“The worldwide community of chemists and chemical engineers is grateful to the authors of these assembled articles and especially to Jianwen Jiang for his diligent service as editor of this timely volume.”

Prof. John Prausnitz
University of California, Berkeley, USA

“The importance of metal–organic frameworks has grown explosively in the past decade, and molecular modeling is playing an important role in this development. This timely book contains reviews by many of the leading modeling researchers in this field and will be essential reading for those interested in this important and rapidly growing field.”

Prof. Randall Q. Snurr
Northwestern University, USA

“In this comprehensive, information-packed edited volume, Jianwen Jiang brings together a collection of chapters on different aspects of modeling metal–organic frameworks. This volume is required reading for researchers interested in this novel class of materials for adsorption, gas separation, and catalysis.”

Prof. A. Z. Panagiotopoulos
Princeton University, USA

“This thirteen-chapter book introduces high-priority subjects on metal-organic frameworks such as their structure and adsorption, separation, and catalytic properties. The unique approach of this book is that these key subjects are overviewed from chemical engineering modeling approaches using various examples with less technical modeling languages. To enable better understanding, the fundamental concepts are well arranged in every chapter, and this book should be helpful to design new MOF families for a specific application on a solid scientific basis.”

Prof. Katsumi Kaneko
Shinshu University, Japan

Metal–organic frameworks (MOFs) have emerged as a new family of nanoporous materials. With the enormous choices of inorganic/organic building blocks, MOFs possess a wide range of surface area, pore size, and functionality and, thus, have been considered versatile materials for many potential applications. This book presents a broad collection of recent modeling studies in the field of MOFs towards potential engineering applications, such as gas storage/separation, carbon capture, catalysis, water treatment, and drug delivery. The subject of this book renders it unique, for while the various topics on MOF’s vast literature, there is not yet a single coherent collection for modeling endeavors. The book will appeal to scientists, engineers, and students in the multidisciplinary intersections of materials science, chemistry, and engineering.

Jianwen Jiang

Metal–Organic Frameworks
Materials Modeling towards Potential Engineering Applications

edited by
Jianwen Jiang
Foreword

Thanks to the diligent work of Omar Yaghi and other creative synthetic chemists, it is now possible to synthesize a variety of metal–organic frameworks (MOFs) that show much promise for gas storage (e.g., methane and hydrogen) and for gas separations, especially those that separate climate-warming carbon dioxide from nitrogen as desired for stack gases from power plants prior to release to the atmosphere.

The possible number of different MOFs is very large. In a finite time, it is not feasible to synthesize even a small fraction of these possible structures. To guide experimentalists toward those structures that are likely to be most useful, theoretical or computational methods are needed. Fortunately, such methods have been under active development for some time. It is therefore now appropriate to assemble a set of articles that describe these methods to indicate their present and future utility.

The worldwide community of chemists and chemical engineers is grateful to the authors of these assembled articles and especially to Jianwen Jiang for his diligent service as editor of this timely volume.

John Prausnitz
University of California, Berkeley, USA
Preface

Metal–organic frameworks (MOFs), also called porous coordination polymers or porous coordination networks, have emerged as a special class of nanoporous materials. Constituted by the enormous choices of metal clusters and organic linkers, MOFs possess a wide range of surface area, pore volume, and functionality; thus they have been considered versatile materials for storage, separation, catalysis, etc. Over the past decade, thousands of MOFs have been synthesized, characterized and tested. The number of MOFs is constantly growing and in principle unlimited. It is, therefore, practically infeasible to experimentally test and select appropriate MOFs from infinite candidates for applications.

With rapidly evolving computational resources, atomistic/molecular modeling has become an indispensable tool in materials science and engineering. Sophisticated modeling at a microscopic level provides wealthy insights that are otherwise experimentally inaccessible and elucidates underlying physics from the bottom up. Furthermore, modeling can secure the fundamental interpretation of experimental observations and guide the rational selection and design of materials.

