Ref.666.86 CHE

Contents

Pr	Preface			
1.	Intro	oduction		
	1.1	The E	volution and Development of Porous Materials	2
		1.1.1	From Natural Zeolites to Synthesized Zeolites	2 3
		1.1.2	From Low-silica to High-silica Zeolites	3
		1.1.3	From Zeolites to Aluminophosphate Molecular Sieves and	
			Other Microporous Phosphates	4
		1.1.4	From 12-Membered-ring Micropores to Extra-large Micropores	5
		1.1.5	From Extra-large Micropores to Mesopores	6
		1.1.6	Emergence of Macroporous Materials	7
		1.1.7	From Inorganic Porous Frameworks to Porous Metal-organic	
			Frameworks (MOFs)	8
	1.2	Main 2	Applications and Prospects	9
		1.2.1	The Traditional Fields of Application and Prospects of	
			Microporous Molecular Sieves	9
		1.2.2	Prospects in the Application Fields of Novel, High-tech, and	
			Advanced Materials	10
		1.2.3	The Main Application Fields and Prospects for Mesoporous	
			Materials	11
	1.3	The D	evelopment of Chemistry for Molecular Sieves and	
		Porous	s Materials	13
		1.3.1	The Development from Synthesis Chemistry to Molecular	
			Engineering of Porous Materials	13
		1.3.2	Developments in the Catalysis Study of Porous Materials	14
2.	Stru	ctural	Chemistry of Microporous Materials	19
	2.1	Introd	• •	19
	2.2	Struct	ural Building Units of Zeolites	23
			Primary Building Units	23
		2.2.2	Secondary Building Units (SBUs)	24
		2.2.3	Characteristic Cage-building Units	25

		2.2.4	Characteristic Chain- and Layer-building Units	29
		2.2.5		32
	2.3	Comp	osition of Zeolites	33
		2.3.1	1	33
			Distribution and Position of Cations in the Structure	34
		2.3.3	Organic Templates	39
	2.4		work Structures of Zeolites	41
		2.4.1		41
		2.4.2	8 1 8	
			in Zeolites	43
		2.4.3	Framework Densities (FDs)	47
		2.4.4	Selected Zeolite Framework Structures	47
	2.5	Zeolit	ic Open-framework Structures	72
		2.5.1	Anionic Framework Aluminophosphates with Al/P ≤ 1	72
		2.5.2	Open-framework Gallophosphates with Extra-large Pores	88
		2.5.3	Indium Phosphates with Extra-large Pores and Chiral	
			Open Frameworks	92
		2.5.4	Zinc Phosphates with Extra-large Pores and Chiral	
			Open Frameworks	93
		2.5.5	Iron and Nickel Phosphates with Extra-large Pores	95
		2.5.6	Vanadium Phosphates with Extra-large Pores and Chiral	
			Open Frameworks	97
		2.5.7	Germanates with Extra-large Pores	100
		2.5.8	Indium Sulfides with Extra-large-pore Open Frameworks	101
	2.6	Summ	hary	104
3	Svnt	hetic (Chemistry of Microporous Compounds (I) –	
•••			tals and Synthetic Routes	117
	3.1		uction to Hydro(solvo)thermal Synthesis	117
	2.1	3.1.1		117
		3.1.2		119
		3.1.3		120
		3.1.4	1	122
		3.1.5		
			Synthetic Routes in the Synthesis of Microporous Crystals	
			and the Preparation of Porous Materials	123
	3.2	Synthe	etic Approaches and Basic Synthetic Laws for Microporous	
		Comp		123
			Hydrothermal Synthesis Approach to Zeolites	125
			Soluethermal Synthesis Approach to Aluminenheerhotes	144

3.2.2	Solvothermal Synthesis Approach to Aluminophosphates	144
3.2.3	Crystallization of Zeolites under Microwave Irradiation	157
3.2.4	Hydrothermal Synthesis Approach in the Presence of	
	Fluoride Source	161

	i luolide Source	101
3.2.5	Special Synthesis Approaches and Recent Progress	164
3.2.6	Application of Combinatorial Synthesis Approach and	
	Technology in the Preparation of Microporous Compounds	168

