

Contents

Preface xv

1	Synthesis of Titanosilicates	1
	<i>Xinqing Lu</i>	
1.1	Introduction	1
1.2	Synthesis of Medium-Pore Titanosilicates	5
1.2.1	TS-1 Synthesis	5
1.2.2	Ti-MWW Synthesis	6
1.2.3	TS-2 Synthesis	8
1.2.4	Synthesis of Other Medium-Pore Titanosilicates	9
1.3	Synthesis of Large-Pore Titanosilicates	9
1.3.1	Ti-Beta Synthesis	9
1.3.2	Ti-MOR Synthesis	10
1.3.3	Ti-MSE Synthesis	12
1.3.4	Synthesis of Other Large-Pore Titanosilicates	13
1.4	Synthesis of Extra-Large-Pore Titanosilicates	14
1.5	Synthesis of Mesoporous Titanosilicates	15
1.6	Synthesis of ETSs	17
1.7	Conclusions	18
	References	18
2	Layered Heteroatom-Containing Zeolites	31
	<i>Hao Xu and Peng Wu</i>	
2.1	Introduction	31
2.2	Traditional Layered Heteroatom-Containing Zeolites	32
2.2.1	Heteroatom-Containing MWW-Type Layered Zeolites and Their Derivative Zeolitic Materials	32
2.2.2	Heteroatom-Containing Layered Zeolites Built from <i>fer</i> -Layers	36
2.3	Novel Layered Heteroatom-Containing Zeolites	41
2.3.1	Heteroatom-Containing MFI-Type Layered Zeolites	41
2.3.2	Germanosilicate-Derived Heteroatom-Containing Zeolites	44
2.4	Conclusions	45
	Acknowledgments	46
	References	46

3 Synthesis and Catalytic Applications of Sn- and Zr-Zeolites 53

Zhiguo Zhu

- 3.1 Introduction 53
- 3.2 Synthesis of Sn- and Zr-Zeolites 55
 - 3.2.1 Bottom-up Approaches 56
 - 3.2.1.1 Hydrothermal Synthesis 56
 - 3.2.1.2 Dry-Gel Conversion Methods 59
 - 3.2.1.3 Interzeolite Transformation 60
 - 3.2.1.4 Structural Reconstruction Strategy 62
 - 3.2.2 Top-Down Approaches 63
 - 3.2.2.1 Direct Metalation 63
 - 3.2.2.2 Demetallation–Metalation 64
- 3.3 General Remarks 66
- 3.4 Catalytic Applications of Sn- and Zr-Zeolites 67
 - 3.4.1 Redox Catalysis 68
 - 3.4.1.1 Baeyer–Villiger Oxidation 68
 - 3.4.1.2 Meerwein–Ponndorf–Verley Redox 70
 - 3.4.2 Lewis Acid Catalysis 71
 - 3.4.2.1 Ring Opening of Epoxides 71
 - 3.4.2.2 Aldol Reaction 72
 - 3.4.2.3 Propane Dehydrogenation 73
 - 3.4.3 Biomass Conversion 73
 - 3.4.3.1 Sugar Isomerization 73
 - 3.4.3.2 5-(Hydroxymethyl)Furfural (HMF) Synthesis 74
 - 3.4.3.3 Synthesis of Lactic Acid or Alkyl Lactates 75
 - 3.4.3.4 γ -Valerolactone Synthesis 76
- 3.5 General Remarks 78
- References 79

4 Synthesis of Germanosilicates 87

Jiuxing Jiang

- 4.1 Introduction 87
 - 4.1.1 General Property of Ge/Si Oxides 87
 - 4.1.2 Germanosilicate Glass 88
- 4.2 Isomorphous Substitution in Germanosilicates 89
 - 4.2.1 Isomorphous Substitution Si in Germanate 89
 - 4.2.2 Isomorphous Substitution Ge in Silicates 92
- 4.3 Inorganic Structure-Directing Effects 93
 - 4.3.1 Structure-Directing Effects of Ge 93
 - 4.3.2 Structure-Directing Effects of F^- 94
- 4.4 Organic Structure-Directing Agents in Germanosilicate Synthesis 94
 - 4.4.1 Organic Structure-Directing Agent Types and Revolutions 94
 - 4.4.2 Two Important Families of OSDA 95
- 4.5 Structure Diversity of Germanosilicates/Silicogermanates 106

