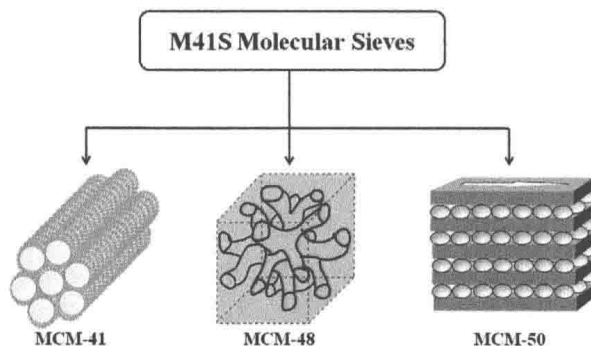


Figure 3

Structures of MCM-41, MCM-48 and MCM-50.

surfactant (cationic/anionic, alkyl chain length), or by post-synthetic techniques. This strategy has successfully led to the synthesis of other mesophases, for example, SBA-15, SBA-1 and HMS [20].

The assembly of these different mesophases depends upon the surfactant organization in the micellar liquid crystalline phase, which serves as a template. The inorganic silicates are cast over the surface of the template by electrostatic interaction. Beck et al. believe that the liquid crystal arrangement is solely credited to surfactants, and the silicate condensation is not the dominant factor in forming the structure [19–21]. Later, Stucky and co-workers proposed another mechanism, in which a cooperative interaction between the surfactant and the silicate precursors (cooperative self-assembly (CSA) mechanism) leads to different mesophases [22]. In general, the LCT mechanism is favoured at high surfactant concentrations, while the CSA mechanism operates at low surfactant concentrations. The CSA mechanism has been widely accepted and extensively evidenced by different advanced characterization techniques [23]. Figure 4 presents the two different mechanisms proposed for the synthesis of mesoporous materials [24].

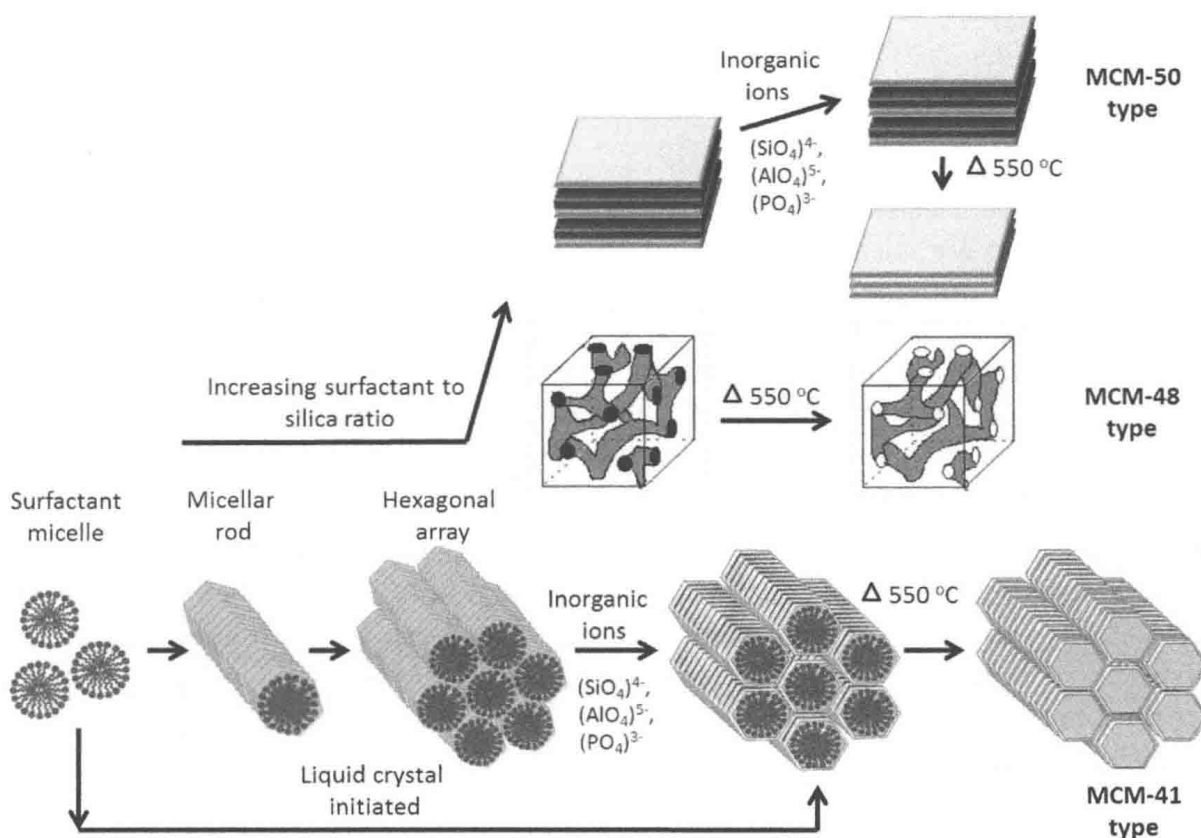


Figure 4

Schematic illustration of (1) the liquid crystal templating mechanism and (2) the cooperative self-assembly mechanism for the formation of ordered mesoporous materials [24].

The trivalent metal ion-substituted mesoporous molecular sieve showed promising catalysts for various organic transformations [25–27]. On the other hand, the introduction of transition metal ions results in redox properties and shown as potential oxidation catalysts [28–30]. However, the amorphous wall properties of these materials limit their application at high temperatures and reactions involving water owing to their poor hydrothermal stability.

#### ***4. Progress in Mesoporous Molecular Sieves Assembled from Microporous Precursors***

The quest to synthesize thermally and mechanically strong mesoporous materials has driven researchers to adopt various synthetic routes and in situ and ex situ methods. During 1992–till present, numerous studies have focused on the synthesis of efficient heterogeneous molecular sieve catalysts with superior characteristics to those of conventional ones. In this regard, the development of hierarchical porous and meso–microcomposite materials is a prospective field for heterogeneous catalysis. Hierarchical or meso/microcomposite materials are generally associated with multidimensional, interconnected pores in an ordered structure, with a high internal surface area and pore volume [31]. Furthermore, these composite materials overcome the diffusion limitation that arises in microporous systems. The interest in such materials is rapidly growing due to their versatile applications in various fields (e.g. nanoscience, catalysis, separation, electronics, optics, optoelectronics, energy, environment and life sciences) [32]. Several synthetic procedures have been adopted to fabricate hybrid materials. The various strategies involve (1) post-synthetic silylation, followed by crystallization; (2) improving the framework wall thickness by aluminium grafting; (3) introducing inorganic salts to improve condensation and cross-linkages in the framework; (4) post-coating of amorphous walls by additional templating agents; (5) developing meso/microcomposites in single- or multistep synthesis or (6) recrystallizing zeolites [33–45].

Broadly, the various routes have been categorized as ‘bottom-up’ or ‘top-down’ methods. In the bottom-up approach, researchers utilize multistep ‘soft templating’ or ‘hard templating’ methods. In soft templating methods, meso/microcomposite materials are prepared either by a direct synthesis route, using a mixture of templates and surfactants for the formation of cubic and hexagonal mesoporous arrays of aluminosilicates [46–49], or by synthesis of mesoporous materials followed by coating of the pore walls with zeolite SBUs [34–38]. In hard templating methods, zeolite seeds are first prepared, and then used to assemble the mesoporous phase [39–45]. On the other hand, in top-down processes, certain framework elements are removed from the zeolitic species (dealumination or desilication) in order to generate mesopores in them. These processes