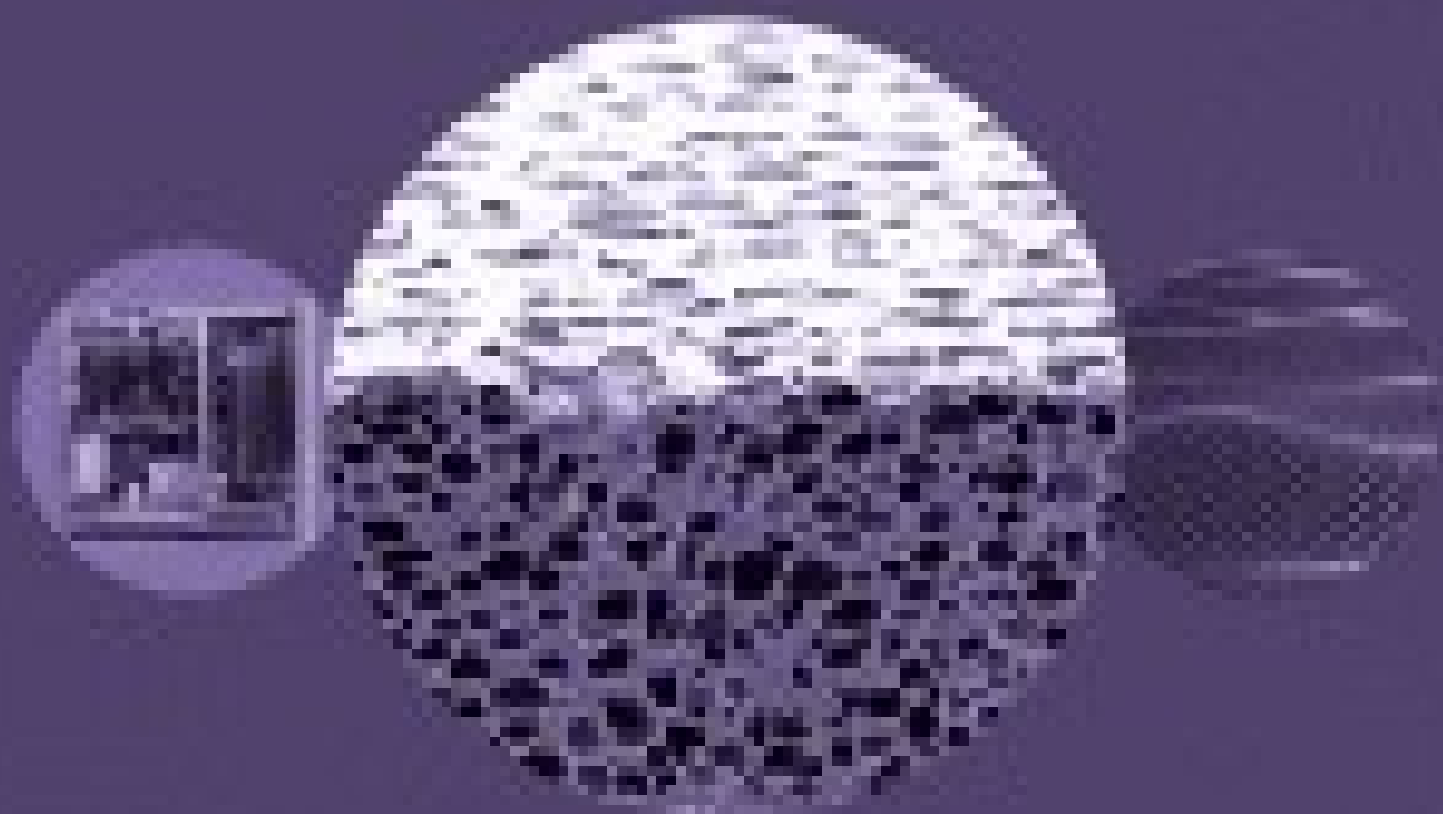


CURRENT TRENDS AND FUTURE DEVELOPMENTS ON (BIO-) MEMBRANES

PROCESSES, MEMBRANES AND MEMBRANE REACTORS



EDITORS
ANGELO SAGLE AND KAMRAN CHAKRABORTY

Preface

In recent years, many research accomplishments in the area of microporous membranes and membrane reactors have been summarized with regard to membrane preparation, modeling, applications, and commercialization, including the state-of-the-art and new challenges, membrane technology and applications, and microporous membranes for gas separation and water treatment, namely hydrogen purification, carbon dioxide separation, and desalination processes. This book evaluates the application potential of microporous membranes such as silica, graphene oxide, zeolite, carbon, and polymeric membranes in membrane reactor systems from both experimental and modeling viewpoints.

