

# Contents

## Preface *xiii*

<b>1</b>	<b>The Stability of Metal–Organic Frameworks</b>	<b>1</b>
	<i>Georges Mouchaham, Sujing Wang, and Christian Serre</i>	
1.1	Introduction	1
1.2	Chemical Stability	2
1.2.1	Strengthening the Coordination Bond	4
1.2.1.1	High-Valence Cations and Carboxylate-Based Ligands	4
1.2.1.2	Low-Valence Cations and Highly Complexing Ligands	9
1.2.1.3	High-Valence Cations and Highly Complexing Ligands	11
1.2.2	Protecting the Coordination Bond	12
1.2.2.1	Introducing Bulky and/or Hydrophobic Groups	12
1.2.2.2	Coating MOFs with Hydrophobic Matrices	13
1.3	Thermal Stability	14
1.4	Mechanical Stability	17
1.5	Concluding Remarks	19
	Acknowledgments	20
	References	20
<b>2</b>	<b>Tuning the Properties of Metal–Organic Frameworks by Post-synthetic Modification</b>	<b>29</b>
	<i>Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat</i>	
2.1	Introduction	29
2.2	Post-synthetic Modification Reactions	30
2.2.1	Covalent Post-synthetic Modification	31
2.2.2	Inorganic Post-synthetic Modification	32
2.2.3	Extent of the Reaction	33
2.3	PSM for Enhanced Gas Adsorption and Separation	34
2.3.1	PSM for Carbon Dioxide Capture and Separation	34
2.3.2	PSM for Hydrogen Storage	35
2.4	PSM for Catalysis	37
2.4.1	Catalysis with MOFs Possessing Metal Active Sites	37
2.4.2	Catalysis with MOFs containing Reactive Organic Functional Groups	39
2.4.3	Catalysis with MOFs as Host Matrices	41

2.5	PSM for Sequestration and Solution Phase Separations	42
2.5.1	Metal Ion Sequestration	42
2.5.2	Anion Sequestration	43
2.5.3	Removal of Organic Molecules from Solution	43
2.6	PSM for Biomedical Applications	44
2.6.1	Therapeutic MOFs and Biosensors	44
2.6.2	PSM by Change of Physical Properties	46
2.7	Post-synthetic Cross-Linking of Ligands in MOF Materials	46
2.7.1	Pre-synthetically Cross-Linked Ligands	47
2.7.2	Post-synthetic Cross-Linking of MOF Linkers	47
2.7.3	Post-synthetically Modifying the Nature of Cross-Linked MOFs	49
2.8	Conclusions	51
	References	51
<b>3</b>	<b>Synthesis of MOFs at the Industrial Scale</b>	<b>57</b>
	<i>Ana D. G. Firmino, Ricardo F. Mendes, João P.C. Tomé, and Filipe A. Almeida Paz</i>	
3.1	Introduction	57
3.2	MOF Patents from Academia versus the Industrial Approach	58
3.3	Industrial Approach to MOF Scale-up	64
3.4	Examples of Scaled-up MOFs	66
3.5	Industrial Synthetic Routes toward MOFs	69
3.5.1	Electrochemical Synthesis	69
3.5.2	Continuous Flow	70
3.5.3	Mechanochemistry and Extrusion	72
3.6	Concluding Remarks	74
	Acknowledgments	75
	List of Abbreviations	75
	References	76
<b>4</b>	<b>From Layered MOFs to Structuring at the Meso-/Macroscopic Scale</b>	<b>81</b>
	<i>David Rodríguez-San-Miguel, Pilar Amo-Ochoa, and Félix Zamora</i>	
4.1	Introduction	81
4.2	Designing Bidimensional Networks	82
4.3	Methodological Notes Regarding Characterization of 2D Materials	84
4.3.1	Morphological and Structural Characterization	84
4.3.2	Spectroscopic and Diffractometric Characterization	88
4.4	Preparation and Characterization	92
4.4.1	Bottom-Up Approaches	92
4.4.1.1	On-Surface Synthesis	92
4.4.1.2	Synthesis at Water/Air or Solvent-to-Solvent Interface	92
4.4.1.3	Synthesis at the Liquid–Liquid Interface	100
4.4.2	Miscellaneous	104
4.4.2.1	Direct Colloidal Formation	104
4.4.2.2	Surfactant Mediated	104
4.4.3	Top-Down Approaches	105
4.4.3.1	Liquid Phase Exfoliation (LPE)	106

