

Contents

Preface *xi*

1	Introduction of Microporous Membranes	1
1.1	Introduction	1
1.2	Historical Development of Membranes	1
1.3	Microporous Materials	4
1.3.1	Carbonaceous Materials	4
1.3.1.1	Activated Carbon	5
1.3.1.2	Carbon Nanotubes	8
1.3.1.3	Graphene	11
1.3.2	Microporous Silica	14
1.3.3	Zeolites	16
1.3.4	Metal–Organic Frameworks	19
1.3.5	Highly Porous Polymers	21
1.3.5.1	High Free Volume Polymers	21
1.3.5.2	Porous Organic Frameworks	23
1.4	Fundamentals of Membrane Separation	27
1.4.1	Membrane Definition	27
1.4.2	Transport Theory	27
1.4.2.1	Membrane Transport for Gas Systems	27
1.4.2.2	Membrane Transport for Liquid Systems	29
1.4.2.3	Transport Mechanism in ED Membrane	32
1.5	Membrane Configurations	35
1.5.1	Membrane Structures	35
1.5.2	Preparation Techniques	36
1.5.2.1	Solution Casting	36
1.5.2.2	Melt Extrusion	36
1.5.2.3	Spinning	37
1.5.2.4	Spin Coating	37
1.5.2.5	Slip Coating Sintering	37
1.5.2.6	Sol–Gel Technique	37
1.5.2.7	Carbonization	38
1.5.3	Membrane Technology	38
1.5.4	Membrane Modules	40
1.5.4.1	Plate-and-Frame Module	41

1.5.4.2	Tubular Membrane Module	41
1.5.4.3	Spiral Wound Module	41
1.5.4.4	Hollow Fiber Module	42
1.6	Features of Microporous Membranes	43
1.7	Conclusions	45
	References	45
2	Microporous Silica Membranes	53
2.1	Introduction	53
2.2	Membrane Synthesis	53
2.2.1	Sol–Gel Synthesis Method	54
2.2.2	Templating Approach	55
2.2.3	Chemical Vapor Deposition	56
2.3	Intermediate Layers	57
2.4	Support	58
2.5	Modification of Silica Membranes	58
2.6	Microporous Silica Membranes for Hydrogen Separation	60
2.7	Microporous Silica Membranes for Carbon Dioxide Separation	63
2.8	Microporous Silica-Based Membranes for Pervaporation Process	66
2.9	Microporous Silica-Based Membranes for Desalination	69
2.10	Conclusions and Future Trends	72
	References	73
3	Carbon-Based Membranes	77
3.1	Introduction	77
3.2	Carbon Membrane Preparations	78
3.2.1	Carbon Molecular Sieve Membranes	78
3.2.1.1	Precursors of Carbon Molecular Sieves	79
3.2.1.2	Pyrolysis Environment for CMS Membranes	80
3.2.1.3	Pretreatments of CMS Membranes	81
3.2.1.4	Posttreatment of CMS Membranes	81
3.2.2	Module Construction of Carbon Membranes	82
3.3	Selective Surface Flow Membranes	84
3.4	Advantages and Disadvantages of Carbon Membranes	86
3.4.1	Advantages of Carbon Membrane Versus Conventional Polymer Membrane	86
3.4.2	Disadvantages of Carbon Membranes	87
3.5	Carbon Nanotubes	87
3.5.1	Types of CNT Membranes	87
3.5.2	CNT Functionalization	90
3.6	Porous Graphene	92
3.7	Carbon-Based Mixed Matrix Membranes (MMMs)	99
3.8	New Advances and Challenging Aspects	102
3.8.1	Concentration Polarization	103
3.8.2	Fouling	104
3.8.3	Mechanical Stability	105
3.8.4	Scalability	106

3.8.5	Cost	106
3.9	Conclusions	107
	References	107
4	Microporous Membranes for Water Purification	115
4.1	Introduction	115
4.2	Types and State-of-the-Art Microporous Membranes in Water Purification	116
4.3	Removal of Water Contaminants (Inorganics, Organics, Biological)	118
4.3.1	Inorganic Pollutants	118
4.3.2	Organic Pollutants	124
4.3.3	Biological Pollutants	131
4.4	Membrane Desalination	134
4.5	Membrane Surface Engineering	144
4.5.1	Membrane Surface Engineering Using Nanoparticles	147
4.5.2	Using Hydrophilic Components to Hydrophobic Membranes	151
4.6	Conclusions	153
	References	153
5	Mixed Matrix Membranes	161
5.1	Introduction	161
5.2	Principles of Mixed Matrix Membranes	161
5.2.1	Polymer Phase	162
5.2.2	Solvents	163
5.2.3	Fabrication and Drying Techniques for MMMs	163
5.2.4	Mass Transport Theory and Models in MMMs	166
5.3	MMMs Made of Zeolites	169
5.3.1	Interfacial Modification with Silane Agents	172
5.3.2	Addition of Low Molecular Weight Materials	172
5.3.3	Annealing	173
5.3.4	Priming Method	173
5.4	MOF-Based MMMs	173
5.4.1	UiO-66 Series	174
5.4.2	Zeolithic Imidazolate Frameworks	176
5.4.3	MIL Series	177
5.4.4	Cu-MOFs	178
5.4.5	MOF-74 Series	179
5.5	POF-Derived MMMs	181
5.6	MMMs Containing Other Porous Fillers	184
5.7	Conclusions	189
	References	189
6	Zeolite Membranes	195
6.1	Introduction	195
6.2	Synthesis Techniques for Zeolite Membranes	196
6.3	Crystal Growth in Zeolite Layers	198