Indeed, this book is intended to serve as a “one-stop” reference resource for important research accomplishments in the area of microporous membranes, membrane reactors, and their applications. This book will be a very valuable reference source for university and college faculties, professionals, postdoctoral research fellows, senior graduate students, and research and development laboratory researchers working in the area of membrane technologies and their applications. Prominent researchers from industry, academia, and government/private research laboratories from across the globe contributed the various chapters. Indeed, the book is an up-to-date record on the major findings and observations in the field of microporous membranes, membrane reactors, and their applications. To this purpose, there are 15 chapters covering all the main subjects in the mentioned field.

Chapter 1 (Ismail, Wan-Salleh, and Sazali) starts by considering the advanced development of carbon membrane, which has been outstanding in gas separation applications compared to other applications, for example, water treatment. The class of microporous carbon membranes is known to possess a wide range of pore size distribution and some promising properties in terms of thermal and chemical resistance. This work critically reviewed the structure, preparation method, characterization, and applications of microporous carbon membranes. The advantages, drawbacks, comparison of data performance, and research requirements are further elaborated upon. Polymer precursor employed, pore structure control, manipulation of heat treatment conditions, and characteristics of the resultant carbon membranes are discussed by comparing each process condition. The chapter outlines the current research in carbon membrane, leading to future research prospectives and pointing out issues that need to be addressed in the future.

In [Chapter 2](#) (Medrano, Llosa-Tanco, Pacheco-Tanaka, and Gallucci), the transport mechanism and modeling of microporous carbon membranes are deeply discussed. This is because, in the last decade, the carbon molecular sieve membranes have gained increased interest as they allow an excellent compromise in performance, in terms of permeability and separation factors, while exhibiting very good chemical and mechanical stability. Their performance is nowadays better than commercial polymeric membranes, although their production costs are still higher and represent one of the main limitations for their large-scale exploitation. In this chapter, a comprehensive overview of the carbon molecular sieve membranes is given. Special attention is paid to the transport mechanism of gases through these membranes, the equations describing this phenomenon, the strategies to follow for maximizing their performance, and finally the potential applications of these membranes.

In [Chapter 3](#) (Iulianelli and Basile), microporous carbon membranes are considered from the point of view of membrane reactors. The chapter explores several aspects of carbon membranes, particularly focusing on the role of the polymer precursors used for their fabrication, the main advantages and drawbacks between supported and unsupported typology, the transport mechanisms, and last but not least the various applications in membrane reactors for carrying out several reaction processes.

In [Chapter 4](#) (Motuzas, Darmawan, Elma, and Wang), the silica in the membrane configuration is seen as one of the most researched materials in the inorganic porous membrane family. In fact, many efforts have been focused on optimization of the preparation venues, development of the characterization methods, and investigation of the potential niches of application of the silica membranes. Since the 1990s, the methyl silica, silica-containing carbon templates, metal oxide/silica, and organosilica structures have been investigated in the membrane configuration. Thermal treatment has also evolved significantly, reducing the preparation time from days to an hour without sacrifice of the membrane quality. Concerning the application in the gas separation, significant input to knowledge has been gathered on hydrogen purification and carbon dioxide removal. The previously mentioned research outcomes are discussed in detail.

[Chapter 5](#) (Kanezashi and Tsoru) relates to the gas permeation properties and pore size evaluation of microporous silica membranes. These membranes have a loose amorphous structure rather than a cristobalite crystal structure, which allows permeation by both helium and hydrogen regardless of their small molecular sizes. Compared with membranes made from other inorganic materials, the potential for thin-layer formations of less than 100 nm via chemical vapor deposition and sol-gel methods dramatically improves He and H₂ permselectivity. Recent research has shown that the choice of Si as a precursor and fluorine doping via the sol-gel method have proven effective in tailoring an amorphous silica structure with pore sizes in the subnanometer range. In this chapter, various methods for subnanometer pore size evaluation are reviewed. One of them is based on a modified gas translation model, and the other one is derived from normalized Knudsen-based permeance that uses a

gas-translation model originally proposed by others for microporous silica membranes. Permeation models, a modified gas translation model, and a solubility site model are compared. The effective molecular size of H₂ for permeation through an amorphous silica network is discussed based on the results of a k_0 plot, activation energy, and the permeance ratio of each model. In addition, theoretical analysis of He and H₂ permeation properties through microporous organosilica membranes derived from bridged organoalkoxysilanes with different linking units is also introduced to discuss the permeation difference between SiO₂ and organosilica networks.

