Contents

Preface *xiii*

1	The Stability of Metal–Organic Frameworks 1 Georges Mouchaham, Sujing Wang, and Christian Serre				
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				
2	Tuning the Properties of Metal–Organic Frameworks by Post-synthetic Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastian Pochat				
	Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat				
2.1	Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat Introduction 29				
2.1 2.2	Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat Introduction 29 Post-synthetic Modification Reactions 30				
2.1	Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat Introduction 29 Post-synthetic Modification Reactions 30 Covalent Post-synthetic Modification 31				
2.1 2.2 2.2.1 2.2.2	Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat Introduction 29 Post-synthetic Modification Reactions 30 Covalent Post-synthetic Modification 31				
2.1 2.2 2.2.1	Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat Introduction 29 Post-synthetic Modification Reactions 30 Covalent Post-synthetic Modification 31 Inorganic Post-synthetic Modification 32 Extent of the Reaction 33				
2.1 2.2 2.2.1 2.2.2 2.2.3	Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat Introduction 29 Post-synthetic Modification Reactions 30 Covalent Post-synthetic Modification 31 Inorganic Post-synthetic Modification 32 Extent of the Reaction 33 PSM for Enhanced Gas Adsorption and Separation 34				
2.1 2.2 2.2.1 2.2.2 2.2.3 2.3	Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat Introduction 29 Post-synthetic Modification Reactions 30 Covalent Post-synthetic Modification 31 Inorganic Post-synthetic Modification 32 Extent of the Reaction 33				
2.1 2.2 2.2.1 2.2.2 2.2.3 2.3 2.3.1	Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat Introduction 29 Post-synthetic Modification Reactions 30 Covalent Post-synthetic Modification 31 Inorganic Post-synthetic Modification 32 Extent of the Reaction 33 PSM for Enhanced Gas Adsorption and Separation 34 PSM for Carbon Dioxide Capture and Separation 34				
2.1 2.2 2.2.1 2.2.2 2.2.3 2.3 2.3.1 2.3.2	Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat Introduction 29 Post-synthetic Modification Reactions 30 Covalent Post-synthetic Modification 31 Inorganic Post-synthetic Modification 32 Extent of the Reaction 33 PSM for Enhanced Gas Adsorption and Separation 34 PSM for Carbon Dioxide Capture and Separation 34 PSM for Hydrogen Storage 35				
2.1 2.2 2.2.1 2.2.2 2.2.3 2.3 2.3.1 2.3.2 2.4	Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat Introduction 29 Post-synthetic Modification Reactions 30 Covalent Post-synthetic Modification 31 Inorganic Post-synthetic Modification 32 Extent of the Reaction 33 PSM for Enhanced Gas Adsorption and Separation 34 PSM for Carbon Dioxide Capture and Separation 34 PSM for Hydrogen Storage 35 PSM for Catalysis 37				
2.1 2.2 2.2.1 2.2.2 2.2.3 2.3 2.3.1 2.3.2 2.4 2.4.1	Modification 29 Andrew D. Burrows, Laura K. Cadman, William J. Gee, Harina Amer Hamzah, Jane V. Knichal, and Sébastien Rochat Introduction 29 Post-synthetic Modification Reactions 30 Covalent Post-synthetic Modification 31 Inorganic Post-synthetic Modification 32 Extent of the Reaction 33 PSM for Enhanced Gas Adsorption and Separation 34 PSM for Carbon Dioxide Capture and Separation 34 PSM for Hydrogen Storage 35 PSM for Catalysis 37 Catalysis with MOFs Possessing Metal Active Sites 37				

vi	Contents						
	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					
	Post-synthetically Modifying the Nature of Cross-Linked MOFs 49						
2.8 Conclusions 51							
	References 51						
	3	Synthesis of MOFs at the Industrial Scale 57					
Ana D. G. Firmino, Ricardo F. Mendes, João P.C. Tomé, and Filipe A. Alme							
	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					
	Concluding Remarks 74						
Acknowledgments 75							
List of Abbreviations 75							
		References 76					
	4	From Layered MOFs to Structuring at the Meso-/Macroscopic Scale 81					
		David Rodríguez-San-Miguel, Pilar Amo-Ochoa, and Félix Zamora					
	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 4.4.2.1	Miscellaneous 104 Direct Colloidal Formation 104					
	4.4.2.1	Surfactant Mediated 104					
	4.4.2.2	Top-Down Approaches 105					
	4.4.3.1	Liquid Phase Exfoliation (LPE) 106					
		1					

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			
4.5.5	•			
4.0	r			
	Acknowledgments 116			
	References 116			
_				
5	Application of Metal–Organic Frameworks (MOFs) for CO ₂			
	Separation 123			
	Mohanned Mohamedali, Hussameldin Ibrahim, and Amr Henni			
5.1	Introduction 123			
5.2	Factors Influencing the Applicability of MOFs for CO ₂ 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 ₂ Separation Using MOFs 139			
5.3.1	Ionic Liquids/MOF Composites 139			
5.3.2	MOF Composites for CO ₂ 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 ₄ 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			