4.4.3.2	Micromechanical Exfoliation	110
4.5	Properties and Potential Applications	111
4.5.1	Gas Separation	111
4.5.2	Electronic Devices	112
4.5.3	Catalysis	113
4.6	Conclusions and Perspectives	115
	Acknowledgments	116
	References	116

## 5 Application of Metal–Organic Frameworks (MOFs) for CO<sub>2</sub> Separation 123

*Mohammed Mohamedali, Hussameldin Ibrahim, and Amr Henni*

5.1	Introduction	123
5.2	Factors Influencing the Applicability of MOFs for CO <sub>2</sub> Capture	124
5.2.1	Open Metal Sites	125
5.2.2	Amine Grafting on MOFs	132
5.2.3	Effects of Organic Ligand	138
5.3	Current Trends in CO <sub>2</sub> Separation Using MOFs	139
5.3.1	Ionic Liquids/MOF Composites	139
5.3.2	MOF Composites for CO <sub>2</sub> Separation	143
5.3.3	Water Stability of MOFs	144
5.3.3.1	Effect of Water on MOFs with Open Metal Sites	146
5.3.3.2	Effects of the Organic Ligand on Water Stability of MOFs	147
5.4	Conclusion and Perspective	150
	References	151

## 6 Current Status of Porous Metal–Organic Frameworks for Methane Storage 163

*Yabing He, Wei Zhou, and Banglin Chen*

6.1	Introduction	163
6.2	Requirements for MOFs as ANG Adsorbents	165
6.3	Brief History of MOF Materials for Methane Storage	167
6.4	The Factors Influencing Methane Adsorption	168
6.4.1	Surface Area	169
6.4.2	Pore Size	170
6.4.3	Adsorption Heat	170
6.4.4	Open Metal Sites	170
6.4.5	Ligand Functionalization	171
6.5	Several Classes of MOFs for Methane Storage	171
6.5.1	Dicopper Paddlewheel-Based MOFs	171
6.5.2	Zn <sub>4</sub> O-Cluster Based MOFs	180
6.5.3	Zr-Based MOFs	182
6.5.4	Al-Based MOFs	186
6.5.5	MAF Series	189
6.5.6	Flexible MOFs for Methane Storage	190
6.6	Conclusion and Outlook	192
	References	195

<b>7</b>	<b>MOFs for the Capture and Degradation of Chemical Warfare Agents</b>	<b>199</b>
	<i>Elisa Barea, Carmen R. Maldonado and Jorge A. R. Navarro</i>	
7.1	Introduction to Chemical Warfare Agents (CWAs)	199
7.2	Adsorption of CWAs	201
7.3	Catalytic Degradation of CWAs	206
7.3.1	Hydrolysis of Nerve Agents and Their Simulants	206
7.3.2	Oxidation of Sulfur Mustard and Its Analogues	211
7.3.3	Multiactive Catalysts for CWA Degradation	212
7.4	MOF Advanced Materials for Protection against CWAs	214
7.5	Summary and Future Prospects	218
	References	219
<b>8</b>	<b>Membranes Based on MOFs</b>	<b>223</b>
	<i>Pasquale F. Zito, Adele Brunetti, Alessio Caravella, Enrico Drioli and Giuseppe Barbieri</i>	
8.1	Introduction	223
8.2	Characteristics of MOFs	224
8.3	MOF-Based Membranes for Gas Separation	225
8.3.1	MOF in Mixed Matrix Membranes	226
8.3.1.1	MOF-based MMMs: Experimental Results	228
8.3.2	MOF Thin-Film Membranes	232
8.3.2.1	Stability of Thin-Film MOF Membranes	242
8.3.3	Modeling the Permeation through MOF-based MMMs	244
	Acknowledgments	246
	References	246
<b>9</b>	<b>Composites of Metal–Organic Frameworks (MOFs): Synthesis and Applications in Separation and Catalysis</b>	<b>251</b>
	<i>Devjyoti Nath, Mohanned Mohamedali, Amr Henni and Hussameldin Ibrahim</i>	
9.1	Introduction	251
9.2	Synthesis of MOF Composites	252
9.2.1	MOF–Carbon Composites	252
9.2.1.1	MOF–CNT Composites	252
9.2.1.2	MOF–AC Composites	255
9.2.1.3	MOF–GO Composites	255
9.2.2	MOF Thin Films	256
9.2.3	MOF–Metal Nanoparticle Composites	262
9.2.3.1	Solution Infiltration Method	263
9.2.3.2	Gas Infiltration Method	266
9.2.3.3	Solid Grinding Method	266
9.2.3.4	Template-Assisted Synthesis Method	266
9.2.4	MOF–Metal Oxide Composites	266
9.2.5	MOF–Silica Composites	272
9.3	Applications of MOF Composites in Catalysis and Separation	274
9.3.1	MOF Composites for Catalytic Application	274

