

---

# Contents

---

Series Preface . . . . .	ix
Preface to Volume 4 . . . . .	xi
Abbreviations . . . . .	xiii
<b>1 An Overview of Zeolite, Zeotype and Mesoporous Solids Chemistry: Design, Synthesis and Catalytic Properties</b> . . . . .	<b>1</b>
<i>Thomas Maschmeyer and Leon van de Water</i>	
1.1 Zeolites, zeotypes and mesoporous solids: synthetic aspects . . . . .	1
1.1.1 Introduction . . . . .	1
1.1.2 Synthetic aspects: template theory for zeolite synthesis . . . . .	2
1.1.3 Synthetic aspects: template theory for mesoporous oxides synthesis . . . . .	7
1.2 Design of extra-large pore zeolites and other micro- and mesoporous catalysts . . . . .	11
1.2.1 Introduction . . . . .	11
1.2.2 Extra-large pore zeolites . . . . .	11
1.2.3 Hierarchical pore architectures: combining micro- and mesoporosity . . . . .	13
1.3 Potential of post-synthesis functionalized micro- and mesoporous solids as catalysts for fine chemical synthesis . . . . .	19
1.3.1 Introduction . . . . .	19
1.3.2 Covalent functionalization . . . . .	20
1.3.3 Noncovalent immobilization approaches . . . . .	25
1.3.4 Single-site catalysts inspired by natural systems . . . . .	29
References . . . . .	30
<b>2 Problems and Pitfalls in the Applications of Zeolites and other Microporous and Mesoporous Solids to Catalytic Fine Chemical Synthesis</b> . . . . .	<b>39</b>
<i>Michel Guisnet and Matteo Guidotti</i>	
2.1 Introduction . . . . .	39
2.2 Zeolite catalysed organic reactions . . . . .	42
2.2.1 Fundamental and practical differences with homogeneous reactions . . . . .	42
2.2.2 Batch mode catalysis . . . . .	45
2.2.3 Continuous flow mode catalysis . . . . .	51
2.2.4 Competition for adsorption: influence on reaction rate, stability and selectivity . . . . .	53

2.2.5	Catalyst deactivation . . . . .	61
2.3	General conclusions . . . . .	63
	References . . . . .	64
<b>3</b>	<b>Aromatic Acetylation . . . . .</b>	<b>69</b>
	<i>Michel Guisnet and Matteo Guidotti</i>	
3.1	Aromatic acetylation . . . . .	69
3.1.1	Acetylation with Acetic Anhydride . . . . .	70
3.1.2	Acetylation with Acetic Acid . . . . .	82
3.2	Procedures and protocols . . . . .	89
3.2.1	Selective synthesis of acetophenones in batch reactors through acetylation with acetic anhydride . . . . .	89
3.2.2	Selective synthesis of acetophenones in fixed bed reactors through acetylation with acetic anhydride . . . . .	90
	References . . . . .	91
<b>4</b>	<b>Aromatic Benzoylation . . . . .</b>	<b>95</b>
	<i>Patrick Geneste and Annie Finiels</i>	
4.1	Aromatic benzoylation . . . . .	95
4.1.1	Effect of the zeolite . . . . .	96
4.1.2	Effect of the acylating agent . . . . .	97
4.1.3	Effect of the solvent. . . . .	97
4.1.4	Benzoylation of phenol and the Fries rearrangement . . . . .	97
4.1.5	Kinetic law . . . . .	99
4.1.6	Substituent effect. . . . .	100
4.1.7	Experimental. . . . .	101
4.2	Acylation of anisole over mesoporous aluminosilicates. . . . .	102
	References . . . . .	103
<b>5</b>	<b>Nitration of Aromatic Compounds . . . . .</b>	<b>105</b>
	<i>Avelino Corma and Sara Iborra</i>	
5.1	Introduction. . . . .	105
5.2	Reaction mechanism. . . . .	106
5.3	Nitration of aromatic compounds using zeolites as catalysts . . . . .	107
5.3.1	Nitration in liquid phase. . . . .	107
5.3.2	Vapour phase nitration . . . . .	116
5.4	Conclusions. . . . .	118
	References . . . . .	118
<b>6</b>	<b>Oligomerization of Alkenes. . . . .</b>	<b>125</b>
	<i>Avelino Corma and Sara Iborra</i>	
6.1	Introduction. . . . .	125
6.2	Reaction mechanisms . . . . .	126
6.3	Acid zeolites as catalysts for oligomerization of alkenes . . . . .	127
6.3.1	Medium pore zeolites: influence of crystal size and acid site density. . . . .	127
6.3.2	Use of large pore zeolites. . . . .	130
6.3.3	Catalytic membranes for olefin oligomerization. . . . .	131
6.4	Mesoporous aluminosilicates as oligomerization catalysts. . . . .	131
6.5	Nickel supported aluminosilicates as catalysts . . . . .	132
	References . . . . .	136

