

Contents

Preface *XI*

Abbreviations *XIII*

1	Introduction	1
	References	4
2	Synthesis Approach of Mesoporous Molecular Sieves	5
2.1	Synthesis	5
2.2	Hydrothermal Synthesis	12
2.2.1	Surfactant	12
2.2.2	Inorganic Precursor	15
2.2.3	Synthesis Temperature	15
2.2.4	Synthetic Media	19
2.2.5	Hydrothermal Treatment	21
2.2.6	Formation Rate	23
2.2.7	Separation and Drying	23
2.3	Removal of Template	24
2.3.1	Calcination	24
2.3.2	Extraction	25
2.3.3	Supercritical Fluid Extraction	25
2.3.4	Microwave Irradiation	26
2.3.5	Ultraviolet Irradiation	27
2.3.6	Microwave Digestion	28
2.3.7	Oxidation of Ammonium Perchlorate	29
2.4	Basic Synthesis	30
2.5	Acidic Synthesis	30
2.6	Nonaqueous Syntheses	33
2.7	Postsynthesis Treatment	37
2.7.1	Hydrothermal Treatment	37
2.7.2	Secondary Synthesis	38
2.7.3	Recrystallization	38
2.8	Stability of Mesoporous Materials	39

2.8.1	Thermal Stability	39
2.8.2	Hydrothermal Stability	41
2.8.3	Mechanical Stability	44
2.9	Pore-Size Control	44
	References	48
3	Mechanisms for Formation of Mesoporous Materials	55
3.1	Introduction	55
3.2	Synthesis Pathways	66
3.3	Mesophase Tailoring	73
3.3.1	Micellar Mesostructure	73
3.3.2	Critical Micelle Concentration	76
3.3.3	The Packing Parameter	76
3.3.4	The Hydrophilic/Hydrophobic Volume Ratio	79
3.3.5	Surfactant Phase Diagram	82
3.3.6	“Acid–Base” Route	84
3.4	Hard-Templating Approach	91
3.4.1	Precursor	92
3.4.1.1	Improving Volume Conversion	94
3.4.1.2	Improving the Interaction between Template and Precursor	97
3.4.1.3	Enhancing the Interaction between Precursors Themselves	98
3.4.2	Conversion of Precursors	100
3.4.3	The Influence of the Template Structure	102
3.4.3.1	Templates with 2D Channeled Pores	103
3.4.3.2	Templates with Cage-Like Pores	104
3.4.3.3	Templates with 3D Helix Channels	104
3.4.4	Replicated Mesoporous Carbon as a Hard Template	107
	References	109
4	Structural Characterization Methods	117
4.1	XRD	117
4.1.1	Basic Principles of XRD	118
4.1.2	XRD Measurement	119
4.1.3	XRD Pattern Analysis	120
4.1.4	SAXS	122
4.2	Electron Microscopy	123
4.2.1	TEM	125
4.2.2	SAED	129
4.2.3	SEM	130
4.2.4	EDX	133
4.2.5	STEM	135
4.3	NMR	136
4.4	Physical Sorption	138
4.4.1	Basic Principles	138
4.4.2	Pore-Size Calculation	141

4.4.3	Window-Size Calculation for Cavity-Like Pores	144
4.4.4	Detection of Micropores and Mesopores	147
4.4.5	Other Probes	148
	References	149
5	Representative Mesoporous Silica Molecular Sieves	153
5.1	D Mesostructures	153
5.1.1	MCM-41	153
5.1.2	SBA-15	161
5.1.3	Other 2D Phases	166
5.1.3.1	FSM-16 and FSM-10	166
5.1.3.2	KSW-2	168
5.1.3.3	SBA-3	168
5.1.3.4	SBA-8	170
5.1.3.5	CMI-1	170
5.1.3.6	AMS-3	171
5.2	3D Hexagonal Phases	171
5.2.1	SBA-2	171
5.2.2	SBA-12	176
5.2.3	IBN-9	178
5.3	Cubic Phases	181
5.3.1	MCM-48, FDU-5 and KIT-6	181
5.3.2	SBA-1 and SBA-6	190
5.3.3	SBA-16	192
5.3.4	FDU-1	195
5.3.5	FDU-2	196
5.3.6	FDU-12 and KIT-5	198
5.3.6.1	FDU-12	198
5.3.7	SBA-11	203
5.3.8	AMS-8 and AMS-10	205
5.4	Disordered Mesostructures	207
5.4.1	HMS and MSU	210
5.4.2	KIT-1	213
5.4.3	TUD-1	213
	References	215
6	Doping in Mesoporous Molecular Sieves	219
6.1	Aluminum Doping	219
6.2	Boron Doping	224
6.3	Gallium and Indium Doping	226
6.4	Germanium and Tin Doping	227
6.5	Transition-Metal Doping	228
6.5.1	Titanium and Zirconium Doping	229
6.5.2	Vanadium and Niobium Doping	231
6.5.3	Chromium and Molybdenum Doping	232

- 6.5.4 Manganese Doping 233
- 6.5.5 Iron and Ruthenium Doping 234
- 6.5.6 Cobalt Doping 236
- 6.5.7 Copper and Zinc Doping 237
- 6.5.8 Hybrid Metal Doping 238
- References 239