This book compiles a broad collection of recent modeling studies in the field of MOFs toward potential engineering applications. It contains 13 chapters and is categorized into 5 different topics:

- In Chapter 1, Caroline Mellot-Draznieks, Ben Slater, and Raimondas Galvelis give an overview of computational approaches for the crystal structure prediction of MOFs. They highlight the simulation-informed principles to design and characterize new MOFs and more systematically understand structure–property relationships.
• Adsorption phenomenon and associated properties of MOFs are summarized in Chapters 2–4. While David Dubbeldam and Krista S. Walton discuss the classical molecular simulations, Michael Fischer and Michael Fröba, as well as Lukáš Grajciar, Miroslav Rubeš, Ota Bludský, and Petr Nachtigall, review theoretical approaches, particularly density functional theory, to describe adsorption on coordinatively unsaturated metal sites in MOFs.

• Chapters 5 and 6 are devoted to both adsorption and diffusion in MOFs. George K. Papadopoulos presents statistical mechanics–based modeling for sorbate equilibria and transport in MOFs. On the other hand, Giovanni Garberoglio highlights the importance of quantum effects to accurately describe hydrogen behavior in MOFs.

• Numerous modeling studies of MOFs are focused on separation, as summarized in a series of chapters. In Chapter 7, Qingyuan Yang, Dahuan Liu, and Chongli Zhong review both adsorption- and membrane-based separation processes for CO\(_2\)-related systems, olefin/paraffin mixtures, and other gas mixtures. Sedá Keskin discusses, in Chapter 8, adsorption-based separation for typical CO\(_2\)-containing gas mixtures in MOFs and membrane-based CO\(_2\) separation in MOFs and mixed-matrix membranes. In Chapter 9, Carlos Nieto-Draghi and Javier Pérez-Pellitero survey the modeling of gas separation in zeolitic imidazolate frameworks. Alternatively, Alexandre F. P. Ferreira, Ana M. Ribeiro, João C. Santos, Marta C. Campo, and Alírio E. Rodrigues demonstrate the modeling of cyclic adsorptive separation in Chapter 10, with emphasis on pilot-scale modeling and process simulation. In Chapter 11, Anjaih Nalaparaju and Jianwen Jiang review the simulation studies of ionic MOFs for gas adsorption and separation, water treatment, biofuel purification, and drug loading.

• Modeling studies of catalysis in MOF-based compounds are documented in Chapters 12 and 13. Qiuju Zhang and Liang Chen, as well as Remedios Cortese and Dario Duca, discuss the catalytic properties of MOFs and several typical chemical reactions catalyzed by MOFs.
From this book, one can clearly witness the increasingly important role of computational modeling in the characterization, screening, and design of MOFs for potential engineering applications. Microscopic insights from the bottom up are imperative to quantitatively unravel fundamental mechanisms, cohesively complement experiments, and effectively facilitate new development in this burgeoning field.

I wish to express my gratitude to the outstanding authors for their invaluable contribution to this book and the editorial team of Pan Stanford Publishing for its technical support.

Jianwen Jiang
Singapore
Contents

Foreword xi
Preface xv

1 Computational Approaches to the Design, Crystal Structure Prediction, and Structure–Property Relationships of Metal–Organic Frameworks 1
Caroline Mellot-Draznieks, Ben Slater, and Raimondas Galvelis

1.1 Introduction 1

1.2 Crystal Structure Prediction 3
  1.2.1 Introduction 3
  1.2.2 The AASBU Method 4
  1.2.3 Large-Scale Enumerative Methods 6

1.3 Using Structure Prediction to Solve the Structures of MOFs 8
  1.3.1 The Decoration Strategy 9
  1.3.2 Ligand Replacement Strategy in Flexible MOFs 11

1.4 Computational Screening of Hypothetical MOFs through Ligand Functionalization 14

1.5 Inventing New Solids: Computational Design of Polyoxometalate Organic Frameworks 18
  1.5.1 Current Context 18
  1.5.2 Computational Design and Evaluation of Hypothetical POMOFs 19
  1.5.3 Thermodynamic Control and Template Effect? 24