6.3.1	Conventional Hydrothermal Synthesis	198
6.3.2	Two-Step Crystallization	199
6.3.3	Crystallization by Microwave Heating	200
6.3.4	Use of Intergrowth Supporting Substances	201
6.3.5	Growth of Oriented Zeolite Layers on Supports	205
6.3.6	Bilayer Membranes	207
6.3.7	Functional Zeolite Films	208
6.3.8	Mixed Matrix Membranes	210
6.4	Microstructures of Zeolite Films	210
6.5	Membrane Characterizations	211
6.6	Conclusions and Outlook	215
	References	216
7	Gas Separations with Zeolite Membranes	225
7.1	Introduction	225
7.2	H ₂ Recovery	226
7.3	Air Separation	228
7.4	CO ₂ Capture	230
7.5	N ₂ /CH ₄ Separation	235
7.6	H ₂ S Capture	238
7.7	Kr/Xe Separation	238
7.8	Post-modification of Zeolite Membranes	245
7.9	Conclusions and Outlook	247
	References	248
8	Pervaporation with Zeolite Membranes	255
8.1	Introduction	255
8.2	Pervaporation Process	255
8.3	Alcohol Dehydration	260
8.4	Organic–Organic Separation	264
8.5	Acid Separation	266
8.6	Membrane Reactors for Various Separations	268
8.6.1	Water Separation	268
8.6.2	Hydrogen Separation in Dehydrogenation Reactions	271
8.6.3	Hydrogen Separation in Water–Gas Shift Reaction	273
8.6.4	Hydrogen Separation in Syngas Production	273
8.6.5	Methanol Separation in Hydrogenation Reaction	274
8.6.6	Metathesis of Propene	274
8.6.7	Separation of Isomers in Isomerization Reaction	275
8.6.8	Other Separations	277
8.7	Conclusions and Outlook	277
	References	278
9	MOF Membranes and Their H₂ Separation Properties	287
9.1	Introduction	287
9.2	Fabrication of MOF Membranes	288
9.2.1	Fabrication Methods for Polycrystalline Membranes	288
9.2.1.1	Direct Synthesis	288

9.2.1.2	Seeded Growth	292
9.2.1.3	Electrochemical Deposition	294
9.2.1.4	Stepwise Dosing of Reagents	296
9.2.1.5	Assembly of MOF Nanocrystals	296
9.2.1.6	Chemical Vapor Deposition	296
9.2.2	Fabrication Methods for SURMOF Membranes	296
9.2.2.1	Liquid-Phase Epitaxy	296
9.2.2.2	Interfacial Synthesis	298
9.3	Controlling and Characterizing MOF Membranes	300
9.3.1	Powder X-Ray Diffraction	302
9.3.2	Nitrogen Adsorption and Desorption	303
9.3.3	Thermal Gravimetric Analysis	304
9.3.4	Scanning Electron Microscopy	305
9.3.5	Inductively Coupled Plasma Optical Emission Spectroscopy	306
9.3.6	NMR Spectroscopy	306
9.3.7	SS-NMR Spectroscopy	307
9.3.8	Diffuse Reflectance Infrared Fourier Transform Spectroscopy	307
9.4	Pore Chemistry for H ₂ Separation	308
9.5	Conclusions	316
	References	316
10	CO₂ Capture with MOF Membranes	323
10.1	Introduction	323
10.2	CO ₂ Capture and Separation Strategies	324
10.2.1	Post-combustion CO ₂ Capture	325
10.2.2	Pre-combustion CO ₂ Capture	326
10.2.3	Oxy-fuel Combustion	326
10.2.4	Chemical Absorption	327
10.2.5	Physical Absorption	328
10.2.6	Physical Adsorption	330
10.2.7	Cryogenic	331
10.2.8	Membrane Technology	331
10.2.8.1	Polymeric Membranes	332
10.2.8.2	Inorganic Membrane	333
10.2.8.3	Zeolite Membrane	333
10.2.8.4	Silica Membrane	334
10.2.8.5	MOF Membrane	334
10.2.9	Chemical-Looping Combustion	334
10.3	Chemistry of MOFs for CO ₂ Recognition	335
10.3.1	Unsaturated Metal Sites	335
10.3.2	Polar Functional Groups	336
10.3.3	Pore Size and Function Control	339
10.3.4	Core–Shell MOF Structure	341
10.3.5	Alkylamine Incorporation	341
10.4	Membrane Design for CO ₂ Separation	344
10.5	Conclusions	353
	References	354

11	MOF Membranes for Vapor or Liquid Separation	361
11.1	Introduction	361
11.2	Selective Separation of Chemicals Via Pervaporation	364
11.2.1	Polycrystalline MOF Membranes for Pervaporation	365
11.2.2	MOF-Based MMMs for PV Process	373
11.3	Organic Solvent Nanofiltration	381
11.4	Chiral Resolution	394
11.5	Stability of MOF Membranes	401
11.6	Conclusions and Outlook	405
	References	406
12	Microporous Organic Framework Materials for Membrane Separations	413
12.1	Introduction	413
12.2	Porous Structures and Free Volumes	413
12.3	Hydrogen Recovery	416
12.4	Carbon Dioxide Capture	419
12.5	Air Separation	423
12.6	Other Gas Separations	427
12.7	Emerging Liquid Separations	428
12.8	Conclusions	431
	References	432
	Index	437