Chapter 6 (Meng and Tsuru) deals with microporous silica membrane reactors. In recent years, catalytic membrane reactors with a microporous inorganic membrane have attracted considerable research interest because of their potentials as an alternative for industrial reaction processes. This chapter focuses on the state of the art in the development of silica-based catalytic membrane reactors for hydrogen production from energy carriers. Recent advances in the preparation of high-performance silica-based microporous membranes are highlighted. Experimental and theoretical investigations into the application of silica-based catalytic membrane reactors for heterogeneous reactions, including reforming of hydrocarbons, water gas shift reaction, dehydrogenation of energy carriers, and iodine–sulfur thermochemical cycle are also discussed.

In **Chapter 7** (Ren and Li), the structure, preparation, characterization, and application of microporous zeolite membrane is presented and discussed. These membranes have great potential in many applications. In this chapter, the structures of zeolite and zeolite membrane are first introduced and summarized. It is shown that in-situ synthesis and secondary growth are the most commonly used methods for the preparation of zeolite membranes, and also that zeolite crystals can grow in hydrothermal or dry gel conditions by oven- or microwave-assisted heating. Moreover, the synthesis of orient and ultrathin zeolite layers, which is an ideal morphology to obtain high performance, is discussed in detail. It is also stressed that the topology, morphology, pore structures, and defects are characterized by many instruments and analyzed to better understand and control the membrane's quality. Finally, applications of zeolite membranes in separation or catalysis are also reviewed.

Chapter 8 (Vaezi, Kojabad, Beiragh, and Babaluo) concerns the transport mechanism and modeling of microporous zeolite membranes. In the development and design of equipment involving microporous zeolite membranes, the proper description of diffusion and transport mechanisms are of vital importance. However, in the opinion of the authors, this subject still needs more clarification. For these reasons, this chapter addresses the diffusion mechanisms of gases through zeolite membranes such as molecular sieving, surface diffusion, and configurational diffusion along with activated transport, which can occur as a facilitator of gas permeation in the case of each of these mechanisms. Also, the effect of temperature as an affecting parameter on the permeance of gases is shown. Subsequently, modeling of various

diffusion mechanisms in microporous zeolite membranes is performed using the Maxwell-Stefan approach. For this, Fickian coefficient introduced for the mentioned mechanisms was converted to Maxwell-Stefan coefficient using the so-called Darken equation. Then, analytical solutions for this model in both cases of weak and strong confinement are presented.

In [Chapter 9](#) (Ghorbani and Bayati), the microporous zeolite membranes are presented in terms of reactors. Zeolite membrane reactors include a combination of membrane separation and reactor (chemical reaction). These membrane reactors improve selectivity and yield of reactions, which are limited by thermodynamic equilibrium. The membrane reactors are commonly used for the selective removal of hydrogen from a hydrogen-producing reaction and tend to shift the thermodynamic equilibrium toward conversion enhancement and product yield. The authors of this chapter studied the removal of hydrogen by CO selective oxidation (Selox) as well as the water-gas shift reaction for conversion of CO to H₂, and removal of volatile organic compounds by the zeolite catalyst membrane reactors. It is shown why these catalyst membrane reactors provide desirable conversion, selectivity, and yield in specific operating conditions.

[Chapter 10](#) (Bernardo) introduces the microporous polymeric membranes by discussing their structure, preparation, characterization, and applications. In recent years, microporous polymers were synthesized via molecular design and by chemical rearrangement induced by controlled thermal treatments. Membranes made from microporous polymers are capable of molecular separation and, thus, could address different purposes. These membranes have shown potential toward the selective transport of gases, pervaporation, organic solvent nanofiltration, and desalination. In particular, this chapter presents the current progress in the fabrication and transport properties of microporous polymeric membranes and new directions of applications.