	3.3	Typica	al Synthetic Procedures for some Important Molecular Sieves	172
7		3.3.1	Linde Type A (LTA)	172
۲ ۰,		3.3.2	Faujasite (FAU)	173
		3.3.3	Mordenite (MOR)	175
M		3.3.4	ZSM-5 (MFI)	176
7		3.3.5	Zeolite Beta (BEA)	177
ĉ		3.3.6	Linde Type L (LTL)	178
		3.3.7	AlPO ₄ -5 (AFI)	178
\tilde{c}_{i}		3.3.8	AIPO ₄ -11 (AEL)	179
e.		3.3.9	SAPO-31	180
ŕ. ·		3.3.10	SAPO-34 (CHA)	181
Ċ.		3.3.11	TS-1 (Ti-ZSM-5)	181
4:	Svn	thetic (Chemistry of Microporous Compounds (II) – Special	
	•		ons, Structures, and Morphologies	191
t. r	4.1	-	etic Chemistry of Microporous Compounds with Special	
5			ositions and Structures	192
1		4.1.1	M(III)X(V)O ₄ -type Microporous Compounds	192
			Microporous Transition Metal Phosphates	194
•			Microporous Aluminoborates	197
		4.1.4	Microporous Sulfides, Chlorides, and Nitrides	199
		4.1.5	Extra-large Microporous Compounds	201
		4.1.6	Zeolite-like Molecular Sieves with Intersecting	
			(or Interconnected) Channels	212
		4.1.7	Pillared Layered Microporous Materials	215
		4.1.8	Microporous Chiral Catalytic Materials	218
	4.2	Synthe	etic Chemistry of Microporous Compounds with Special	
		Morph	nologies	226
•		4.2.1	Single Crystals and Perfect Crystals	226
		4.2.2	Nanocrystals and Ultrafine Particles	235
		4.2.3	The Preparation of Zeolite Membranes and Coatings	241
		4.2.4	Synthesis of Microporous Material with Special	
			Aggregation Morphology in the Presence of Templates	248
		4.2.5	Applications of Zeolite Membranes and Films	251
5	Crv	stalliza	tion of Microporous Compounds	267
			ng Materials of Zeolite Crystallization	268
	211	5.1.1	Structures and Preparation Methods for Commonly	200
			Used Silicon Sources	268
		5.1.2	Structure of Commonly Used Aluminum Sources	284
	5.2		illization Process and Formation Mechanism of Zeolites	285
		5.2.1	Solid Hydrogel Transformation Mechanism	287
		5.2.2	Solution-mediated Transport Mechanism	289
		5.2.3	Important Issues Related to the Solution-mediated Transport	
			Mechanism	294
		5.2.4	Dual-phase Transition Mechanism	305

	5.3	ure-directing Effect (SDE) and Templating in the Crystallization		
		Proces	ss of Microporous Compounds	307
		5.3.1	Roles of Guest Molecules (Ions) in the Creation of Pores	307
		5.3.2	Studies on the Interaction between Inorganic Host and Guest	
			Molecules via Molecular Simulation	324
		5.3.3	Conclusions and Prospects	325
	5.4	Crysta	Ilization Kinetics of Zeolites	326
6.	Prep	aratio	n, Secondary Synthesis, and Modification of Zeolites	345
	6.1	Prepar	ation of Zeolites – Detemplating of Microporous Compounds	345
		6.1.1	High-temperature Calcination	345
		6.1.2	Chemical Detemplating	347
		6.1.3	Solvent-extraction Method	348
	6.2	Outlin	e of Secondary Synthesis	350
	6.3	Cation	e-exchange and Modification of Zeolites	351
		6.3.1	e	351
		6.3.2	Modification of FAU Zeolite through Ion-exchange	357
	6.4	Modif	ication of Zeolites through Dealumination	361
		6.4.l		361
		6.4.2	High-temperature Dealumination and Ultra-stabilization	362
		6.4.3	Chemical Dealumination and Silicon Enrichment of Zeolites	364
	6.5		rphous Substitution of Heteroatoms in Zeolite Frameworks	373
		6.5.1	Galliation of Zeolites - Liquid-Solid Isomorphous Substitution	374
		6.5.2	Secondary Synthesis of Titanium-containing Zeolites –	
			Gas-Solid Isomorphous Substitution Technique	377
		6.5.3	Demetallation of Heteroatom Zeolites through High-temperature	
			Vapor-phase Treatment	378
	6.6		el and Surface Modification of Zeolites	379
		6.6.1	8	380
		6.6.2		381
		6.6.3	External Surface-modification Method	383
7.			ational Design and Synthesis of Inorganic Microporous	
		erials		397
	7.1	Introd		397
	7.2		ure-prediction Methods for Inorganic Microporous Crystals	398
		7.2.1		• • • •
			by Simulated Annealing Method	399
		7.2.2	Generation of 3-D Frameworks by Assembly of 2-D Nets	401
		7.2.3	Automated Assembly of Secondary Building Units	10.6
		- - ·	(AASBU Method)	406
		7.2.4	Prediction of Open-framework Aluminophosphate Structures	
			by using the AASBU Method with Lowenstein's Constraints	412
		7.2.5	Design of Zeolite Frameworks with Defined Pore Geometry	41.5
			through Constrained Assembly of Atoms	415