7	MOFs for the Capture and Degradation of Chemical Warfare
	Agents 199
7.1	Elisa Barea, Carmen R. Maldonado and Jorge A. R. Navarro
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 7.3.2	Hydrolysis of Nerve Agents and Their Simulants 206 Oxidation of Sulfur Mustard and Its Analogues 211
7.3.2	Multiactive Catalysts for CWA Degradation 212
7.3.3 7.4	MOF Advanced Materials for Protection against CWAs 214
7.5	Summary and Future Prospects 218
7.0	References 219
8	Membranes Based on MOFs 223
	Pasquale F. Zito, Adele Brunetti, Alessio Caravella, Enrico Drioli and Giuseppe
	Barbieri
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
9	Composites of Metal-Organic Frameworks (MOFs): Synthesis
,	and Applications in Separation and Catalysis 251
	Devjyoti Nath, Mohanned Mohamedali, Amr Henni and Hussameldin Ibrahim
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 9.3.3 9.4	MOF Composites for Gas Adsorption and Storage Applications MOF Composites for Liquid Separation Applications 285 Conclusions 286 References 286	276		
10	Tuning of Metal-Organic Frameworks by Pre- and Post-synthetic Functionalization for Catalysis and Separations 297 Christopher F. Cogswell, Zelong Xie, and Sunho Choi			
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			
	Delta of Defenda to Constitute 244			
11	Role of Defects in Catalysis 341			
11.1	Zhenlan Fang and Qiang Ju Introduction 341			
11.1	Definition of MOF Defect 342			
11.3	Classification of MOF Defects 343			
11.3.1	Defects Classified by Defect Dimensions 343			
11.3.1	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			
	Inherent Surface Defect 344			
	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
	Defects Formed by Post-synthetic Treatment 351
11.5	Characterization of Defects 352
11.5.1	Experimental Methods for Analyzing Defects 352
	Assessing Presence of Defects 352
	Imaging Defects 355
	Probing Chemical and Physical Environment of Defects 357
	Distinguish between Isolated Local and Correlated Defects 358
	Theoretical Methods 359
11.6	The Role of Defect in Catalysis 363
	External Surface Linker Vacancy 363
	Inherent Linker Vacancy of Framework Interior 366
	Intentionally Implanted Defects 367
	Implanted Linker Vacancy by TML Strategy 367
	Implanted Linker Vacancy by LML Strategy 368
	Implanted Linker Vacancy by Post-synthetic Treatment 369
	Implanted Linker Vacancy by Fast Precipitation 370
	Implanted Linker Vacancy by MOF Partial Decomposition 370
11.7	Conclusions and Perspectives 372
	Acknowledgment 372
	References 372
12	MOFs as Heterogeneous Catalysts in Liquid Phase Reactions 379
	Maksym Opanasenko, Petr Nachtigall, and Jiří Čejka
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
10.00	Reaction 392
12.3.2	Dynamically Formed Defects as Active Sites: Knoevenagel
10.4	Condensation 394
12.4	Concluding Remarks and Future Prospects 395
	References 396
13	Encapsulated Metallic Nanoparticles in Metal-Organic Frameworks:
	Toward Their Use in Catalysis 399
	Karen Leus, Himanshu Sekhar Jena, and Pascal Van Der Voort
13.1	Introduction 399
13.1.1	Impregnation Methods 400

13.1.1.1	Liquid Phase Impregnation 400				
	Solid Phase Impregnation 401				
	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					
13.7	Conclusions and Outlook 437				
	References 438				
4.4	MOE Comments of Francisco in Discontinuity 1477				
14	MOFs as Supports of Enzymes in Biocatalysis 447				
1 / 1	Sérgio M. F. Vilela and Patricia Horcajada				
14.1	Introduction 447				
14.2	MOFs as Biomimetic Catalysts 449				
14.3	Enzyme Immobilization Strategies 454 Surface Immobilization 455				
14.3.1					
14.3.2 14.3.3	Diffusion into the MOF Porosity 456				
14.3.3 14.4	In Situ Encapsulation/Entrapment 457				
14.4.1	Biocatalytic Reactions Using Enzyme–MOFs 459 Esterification and Transesterification 463				
14.4.1					
14.4.3	Hydrolysis 464 Oxidation 466				
14.4.4					
14.4.5	4				
14.4.3	of Enzyme–MOFs 468				
14.5	Conclusions and Perspectives 469				
11.0	Acknowledgments 470				
	References 471				
15	MOFs as Photocatalysts 477				
	Sergio Navalón and Hermenegildo García				
15.1	Introduction 477				
15.2	Properties of MOFs 482				
15.3	Photophysical Pathways 483				
15.4	Photocatalytic H ₂ Evolution 490				
15.5	Photocatalytic CO ₂ 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				