4.5.1	Relationship Between Composition and Structure	106
4.5.2	Pore Opening	106
4.6	Possibility of Elimination of Ge and Catalytic Research of Germanosilicates	108
4.6.1	The Price Concern of Ge	108
4.6.2	Removal of Ge in Zeolite Synthesis	108
4.6.3	Removal of Ge with Post-synthesis	109
4.6.4	Catalytic Research of Germanosilicates	112
4.7	Conclusions and Outlook	112
	References	112
5	Structural Modifications on Germanosilicates	119
	<i>Ondřej Veselý, Maksym Opanasenko, and Jiří Čejka</i>	
5.1	Introduction	119
5.2	Germanosilicates to Layered Precursors	121
5.2.1	UTL to IPC-1P	121
5.3	ADOR Strategy for Developing New Zeolite Structures	125
5.3.1	Assembly	126
5.3.2	Disassembly	127
5.3.3	Organization	127
5.3.4	Reassembly	127
5.3.5	Liquid-phase ADOR	128
5.3.5.1	The UTL Case	129
5.3.5.2	The CIT-13 Case	132
5.3.5.3	The UOV Case	134
5.3.5.4	The IWW Case	134
5.3.6	Vapor-phase ADOR	135
5.3.7	Reductive Degermanation	136
5.3.8	Solid-state Transformations	137
5.4	Structure Stabilization	139
5.4.1	Degermanation	139
5.4.2	Functionalization With Catalytic Sites	140
5.4.3	Slow Disassembly	141
5.4.4	Reverse ADOR	141
5.5	Germanosilicate-Derived Catalysts	142
5.5.1	Summary and Perspectives	144
	Acknowledgements	146
	References	146
6	Heteroatom-Containing Dendritic Mesoporous Silica Nanoparticles	153
	<i>Bo Peng, Jia-Feng Zhou, Meng Ding, Laurent Bonneviot, and Kun Zhang</i>	
6.1	Introduction	153
6.2	Main Synthetic Methods and Formation Mechanism of Pure Silica-Based Dendritic Mesoporous Silica Nanoparticles (DMSNs)	155

6.2.1	Main Synthetic Methods of Dendritic Mesoporous Silica Nanoparticles (DMSNs) 155
6.2.2	Unified Formation Mechanism of Dendritic Mesoporous Silica Nanoparticles 155
6.3	Synthesis of Heteroatom-Containing DMSNs and Their Catalytic Applications 164
6.3.1	One-Pot Doping Strategy for DMSNs Containing Heteroatoms (Al/Ti/V/Sn/Mn/Fe/Co) 165
6.3.2	Post-grafting for Surface Metal Complexes 167
6.3.3	Loading of Metal and/or Metal Oxide Nanoparticles Within the Nanopores 169
6.4	Summary and Perspectives 173
	Acknowledgments 173
	References 173
7	Chemical Post-Modifications of Titanosilicates 181
	<i>Fang Nan, Liu Dongxu, Yu Yunkai, and Liu Yueming</i>
7.1	Introduction 181
7.2	Diffusion and Adsorption/Desorption 182
7.2.1	Hierarchical Titanosilicates 182
7.2.2	Surface Hydrophilicity and Hydrophobicity 183
7.3	Surface Reaction 184
7.3.1	Ti Active Sites Content 184
7.3.2	Ti Active Sites Distribution 186
7.3.3	Ti Active Sites Properties 187
7.3.3.1	Electrophilicity of Ti Active Sites 187
7.3.3.2	Coordinate State of Ti Active Sites 191
7.3.3.3	Adjacent Silanol Groups of Ti Active Sites 193
7.4	Solvent Effect 196
7.4.1	Effect of Solvent on Diffusion 197
7.4.2	Effect of Solvent on Adsorption/Desorption 199
7.4.3	Effect of Solvent on Surface Reactions 200
7.4.3.1	Effect on the Formation on Ti—O—O—H 200
7.4.3.2	Effect on the Stability of Ti—O—O—H 202
7.4.3.3	Effect on the Transfer of Ti—O—O—H 203
7.5	Conclusions and Prospects 204
	References 204
8	Spectroscopic Characterization of Heteroatom-Containing Zeolites 217
	<i>Guodong Qi, Jun Xu, and Feng Deng</i>
8.1	X-Ray Technique 217
8.1.1	XRD Determination of Framework Structure and Heteroatoms in Zeolites 217