The next work, [Chapter 11](#) (Rafiee, Seyedhoseinie, and Ghasemzadeh), deals with both the transport mechanism and modeling of microporous polymeric membranes. Some of the most commonly used microporous polymeric membranes are first explained. These membranes having excellent selectivity and high permeability are crucial to efficient membrane gas separation and adsorption. Generally, membrane performance is directly linked to controlled pore formation. The origin of the activation of gas transport in micropores is analyzed by the evolution of the adsorption potentials of a gas molecule in pores with decreasing pore diameter. Also, various simulation methods (computational fluid dynamics, molecular dynamics, and Monte Carlo) have been studied to estimate solubility properties of these membranes. The results indicate that a low solubility environment will also not lead to steady state and will promote a transient process based on tortuosity. Alternative solutions for increasing the topological difficulty of the landscape for diffusion include the use of polymers characterized by high glass temperatures, cross-linked polymers, or copolymers. However, the model parameters are not directly related to the polymer structure.

In [Chapter 12](#) (Vital), the microporous polymers, a new class of organic polymeric materials with pore sizes below 2 nm and consequently high surface areas, are seen in terms of membrane reactors. This chapter provides a brief overview of microporous polymers, with particular attention paid to the materials suitable for membrane preparation and those with catalytic properties. The possibility of using microporous polymer membranes in membrane reactors, such as forced-flow reactors and pervaporation units, is also discussed.

In [Chapter 13](#) (Ghasemzadeh, Zeynali and Basile), a comparison of traditional chemical separation processes with membrane separation shows it is much simpler and more efficient. An ideal membrane for molecular separation should be as thin as possible to maximize its solvent flux, mechanically robust to prevent it from fracture, and have well-defined pore sizes to guarantee its selectivity. Among others, graphene is an excellent platform for developing size-selective membranes because of its atomic thickness, high mechanical strength, and chemical inertness. In this chapter, the recent advancements on the fabrication of nanoporous graphene membranes and graphene oxide membranes for molecular separation are reviewed. In particular, the methods of fabricating these membranes are summarized, and the mechanisms of molecular separation based on these two types of graphene membranes are compared. The challenges of synthesizing nanoporous graphene membranes and engineering the performances of graphene oxide membranes are discussed as well.

In [Chapter 14](#) (Ghasemzadeh, Nouri, Zeynali, and Basile), the transport mechanism and modeling of microporous graphene membranes are considered and discussed. Presently, in our day-to-day separation process, there are many observations to better understand the relationship between the flows of any species; it may be heat, matter, or charge and a particular force driving that flow. Therefore, mass flows from the higher concentration to the lower concentration, the concentration difference being the driving force. In this case, membrane-based separation technology has attracted great interest in many separation fields due to its advantages of easy operation, energy efficiency, easy scale-up, and environmental friendliness. The development of novel membrane materials and membrane structures is in urgent demand to promote membrane-based separation technology. Graphene-based membranes, as an emerging nano-building membrane, has showed great potential in the membrane-based separation field. In recent years, various types of graphene membranes have indicted high potentials for both aspects of gas and liquid separations. Therefore, in the state of art of this chapter, after discussing progresses in graphene-based membranes, the performance of various graphene membranes is introduced, followed by evaluation of transport mechanisms of various graphene membranes in separation processes. Consequently, application of graphene membranes is also studied from modeling point of views.

In [Chapter 15](#) (Tilebon, Ghasemzadeh, and Basile), microporous graphene membranes are seen in their role as membrane reactors. Graphene-based membranes have several uncommon properties such as structural strength that can improve its separation performance. As one of the

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most promising approaches in chemical process intensification, membrane reactor technology has attracted great attention in the last few years, and this subject is still currently undergoing rapid development and innovation. Nevertheless, few studies are focused on the evaluation of graphene-based membrane reactor performances, which implies a lot of challenges in applications. For these reasons, this chapter addresses research and development of graphene-based membrane reactor applications. Indeed, after discussing about progress in membrane reactor technology, the performance of various graphene membranes is introduced, followed by the evaluation of employing graphene membranes for various chemical reactions from both aspects of modeling and experimental works.

We wish to take this occasion to deeply thank all the authors for their excellent work, especially in reviewing, sometimes many times, their chapters.

Also special thanks to the staff of Elsevier for their irreplaceable help.