7 Morphology Control 243

- 7.1 The Methods and Techniques 243
- 7.2 Typical Morphologies 244
 - 7.2.1 Fibers and Rods 244
 - 7.2.2 Thin Films 254
 - 7.2.3 Monoliths 260
 - 7.2.4 Spheres 266
 - 7.2.5 Single Crystals 270
- 7.3 Magnetically Responsive Ordered Mesoporous Materials 273
 - 7.3.1 Magnetic Nanomaterials and Mesoporous Materials 273
 - 7.3.2 Synthesis of Magnetic Mesoporous Materials 274
 - 7.3.3 Sol-Gel Coating Approach 274
 - 7.3.4 Postloading Approach 283
 - 7.3.5 Nanocasting Synthesis 286
- References 287

8 Mesoporous Nonsilica Materials 293

- 8.1 Mesoporous Carbon 293
 - 8.1.1 Nanocasting 294
 - 8.1.1.1 Morphology Control 297
 - 8.1.1.2 Pore-Wall Structure Control 316
 - 8.1.1.3 Special Mesostructured Templates 324
 - 8.1.2 Surfactant Self-Assembly 325
 - 8.1.2.1 Electrostatic Interaction 325
 - 8.1.2.2 Compatibility between Block Copolymers and Precursors 327
 - 8.1.2.3 Morphology Control 336
 - 8.1.2.4 Hybrid Mesoporous Carbon Materials 337
 - 8.1.2.5 Phenolic Resol and Titanium Complex 340
- 8.2 Mesoporous Polymers 341
 - 8.2.1 Nanocasting 341
 - 8.2.2 Direct Synthesis 348
 - 8.2.2.1 *In-Situ* Crosslinkage of Micelles 348
 - 8.2.2.2 Selective Etching of One Block in Ordered Aggregates of Block Copolymer 350
 - 8.2.3 Surfactant Self-Assembly 351
- 8.3 Mesoporous Nonsiliceous Oxides 351
 - 8.3.1 Surfactant Self-Assembly 352
 - 8.3.2 Nanocasting 354

8.3.2.1	Mesoporous Silica Hard Template	354
8.3.2.2	Precursors and Filling Methods	363
8.3.2.3	Mesoporous Carbon Hard Template	370
8.4	Mesoporous Metals	371
8.4.1	LCT Mechanism	371
8.4.2	Nanocasting	374
8.5	Mesoporous Metal Chalcogenides	378
8.5.1	Cadmium, Zinc, Indium, Copper Chalcogenides	378
8.5.1.1	Soft-Templating Synthesis	378
8.5.1.2	Nanocasting Synthesis	381
8.5.2	Sn, Ge, Sb, Mo, W Chalcogenides	382
8.5.2.1	Soft-Templating Synthesis	382
8.5.2.2	Nanocasting Synthesis	384
8.6	Ordered Mesoporous Nonoxide Ceramic Materials	386
8.6.1	Mesoporous SiC Materials	386
8.6.2	Mesoporous Silicon Nitride and Oxynitride Materials	391
8.6.3	Mesoporous SiOC Materials	395
8.6.4	Mesoporous SiCN and SiBCN Materials	396
8.6.4.1	Nanocasting Synthesis	396
8.6.4.2	Direct Synthesis Based on Block Copolymer Self-Assembly	398
8.6.5	Mesoporous BN, B ₄ C and BCN Materials	402
8.6.6	Mesoporous Carbon Nitride Materials	404
8.6.7	Mesoporous Phosphorus Nitrides	407
8.7	Mesoporous Metal Nitrides, Carbides and Fluorides	408
8.7.1	Mesoporous Metal Nitrides	408
8.7.2	Mesoporous Metal Fluoride Materials	411
8.7.3	Mesoporous Metal Carbides	412
	References	414
9	Organic Group Functionalized Mesoporous Silicas	429
9.1	Synthetic Approaches	430
9.1.1	Grafting ("Two-Step") Method	430
9.1.2	Cocondensation ("One-Pot") Approach	434
9.1.3	Interaction of the Pore Wall with Organic Functional Group	436
9.1.3.1	Loading of Organic Groups	436
9.1.3.2	Mesostructure and Morphology	440
9.1.3.3	Condensation of Silanes	442
9.1.3.4	Distribution of Organic Functional Groups	444
9.2	Combinatorial Synthesis	446
9.3	Accessibility to the Active Site and Applications	451
9.3.1	Spatial Effect	451
9.3.2	Further Reactive Ability	453
9.3.3	Adsorption Properties	455

9.4	Conclusions	459
	References	459
10	Applications of Mesoporous Molecular Sieves	465
10.1	Catalysts and Carriers	465
10.1.1	Inclusion of Dispersed Atomic-Level Heteroatoms or Oxide Species	465
10.1.1.1	Acidic Catalysis	466
10.1.1.2	Basic Catalysis	469
10.1.1.3	Oxidation Catalysis	470
10.1.2	Loading Highly Dispersed Metals and Their Nanoparticles	472
10.1.3	Loading of Molecular Catalysts	474
10.1.4	Nonsilica Mesoporous Materials as Carriers	478
10.2	Biology, Separation and Adsorption	479
10.2.1	Biological Field	479
10.2.2	Separation and Adsorption	487
10.3	Photoelectric Applications	488
10.4	High-Tech Fields Such as Electromagnetism	492
10.4.1	Electrochemical Capacitors	492
10.4.1.1	Double-Layer Capacitor	493
10.4.1.2	Pseudocapacitance Capacitor	497
10.4.1.3	Lithium Ion Battery	499
10.4.1.4	Lithium–Sulfur Battery	502
10.4.1.5	Fuel Cells	504
	References	506
11	Outlook	513
	Index	519