٠.		7.2.6	Design of 2-D 3.4-Connected Layered Aluminophosphates	
ķ			with $Al_3P_4O_{16}^{3-}$ Stoichiometry	426
		7.2.7	Hypothetical Zeolite Databases	429
z'	7.3	Towar	ds Rational Synthesis of Inorganic Microporous Materials	430
£		7.3.1	Data Mining-aided Synthetic Approach	430
· .		7.3.2	Template-directed Synthetic Approach	433
2.1		7.3.3	Rational Synthesis through Combinatorial Synthetic Route	454
٤		7.3.4	Building-block Built-up Synthetic Route	455
ż.	7.4	Prospe		459
4.		1		
8.	Synt	hesis, S	Structure, and Characterization of Mesoporous Materials	467
ł,e-	8.1	Introd	uction	468
į.	8.2	Synthe	esis Characteristics and Formation Mechanism of Ordered	
tri		Mesor	porous Materials	472
:		8.2.1	Mesostructure Assembly System: Interaction Mechanisms	
<u>*</u> 77			between Organics and Inorganics	472
ζ.		8.2.2	Formation Mechanism of Mesostructure: Liquid-crystal	
			Template and Cooperative Self-assembly	478
		8.2.3	Surfactant Effective Packing Parameter: g and Physical	
è			Chemistry of Assembly and Interface Considerations	489
× .	8.3	Mesor	porous Silica: Structure and Synthesis	494
ę?		8.3.1	Structural Characteristics and Characterization Techniques	
ξ.			for Mesoporous Silica	494
,		8.3.2	2-D Hexagonal Structure: MCM-41, SBA-15, and SBA-3	497
ż		8.3.3	Cubic Channel Mesostructures: MCM-48, FDU-5, and Im3m	
ដុំ គំរ			Materials	505
P •		8.3.4	Caged Mesostructures	508
5		8.3.5	Deformed Mesophases, Low-order Mesostructures, and	
Ū.			Other Possible Mesophases	520
~		8.3.6	Phase Transformation and Control	525
Ð	8.4	Pore (Control	526
Ç		8.4.1	Pore-size and Window-size Control	526
\$		8.4.2	Macroporous Material Templating Synthesis	529
		8 .4.3	The Synthesis of Hierarchical Porous Silica Materials	531
٢	8.5	Synthe	esis Strategies	533
1		8.5.1	Synthesis Methods	533
í.		8.5.2	Surfactant, its Effect on Product Structure and Removal from	
			Solid Product, and Nonsurfactants template	535
t i		8.5.3	Stabilization of Silica Mesophases and Post-synthesis	
:			Hydrothermal Treatment	541
•		8.5.4	Zeolite Seed as Precursor and Nanocasting with Mesoporous	
			Inorganic Solids	547
/4		8.5.5	Synthesis Parameters and Extreme Synthesis Conditions	550
•	8.6	Comp	osition Extension of Mesoporous Materials	558
<		8.6.1	Chemical Modification	558
		8.6.2	Synthesis Challenges for Nonsilica Mesoporous Materials	561

		8.6.3	Metal-containing Mesoporous Silica-based Materials	562
		8.6.4	Inorganic-Organic Hybrid Materials	563
		8.6.5	Metal Oxides, Phosphates, Semiconductors, Carbons,	
			and Metallic Mesoporous Materials	565
	8.7	Morph	nology and Macroscopic Form of Mesoporous Material	572
		8.7.1	'Single Crystal' and Morphologies of Mesoporous Silicas	573
		8.7.2	Macroscopic Forms	575
	8.8	Possib	le Applications, Challenges, and Outlook	583
		8.8.1	Possible Applications	583
		8.8.2	Challenges and Outlook	584
9.	Poro	ous Hos	st–Guest Advanced Materials	603
	9.1	Metal	Clusters in Zeolites	604
		9.1.1	Definition of Metal Clusters	604
		9.1.2	Preparation Approaches to Metal Clusters	605
		9.1.3	Alkali Metal Clusters	607
		9.1.4	Metal Clusters of Silver	612
		9.1.5	Noble Metal (Platinum, Palladium, Rhodium, Ruthenium,	
			Iridium, Osmium) Clusters	613
		9.1.6	Other Metal Clusters	614
		9.1.7	Clusters of Metal Oxides or Oxyhydroxide	615
	9.2	Dyes i	in Zeolites	616
	9.3	Polym	ers and Carbon Materials in Zeolites	621
		9.3.1	Polymers in Zeolites	621
		9.3.2	Preparation of Porous Carbon using Zeolites	623
			Fullerenes Assembled in Zeolites	624
		9.3.4	Carbon Nanotube Growth in Zeolites	625
	9.4	Semic	onductor Nanoparticles in Zeolites	631
	9.5		Complexes in Molecular Sieves	636
		9.5.1		636
		9.5.2	Incorporation of Metal-Schiff Base Complexes	640
		9.5.3	Incorporation of Porphyrin and Phthalocyanine Complexes	642
		9.5.4	Incorporation of Other Metal Complexes	644
	9.6	Metal-	-Organic Porous Coordination Polymers	647
		9.6.1	Transition Metal-Multicarboxylate Coordination Polymers	647
		9.6.2	Coordination Polymers with N-containing Multidentate	
			Aromatic Ligands	648
		9.6.3	Coordination Polymers with N- and O-containing Multidentate	
			Ligands	650
		9.6.4	Zinc-containing Porous Coordination Polymers	651
		9.6.5	Adsorption Properties and H ₂ Storage of MOFs	652
Fu	rther	Readi	ng	667
_	_			

Index

673