8.1.2	XAS Characterization of Metals in Zeolite	219
8.1.3	XPS Analysis of the Chemical State of Metal Species	222
8.2	Ultraviolet-Visible-Near Infrared (UV-VIS-NIR) Spectroscopy	224
8.2.1	UV-VIS-NIR Characterization of Framework and Non-Framework Metal Species	224
8.2.2	UV-VIS-NIR Characterization of Metal Species on Ion Exchange Sites of Zeolites	226
8.3	Raman Spectroscopy	227
8.3.1	Raman Study of Synthesis Mechanism and Assembly of Metal-Zeolites	228
8.3.2	Raman Characterization of Active Metal-Oxygen Species in Zeolites	228
8.4	Solid-State NMR Spectroscopy	230
8.4.1	Solid-State NMR Characterization of Metal Elements in Zeolites	231
8.4.2	Solid-State Correlation NMR Measurement of Active Site Proximity and Host-Guest Interactions	233
8.4.3	In Situ Solid-State NMR for the Study of Reaction Mechanisms	235
8.5	Conclusions	238
	Acknowledgments	239
	References	239
9	Theoretical Calculations of Heteroatom Substituted Zeolites	253
	<i>Xin Yu, Wenjun Dong, Wei Chen, and Anmin Zheng</i>	
9.1	Introduction	253
9.2	Ti-Doped Zeolites	254
9.2.1	Preferred Tetrahedral (T) Sites for Substitution	255
9.2.2	Lewis Acid	257
9.2.3	Active Site with H ₂ O ₂	258
9.2.4	Reaction Mechanism	261
9.2.4.1	Epoxidation of Olefins	261
9.2.4.2	Ammonoximation and Oxidation of Cyclohexanone	263
9.2.4.3	Oxidation Desulfurization Reactions	265
9.3	Sn-Doped Zeolites	267
9.3.1	Preferred Substitution T Sites and Acidity	267
9.3.2	Reaction Mechanism	268
9.3.2.1	Glucose Isomerization to Fructose and Epimerization to Mannose	268
9.3.3	Other Catalytic Reactions	272
9.4	Other Metal-Substituted Zeolites	273
9.5	Summary and Outlook	276
	Acknowledgments	276
	References	277

10	Catalytic Ammoximation of Ketones or Aldehydes Using Titanosilicates 283 <i>Rusi Peng, Hao Xu, Chengwei Zhai, Mingyuan He, and Peng Wu</i>
10.1	Introduction 283
10.2	The Development of Titanosilicates in Ammoximation of Ketones and Aldehydes 284
10.3	Ammoximation Mechanism and Product Distributions of Representative Ketones and Aldehydes 288
10.3.1	Titanosilicate-Catalyzed Ammoximation Mechanism 288
10.3.2	Product Distributions for Ammoximation of Representative Carbonyl Compounds 290
10.4	Enhancing Ammoximation Performances in Titanosilicate/H ₂ O ₂ System 295
10.4.1	Improvement of Catalytic Ammoximation Activity 296
10.4.1.1	Regulation of Ti Active Sites 296
10.4.1.2	Enhancement of Diffusion Properties 298
10.4.1.3	Improvement of Hydrophobicity 299
10.4.1.4	Regulation of Acid Sites 300
10.4.2	Improvement of Catalytic Ammoximation Stability 300
10.5	Ketone Ammoximation Technology for Industrial Processes 302
10.6	Titanosilicate-Based Bifunctional Catalysts for Process Intensified or Tandem Ammoximation Reactions 306
10.7	Conclusions and Perspectives 310 Acknowledgments 311 References 311
11	Titanosilicate-Based Alkene Epoxidation Catalysis 323 <i>Changjiu Xia and Xiang Feng</i>
11.1	Introduction 323
11.2	Reaction Chemistry of Alkene Epoxidation Catalyzed by Titanosilicate Zeolites 326
11.3	Typical Alkene Epoxidation Cases 329
11.3.1	Propylene Epoxidation for PO Production 329
11.3.2	Propylene Chloride Epoxidation 331
11.3.3	Ethylene Epoxidation to EO, EG, and Ethers 334
11.4	Industrial Propylene Epoxidation Techniques and Processes 336
11.5	Conclusion and Outlook 339 Acknowledgments 339 References 340
12	Propylene Epoxidation with Cumene Hydroperoxide/Titanosilicates 345 <i>Le Xu and Hailang Liu</i>
12.1	Introduction 345
12.2	Traditional Route for PO Production (Chlorohydrin Process) 347
12.3	Co-production Route for PO Production (PO/TBA and PO/SM Processes) 347