<b>7 Microporous and Mesoporous Catalysts for the Transformation of Carbohydrates</b> . . . . .	141
<i>Claude Moreau</i>	
7.1 Introduction . . . . .	141
7.2 Hydrolysis of sucrose in the presence of H-form zeolites . . . . .	142
7.3 Hydrolysis of fructose and glucose precursors . . . . .	143
7.4 Isomerization of glucose into fructose . . . . .	144
7.5 Dehydration of fructose and fructose-precursors. . . . .	145
7.6 Dehydration of xylose. . . . .	146
7.7 Synthesis of alkyl-D-glucosides . . . . .	147
7.7.1 Synthesis of butyl-D-glucosides . . . . .	147
7.7.2 Synthesis of long-chain alkyl-D-glucosides . . . . .	150
7.8 Synthesis of alkyl-D-fructosides . . . . .	151
7.9 Hydrogenation of glucose . . . . .	151
7.10 Oxidation of glucose . . . . .	153
7.11 Conclusions . . . . .	154
References . . . . .	154
<b>8 One-pot Reactions on Bifunctional Catalysts</b> . . . . .	157
<i>Michel Guisnet and Matteo Guidotti</i>	
8.1 Introduction . . . . .	157
8.2 Examples . . . . .	158
8.2.1 One-pot transformations involving successive hydrogenation and acid–base steps. . . . .	158
8.2.2 One-pot transformations involving successive oxidation and acid–base steps . . . . .	166
References . . . . .	168
<b>9 Base-type Catalysis</b> . . . . .	171
<i>Didier Tichit, Sara Iborra, Avelino Corma and Daniel Brunel</i>	
9.1 Introduction . . . . .	171
9.2 Characterization of solid bases. . . . .	172
9.2.1 Test reactions . . . . .	172
9.2.2 Probe molecules combined with spectroscopic methods . . . . .	174
9.3 Solid base catalysts . . . . .	175
9.3.1 Alkaline earth metal oxides. . . . .	175
9.3.2 Catalysis on alkaline earth metal oxides . . . . .	177
9.3.3 Hydrotalcites and related compounds . . . . .	183
9.3.4 Organic base-supported catalysts . . . . .	187
9.4 Conclusions . . . . .	195
References . . . . .	195
<b>10 Hybrid Oxidation Catalysts from Immobilized Complexes on Inorganic Microporous Supports</b> . . . . .	207
<i>Dirk De Vos, Ive Hermans, Bert Sels and Pierre Jacobs</i>	
10.1 Introduction and scope . . . . .	207
10.2 Oxygenation potential of heme-type complexes in zeolite. . . . .	211
10.2.1 Metallo-phthalocyanines encapsulated in the cages of faujasite-type zeolites . . . . .	211
10.2.2 Oxygenation potential of metallo-phthalocyanines encapsulated in the mesopores of VPI-5 $\text{AlPO}_4$ . . . . .	215

10.2.3	Oxygenation potential of zeolite encapsulated metallo-porphyrins . . . . .	216
10.3	Oxygenation potential of zeolite encapsulated nonheme complexes . . . .	220
10.3.1	Immobilization of <i>N,N'</i> -bidentate complexes in zeolite Y . . . .	220
10.3.2	Ligation of zeolite exchanged transition ions with bidentate aza ligands . . . . .	224
10.3.3	Ligation of zeolite exchanged transition ions with tri- and tetra-aza(cyclo)alkane ligands . . . . .	225
10.3.4	Ligation of zeolite exchanged transition ions with Schiff base-type ligands . . . . .	228
10.3.5	Zeolite effects with <i>N,N'</i> -bis(2-pyridinecarboxamide) complexes of Mn and Fe in zeolite Y . . . . .	231
10.3.6	Zeolite encapsulated chiral oxidation catalysts . . . . .	233
10.4	Conclusions . . . . .	235
	Acknowledgements . . . . .	235
	References . . . . .	235
	Subject Index . . . . .	241