1.6 Exploring the Energy Landscapes of MOFs 26
  1.6.1 Importance of Dispersive Forces in MOFs 26
  1.6.2 Energy Landscape of Zeolitic Imidazolate Frameworks 26
  1.6.3 Understanding the Energy Landscape of Nonchiral and Chiral MOFs 30
Contents

1.7 Exploring Physical Properties of MOFs 32
   1.7.1 Estimation of Band Gaps 32
   1.7.2 Mechanical Properties 37
1.8 Modelling Defects in MOFs 40
1.9 Concluding Remarks 41

2 On the Application of Classical Molecular Simulations of Adsorption in Metal–Organic Frameworks 53
   David Dubbeldam and Krista S. Walton
   2.1 Introduction 53
   2.2 Geometric Properties 56
      2.2.1 Visualization of the Topology 56
      2.2.2 Studying Adsorption Sites 58
      2.2.3 Void Fraction 60
      2.2.4 Surface Areas 62
      2.2.5 Pore Size Distributions 66
   2.3 Single-Component Adsorption 69
      2.3.1 Adsorption 69
      2.3.2 Isotherm Shapes 70
      2.3.3 Maximum Loading 74
      2.3.4 Clustering of Molecules 75
      2.3.5 Excess vs. Absolute Adsorption 78
      2.3.6 Taking Flexibility into Account or Not? 81
      2.3.7 Polarization 83
   2.4 Mixture Adsorption Isotherms 85
      2.4.1 Experimental Measurements of Mixture Adsorption 85
      2.4.2 Ideal Adsorption Solution Theory 86
      2.4.3 Breakthrough Curves 89
   2.5 Screening 95
      2.5.1 Case Study: Hexane Isomers 95
      2.5.2 Screening Strategies 99

3 Modeling the Adsorption of Small Molecules at Coordinatively Unsaturated Metal Sites: Density Functional Theory and Molecular Mechanics Approaches 113
   Michael Fischer and Michael Fröba
   3.1 Introduction 114
3.2 A Short Review of Experimental Methods 119
3.3 Electronic Structure Methods 121
  3.3.1 Hydrogen 122
  3.3.2 Methane 129
  3.3.3 Carbon Dioxide 130
  3.3.4 Other Small Molecules 134
3.4 Molecular Mechanics Methods 136
  3.4.1 Hydrogen 137
  3.4.2 Methane 140
  3.4.3 Carbon Dioxide 143
  3.4.4 Other Small Molecules 146
3.5 Bridging the Gap: Toward an Improved Modeling of Metal–Adsorbate Interactions 149
3.6 Conclusions 157

4 Accurate ab initio Description of Adsorption on Coordinatively Unsaturated Sites in Metal–Organic Frameworks 175
  Lukáš Grajičar, Miroslav Rubeš, Ota Bludský, and Petr Nachtigall
4.1 Introduction 176
4.2 Methods and Models 177
  4.2.1 Cluster and Periodic Models of Cu-BTC 177
  4.2.2 Methods 178
    4.2.2.1 Density functional theory 178
    4.2.2.2 Post-Hartree-Fock methods 180
    4.2.2.3 DFT/CC method 181
4.3 Electronic Structure of Coordinatively Unsaturated Sites in Cu-BTC 182
  4.3.1 Spin Coupling in Cu-BTC 182
  4.3.2 Evaluation of Method Accuracy: The Cu(COOH)_2 Model 185
  4.3.3 Paddlewheel Model 188
4.4 Adsorption in Cu-BTC: Electrostatic vs. Dispersion Interactions 191
  4.4.1 H_2O 191
  4.4.2 CO 192
  4.4.3 CO_2 193
4.4.4 CH₄
4.4.5 C₃H₈ and C₃H₆
4.5 Summary

5 Modeling Sorbate Equilibria and Transport in Porous Coordination Polymers
George K. Papadopoulos
5.1 Introduction
5.2 Sorbent Digitization
  5.2.1 Atomistic Reconstruction
5.3 Basics of Sorbate Equilibria and Transport
  5.3.1 Sorption Thermodynamics
    5.3.1.1 Rigid sorbent model
    5.3.1.2 Flexible sorbent model
  5.3.2 Molecular Dynamics
5.4 Conclusions