Angelo Basile,
Kamran Ghasemzadeh

Contributors

Ali Akbar Babaluo Nanostructure Material Research Center (NMRC), Sahand University of Technology, Tabriz, Iran

Angelo Basile CNR-ITM (Institute on Membrane Technology of the Italian National Research Council), Rende, Italy

Behrouz Bayati Chemical Engineering Department, Ilam University, Ilam, Iran

Masoud Majidi Beiragh Nanostructure Material Research Center (NMRC), Sahand University of Technology, Tabriz, Iran

Paola Bernardo Institute on Membrane Technology, ITM-CNR, Rende, Italy

Adi Darmawan Department of Chemistry, Diponegoro University, Semarang, Indonesia

Muthia Elma Chemical Engineering Department, Lambung Mangkurat University, Banjarbaru, Indonesia

F. Gallucci Inorganic Membranes and Membrane Reactors (SIR), Sustainable Process Engineering (SPE), Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

K. Ghasemzadeh Faculty of Chemical Engineering, Urmia University of Technology, Urmia, Iran

Asma Ghorbani Chemical Engineering Department, Ilam University, Ilam, Iran

Ahmad Fauzi Ismail Advanced Membrane Technology Research Centre (AMTEC); School of Chemical and Energy Engineering Faculty of Engineering, Universiti Teknologi Malaysia, Johor Darul Takzim, Malaysia

Adolfo Iulianelli CNR-ITM (Institute on Membrane Technology of the Italian National Research Council), Rende, Italy

Masakoto Kanezashi Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, Japan

Mahdi Elyasi Kojabad Nanostructure Material Research Center (NMRC), Sahand University of Technology, Tabriz, Iran

Yanshuo Li School of Material Science and Chemical Engineering, Ningbo University, Ningbo, China

M.A. Llosa-Tanco Energy and Environment Division, Tecnalia Research & Innovation, Donostia-San Sebastian, Spain

J.A. Medrano Inorganic Membranes and Membrane Reactors (SIR), Sustainable Process Engineering (SPE), Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

Lie Meng School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ, United States

Contributors

- Julius Motuzas** The University of Queensland, FIM²Lab-Functional and Interfacial Materials and Membranes Laboratory, School of Chemical Engineering, Brisbane, QLD, Australia
- M. Nouri** CNR-ITM (Institute on Membrane Technology of the Italian National Research Council), Rende, Italy
- D.A. Pacheco-Tanaka** Energy and Environment Division, Tecnalia Research & Innovation, Donostia-San Sebastian, Spain
- R. Rafiee** Faculty of Chemical Engineering, Urmia University of Technology, Urmia, Iran
- Xiuxiu Ren** School of Petrochemical Engineering, Changzhou University, Changzhou, China
- Wan Norharyati Wan Salleh** Advanced Membrane Technology Research Centre (AMTEC); School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Darul Takzim, Malaysia
- Norazlianie Sazali** Advanced Membrane Technology Research Centre (AMTEC); School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Darul Takzim, Malaysia
- M. Seiiedhoseiny** Faculty of Chemical Engineering, Urmia University of Technology, Urmia, Iran
- S.M. Sadati Tilebon** Chemical Engineering Department, Iran University of Science & Technology, Tehran, Iran
- Toshinori Tsuru** Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, Japan
- Mohammad Javad Vaezi** Nanostructure Material Research Center (NMRC), Sahand University of Technology, Tabriz, Iran
- J. Vital** Faculty of Science and Technology, Universidade de Lisboa, LAQV-REQUIMTE, Caparica, Portugal
- David K. Wang** The University of Sydney, School of Chemical and Biomolecular Engineering, Sydney, NSW, Australia
- R. Zeynali** Faculty of Chemical Engineering, Urmia University of Technology, Urmia, Iran

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Radarweg 29, PO Box 211, 1000 AE Amsterdam, Netherlands
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States

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Library of Congress Cataloging-in-Publication Data

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

British Library Cataloguing-in-Publication Data

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

ISBN: 978-0-12-816350-4

For information on all Elsevier publications
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Publisher: Joe Hayton

Acquisition Editor: Kostas Marinakis

Editorial Project Manager: Vincent Gabrielle

Production Project Manager: Omer Mukthar

Cover Designer: Miles Hitchen

Typeset by SPi Global, India