9.3.2	MOF Composites for Gas Adsorption and Storage Applications	276
9.3.3	MOF Composites for Liquid Separation Applications	285
9.4	Conclusions	286
	References	286
<b>10</b>	<b>Tuning of Metal–Organic Frameworks by Pre- and Post-synthetic Functionalization for Catalysis and Separations</b>	<b>297</b>
	<i>Christopher F. Cogswell, Zelong Xie, and Sunho Choi</i>	
10.1	Introduction	297
10.1.1	Terminology for Functionalization on MOFs	297
10.1.2	General Design Parameters for Separations and Catalysis	299
10.2	Pre-synthetic Functionalization	303
10.2.1	Explanation of this Technique	303
10.2.2	Separations Applications	304
10.2.3	Catalytic Applications	307
10.3	Type 1 or Physical Impregnation	309
10.3.1	Explanation of this Technique	309
10.3.2	Separations Applications	310
10.3.3	Catalytic Applications	312
10.4	Type 2 or Covalent Attachment	313
10.4.1	Explanation of this Technique	313
10.4.2	Separations Applications	314
10.4.3	Catalytic Applications	316
10.5	Type 3 or <i>In Situ</i> Reaction	318
10.5.1	Explanation of this Technique	318
10.5.2	Separations Applications	319
10.5.3	Catalytic Applications	321
10.6	Type 4 or Ligand Replacement	321
10.7	Type 5 or Metal Addition	322
10.7.1	Explanation of this Technique	322
10.7.2	Separations Applications	325
10.7.3	Catalytic Applications	325
10.8	Conclusions	326
	References	327
<b>11</b>	<b>Role of Defects in Catalysis</b>	<b>341</b>
	<i>Zhenlan Fang and Qiang Ju</i>	
11.1	Introduction	341
11.2	Definition of MOF Defect	342
11.3	Classification of MOF Defects	343
11.3.1	Defects Classified by Defect Dimensions	343
11.3.2	Defects Classified by Distribution, Size, and State	343
11.3.3	Defects Classified by Location	343
11.4	Formation of MOF Defects	343
11.4.1	Inherent Defects of MOFs	343
11.4.1.1	Inherent Surface Defect	344
11.4.1.2	Inherent Internal Defect	344