6 Modeling Quantum Effects on Adsorption and Diffusion of Hydrogen in Metal–Organic Frameworks
Giovanni Garberoglio
6.1 The Hydrogen Molecule and Its Isotopologues
  6.1.1 Models for the Hydrogen Molecule
6.2 Computer Simulations of Quantum Statistical Mechanics
  6.2.1 Diagonalization of the Hamiltonian
  6.2.2 The Path-Integral Approach
  6.2.3 Probability Distribution for the Ring-Polymer Configurations
  6.2.4 Using the Path-Integral Method: Radial Distribution Functions of Adsorbed Hydrogen
  6.2.5 Monte Carlo Sampling of the Path-Integral Expressions
  6.2.6 Approximating the Path Integral: Centroid and Semiclassical Approaches
  6.2.7 Path-Integral Approach to Rotational Degrees of Freedom
6.3 Modeling Adsorption of Quantized Molecules
6.3.1 Quantum Effects on Hydrogen Adsorption in Metal–Organic Frameworks 280
6.3.2 Isotopic Effects on Adsorption and Quantum Sieving 282
6.4 Modeling the Dynamics of Quantized Molecules 285
6.4.1 Reverse Kinetic Isotope Effect in Diffusion 287

7 Molecular Modeling of Gas Separation in Metal–Organic Frameworks 295
Qingyuan Yang, Dahuan Liu, and Chongli Zhong
7.1 Introduction 295
7.2 Development of Research Methods 297
7.2.1 Charge Calculations 297
7.2.2 Evaluation of Electrostatic Characteristic of MOFs 299
7.2.3 Methodology for Large-Scale Screening of MOFs 301
7.3 Adsorption-Based Separation 302
7.3.1 CO2-Related Systems 303
7.3.2 Gas Mixtures of Olefin and Paraffin 308
7.3.3 Other Gas Mixtures 311
7.4 Membrane-Based Separation 311
7.4.1 CO2 Related Systems 312
7.4.2 Gas Mixtures of Olefin and Paraffin 317
7.4.3 Other Gas Mixtures 318
7.5 Strategy for Separation Enhancement 319
7.5.1 Tailoring Pore Size and Shape 319
7.5.2 Catenation 320
7.5.3 Chemical Modification 321
7.6 Summary and Suggestions 323

8 Molecular Modeling of Metal–Organic Frameworks for Carbon Dioxide Separation Applications 339
Seda Keskin
8.1 Introduction 341
8.2 Molecular Modeling Methods 342
8.2.1 Monte Carlo Simulations 342
8.2.2 Molecular Dynamics Simulations 343
8.2.3 Force Fields for CO₂ and MOFs 344
8.2.4 Modeling of MOFs 345
8.3 Adsorption-Based Carbon Dioxide Separation 348
  8.3.1 CO₂/CH₄ Separations 348
  8.3.2 CO₂/N₂ Separations 351
  8.3.3 CO₂/H₂ Separations 354
  8.3.4 CO₂/CO Separations 357
  8.3.5 Other CO₂ Separations 358
  8.3.6 Comparing MOFs with Other Nanoporous Materials for CO₂ Separations 359
8.4 MOFs for Membrane-Based Carbon Dioxide Separation 360
8.5 Diffusion of Carbon Dioxide in MOFs 365
8.6 Summary and Outlook 366