12.4	PO-Only Production Routes (HPPO and CMHPPO Routes)	349
12.5	Catalyst Design for PO-Only Routes	350
12.5.1	Mesoporous Ti-Doped Catalysts for CMHPPO Process	352
12.5.2	Hierarchical Titanosilicates for CMHPPO Process	357
12.6	Industrial CMHPPO Process	362
12.7	Conclusions and Outlooks	363
	References	364
13	Hydroxylation of Benzene and Phenol on Zeolite Catalysts	367
	<i>Shiying Li, Shanhui Zhu, Sen Wang, Mei Dong, and Weibin Fan</i>	
13.1	Introduction	367
13.2	Hydroxylation of Benzene to Phenol	368
13.2.1	Gas-Phase Reactions	368
13.2.1.1	Heteroatomic Molecular Sieves as Catalysts	368
13.2.1.2	Fe-Containing Molecular Sieves as Catalysts	371
13.2.1.3	Other Methods for Benzene Hydroxylation to Phenol	377
13.2.2	Liquid-Phase Reactions	378
13.2.2.1	Fe-Containing Molecular Sieves as Catalysts	378
13.2.2.2	Microporous Crystalline Titanosilicates as Catalysts	379
13.2.2.3	Catalytic Recyclability of Fe- and Ti-Containing Zeolites	381
13.3	Hydroxylation of Phenol to DHB	381
13.3.1	Fe-Containing Molecular Sieves as Catalysts	382
13.3.1.1	Effect of Reaction Conditions	382
13.3.1.2	Catalytic Recyclability	383
13.3.1.3	Improving Catalytic Performance by Developing Hierarchically Porous Structure	383
13.3.1.4	Catalytic Mechanism	384
13.3.2	Titanosilicate Molecular Sieves as Catalysts	387
13.3.2.1	Effect of Pore Structure	387
13.3.2.2	Effect of Solvent	389
13.3.2.3	Effect of Reaction Conditions	391
13.3.2.4	Stability of Ti Species	392
13.3.3	Transition Metal Complexes Encapsulated in Zeolite Y as Catalysts	393
13.4	Summary	394
	Acknowledgments	395
	References	395
14	Bifunctional Titanosilicate Systems for the Gas-Phase Catalytic Propylene Epoxidation with Hydrogen and Oxygen	403
	<i>Gang Wang, Qianhong Wang, Zhihua Zhang, Xuezhi Duan, and Xinggui Zhou</i>	
14.1	Introduction	403
14.2	Advances in the Catalytic Propylene Epoxidation with H ₂ and O ₂	404
14.2.1	Mechanistic Insights into Au-Ti Synergy	404
14.2.2	Effects of Au Particle Properties	406

14.2.2.1	Au Particle Sizes	406
14.2.2.2	Au Oxidation States	408
14.2.2.3	Au Sites Location	408
14.2.3	Effects of Materials' Properties for Immobilizing Au Particles	408
14.2.3.1	Ti-SiO ₂ Materials	410
14.2.3.2	Mesoporous Ti-Containing Materials	410
14.2.3.3	Microporous Ti-Containing Materials	411
14.2.3.4	Effects of Hydrophobicity	412
14.2.4	Effect of Promoters	413
14.3	Conclusions and Outlook	415
	Conflicts of Interest	416
	References	416
15	Zeolites Containing Heteroatoms/Metal Nanoparticles for Catalytic Conversion of Light Alkanes	423
	<i>Hang Zhou, Liang Wang, and Feng-Shou Xiao</i>	
15.1	Introduction	423
15.2	Metal Nanoclusters and Heteroatoms in Zeolite for Propane Dehydrogenation	424
15.2.1	Zeolite-Based Catalysts for Non-Oxidative PDH	425
15.2.2	Zeolite-Based Catalysts for Oxidative PDH	426
15.3	Metallosilicates for Ethane Dehydrogenation	430
15.3.1	Metallosilicates for Non-Oxidative Dehydrogenation of Ethane	430
15.3.2	Metallosilicates for Oxidative Dehydrogenation of Ethane	431
15.4	Zeolite Catalysts for Selective Oxidation of Methane	432
15.4.1	Bionic Catalysis of Methane to Methanol Using Metallosilicates	434
15.4.2	In situ Synthesizing Hydrogen Peroxide for Low-Temperature Methane Oxidation Using Metal@zeolite	435
15.4.3	Direct Metal Oxidation with Oxygen by Zeolite-Supported Nanoparticle Catalysts	436
15.5	Summary and Outlook	439
	Acknowledgments	440
	References	440
16	Design and Applications of Single-Site Photocatalysis Using Metallosilicates	447
	<i>Priyanka Verma and Hiromi Yamashita</i>	
16.1	Introduction	447
16.2	Ti-Based Single-Site Photocatalysis Within Zeolites and Mesoporous Silica	449
16.3	Single-Site Photocatalysis Based Thin Films	450
16.3.1	Thin Films with Ti-Oxide Species	450
16.3.2	Thin Films with Various Metal Oxide Species (Mo, V, Cr, and W)	452
16.4	Visible-Light Sensitive Single-Site Photocatalysis	454

16.5	Nano-Sized Metal Preparation Using Single-Site Photocatalyst	456
16.5.1	Preparation of Monometallic NPs	456
16.5.2	Preparation of Bimetallic Metal NPs	457
16.6	Conclusions	458
	Acknowledgments	461
	References	461
	Index	465