11.4.1.3	Post-crystallization Cleavage	345
11.4.2	Intentionally Implanted Defects via Defect Engineering	346
11.4.2.1	Defects Introduced during <i>De Novo</i> Synthesis	347
11.4.2.2	Defects Formed by Post-synthetic Treatment	351
11.5	Characterization of Defects	352
11.5.1	Experimental Methods for Analyzing Defects	352
11.5.1.1	Assessing Presence of Defects	352
11.5.1.2	Imaging Defects	355
11.5.1.3	Probing Chemical and Physical Environment of Defects	357
11.5.1.4	Distinguish between Isolated Local and Correlated Defects	358
11.5.2	Theoretical Methods	359
11.6	The Role of Defect in Catalysis	363
11.6.1	External Surface Linker Vacancy	363
11.6.2	Inherent Linker Vacancy of Framework Interior	366
11.6.3	Intentionally Implanted Defects	367
11.6.3.1	Implanted Linker Vacancy by TML Strategy	367
11.6.3.2	Implanted Linker Vacancy by LML Strategy	368
11.6.3.3	Implanted Linker Vacancy by Post-synthetic Treatment	369
11.6.3.4	Implanted Linker Vacancy by Fast Precipitation	370
11.6.3.5	Implanted Linker Vacancy by MOF Partial Decomposition	370
11.7	Conclusions and Perspectives	372
	Acknowledgment	372
	References	372
<b>12</b>	<b>MOFs as Heterogeneous Catalysts in Liquid Phase Reactions</b>	<b>379</b>
	<i>Maksym Opanasenko, Petr Nachtigall, and Jiří Čejka</i>	
12.1	Introduction	379
12.2	Synthesis of Different Classes of Organic Compounds over MOFs	380
12.2.1	Alcohols	380
12.2.2	Carbonyl and Hydroxy Carbonyl Compounds	383
12.2.3	Carboxylic Acid Derivatives	385
12.2.4	Acetals and Ethers	389
12.2.5	Terpenoids	390
12.3	Specific Aspects of Catalysis by MOFs	392
12.3.1	Concept of Concerted Effect of MOF's Active Sites: Friedländer Reaction	392
12.3.2	Dynamically Formed Defects as Active Sites: Knoevenagel Condensation	394
12.4	Concluding Remarks and Future Prospects	395
	References	396
<b>13</b>	<b>Encapsulated Metallic Nanoparticles in Metal–Organic Frameworks: Toward Their Use in Catalysis</b>	<b>399</b>
	<i>Karen Leus, Himanshu Sekhar Jena, and Pascal Van Der Voort</i>	
13.1	Introduction	399
13.1.1	Impregnation Methods	400

13.1.1.1	Liquid Phase Impregnation	400
13.1.1.2	Solid Phase Impregnation	401
13.1.1.3	Gas Phase Impregnation	401
13.1.2	Assembly Methods	402
13.2	Nanoparticles in MOFs for Gas and Liquid Phase Oxidation Catalysis	405
13.3	Nanoparticles in MOFs in Hydrogenation Reactions	411
13.4	Nanoparticles in MOFs in Dehydrogenation Reactions	424
13.5	Nanoparticles in MOFs in C–C Cross-Coupling Reactions	430
13.6	The Use of Nanoparticles in MOFs in Tandem Reactions	433
13.7	Conclusions and Outlook	437
	References	438
<b>14</b>	<b>MOFs as Supports of Enzymes in Biocatalysis</b>	<b>447</b>
	<i>Sérgio M. F. Vilela and Patricia Horcajada</i>	
14.1	Introduction	447
14.2	MOFs as Biomimetic Catalysts	449
14.3	Enzyme Immobilization Strategies	454
14.3.1	Surface Immobilization	455
14.3.2	Diffusion into the MOF Porosity	456
14.3.3	<i>In Situ</i> Encapsulation/Entrapment	457
14.4	Biocatalytic Reactions Using Enzyme–MOFs	459
14.4.1	Esterification and Transesterification	463
14.4.2	Hydrolysis	464
14.4.3	Oxidation	466
14.4.4	Synthesis of Warfarin	468
14.4.5	Other Applications Based on the Catalytic Properties of Enzyme–MOFs	468
14.5	Conclusions and Perspectives	469
	Acknowledgments	470
	References	471
<b>15</b>	<b>MOFs as Photocatalysts</b>	<b>477</b>
	<i>Sergio Navalón and Hermenegildo García</i>	
15.1	Introduction	477
15.2	Properties of MOFs	482
15.3	Photophysical Pathways	483
15.4	Photocatalytic H <sub>2</sub> Evolution	490
15.5	Photocatalytic CO <sub>2</sub> Reduction	493
15.6	Photooxidation Reactions	494
15.7	Photocatalysis for Pollutant Degradation	496
15.8	Summary and Future Prospects	497
	Acknowledgements	498
	References	498