9 Modeling of Zeolitic-Like Hybrid Materials for Gas Separation 381
  Carlos Nieto-Draghi and Javier Pérez-Pellitero
  9.1 Introduction 382
  9.2 Development of Force Fields for ZIFs 384
    9.2.1 Standard Force Fields 384
    9.2.2 Dedicated Rigid Force Fields for ZIFs 385
    9.2.3 Dedicated Flexible Force Fields for ZIFs 388
  9.3 Molecular Modeling of Adsorption in ZIFs 390
    9.3.1 Basic Concepts of Adsorption 391
    9.3.2 General Behavior of Adsorption in ZIFs 392
      9.3.2.1 Metal sites and ligand adsorption 392
      9.3.2.2 Importance of electrostatics in adsorption 393
    9.3.3 Adsorption of Alkanes in ZIFs 394
    9.3.4 CO₂ Adsorption in ZIFs 397
    9.3.5 Impact of Functionality on Adsorption 399
  9.4 Membrane Separation in ZIFs 401
    9.4.1 Basic Concepts of Diffusion and Permeation 401
    9.4.2 Diffusion Behavior of CO₂ and Other Gases in ZIFs 402
  9.5 New Perspectives on Modeling and Applications 406
    9.5.1 Correlative Models and in silico Screening 406
## Contents

9.5.2 Prediction of New Solid Structures 408
9.6 Conclusions 409

10 Modeling Adsorptive Separations Using Metal–Organic Frameworks 419
Alexandre F. P. Ferreira, Ana M. Ribeiro, João C. Santos, Marta C. Campo, and Alírio E. Rodrigues
10.1 Introduction 420
10.2 Adsorptive Gas-Phase Separation Processes 424
10.2.1 Propylene/Propane Separation by PSA 425
10.3 Future Challenges 438
10.4 Summary 440

11 Computer Simulations of Ionic Metal–Organic Frameworks 451
Anjaiah Nalaparaju and Jianwen Jiang
11.1 Introduction 452
11.2 Simulation Studies 454
11.2.1 Locations of Nonframework Ions 454
11.2.2 Gas Adsorption and Separation 458
11.2.2.1 Adsorption of pure gases 459
11.2.2.2 Separation of CO₂-containing mixtures 463
11.2.3 Water Treatment 468
11.2.4 Biofuel Purification 471
11.2.5 Drug Loading 473
11.3 Summary 474

12 Computational Modeling of Catalysis in Metal–Organic Frameworks 483
Qiuju Zhang and Liang Chen
12.1 Introduction 483
12.2 Experimentally Generating Active Sites in MOF-Based Catalysts 485
12.2.1 Intrinsic Active Sites on the Framework 485
12.2.2 MOF-Encapsulated Active Species 486
12.2.3 Incorporating Active Sites 488
12.2.4 Active Sites Attached through Postsynthetic Modification 489
12.3 Computational Modeling of MOF-Based Catalysts

12.3.1 Catalyzed Reaction by Open Metal Nodes

12.3.2 Knoevenagel Condensation by Framework Aniline-Like Groups

12.3.3 Incorporating W Ions into Cu-BTC to Activate CO₂

12.3.4 Encapsulation of Active Sites

12.4 Applications and Outlook

13 Modeled Catalytic Properties of MOF-Based Compounds

Remedios Cortese and Dario Duca

13.1 Introduction

13.2 Microporous Materials and Modeling

13.3 Heterogeneous Catalysis: Methods and Models

13.4 Adsorption Models

13.5 Modeling Catalysis within MOFs

13.5.1 Formaldehyde Catalytic Addition to Propylene on MOF-11

13.5.2 Cyclo-[(S)-Phenylalanyl-(S)-Histidyl] Benzaldehyde-Complex Synthesis on MOFs

13.5.3 Knoevenagel Condensation between Benzaldehyde and Ethyl Cyanoacetate inside IRMOF-3

13.5.4 Electronic Effects of 5,5’-Substituents on the Enantioselectivity of (Salen)Mn Catalysts

13.5.5 Steric Effects on Enantioselective Epoxidation Catalyzed by (Salen)Mn in MOFs

13.5.6 Effects of Lewis Acidity in Citronellal Cyclization Catalyzed by UiO-66

13.5.7 Epoxidation of Cyclohexene Catalyzed by Coordinatively Saturated Vanadium MIL-47

13.5.8 Hydroperoxide Decomposition over Cu and Co Cations Embodied in MOFs

Index