

Contents

1 INTRODUCTION	1
References 12	
Further Reading 12	
Problems 12	
2 CATALYSIS IN SOLUTIONS	15
Introduction 15	
Acid-Base Catalysis 19	
2.2.1 Catalysis in the Gas Phase 19	
2.2.2 Catalysis in Dilute Aqueous Solution 19	
2.2.3 General and Specific Acid and Base Catalysis 26	
2.2.4 Catalysis in Concentrated Strong Acid Solutions 31	
2.2.5 Catalysis by Bases 34	
2.2.6 Stepwise and Concerted Reactions 37	
2.2.7 Catalysis by Metal Ions 40	
√2.2.8 Hydrocarbon Conversion 40	
Carbenium Ion Reactions 40	
Catalytic Reactions Involving Carbenium Ion Intermediates 52	
2.3 Catalysis by Electron Transfer 60	
2.3.1 Simple Redox Reactions 602.3.2 Oxidation Involving Free-Radical Intermediates 62	
2.4 Organometallic Catalysis 67	
2.4.1 Introduction 67	

List of Notation xix

	Bonding and Structure of Transition Metal
	Complexes 68
	Reactions of Transition Metal Complexes 77
	Patterns of Reactivity of the Transition Metals 79
	2.4.2 Examples of Organometallic Catalysis 79
	Olefin Hydrogenation 79
	Olefin Hydroformylation 91
	Methanol Carbonylation 98
	Olefin Polymerization 102
	Olefin Metathesis 109
	Partial Oxidation 112
	C-H Bond Activation 117
	2.4.3 Catalysis by Metal Clusters 118
2.5	Catalysis by Macromolecules 123
2.6	Phase Transfer Catalysis 127
2.7	Catalysis by Micelles 129
2.8	The Influence of Diffusion 130
2.9	Process Engineering 133
	2.9.1 Separation 133
	2.9.2 Corrosion 133
	2.9.3 Heat Transfer 133
Refe	erences 134
Fur	ther Reading 137
Prol	blems 138
•	CATALVOIS DV DATAVALO
3	CATALYSIS BY ENZYMES
	Introduction 143
	Composition and Structure of Enzymes 144
	Reactions Catalyzed by Enzymes 152
	Nature of Catalytic Sites: the Uniqueness of Enzymes as
	Catalysts 154
3 5	Examples of Enzyme Structure and Catalysis 159
	3.5.1 Organic Catalysis 159
	Lysozyme 160
	Ribonuclease 166
	3.5.2 Metalloenzyme Catalysis 169
	Carbonic Anhydrase 173
	A Free-radical Reaction Catalyzed by
	Vitamin B_{12} 175.
	3.5.3 Summary 176
3.6	Supported Enzymes 177

Further Reading 179 Problems 180
Problems 180
4 CATALYSIS BY POLYMERS 182
4.1 The Nature of Polymers 182
4.2 Attachment of Catalytic Groups to Polymer Supports 184
4.3 Catalysis in Polymer Gels 186
4.4 Adsorption and the Kinetics of Polymer-Catalyzed Reactions 188
4.5 Interactions of Catalytic Groups: the Role of the Support 205
4.6 Bifunctional and Multifunctional Catalysis 210
4.7 Porous Polymers and Surface Catalysis 220
4.8 Intraparticle Transport Influence 224
4.8.1 The Thiele Model: the Influence of Intraparticle Mass
Transport on Catalysis 224 4.8.2 The Influence of Intraparticle Heat Transport 236
4.8.2 The Influence of Intraparticle Heat Transport 236 4.9 Applications of Polymer Catalysts 238
4.10 Extraparticle Transport Influence 240
References 244
Further Reading 246
Problems 246
5 CATALYSIS IN MOLECULAR-SCALE CAVITIES 254
Structures of Crystalline Solids 254
Structures of Zeolites (Crystalline Aluminosilicates) 259
5.2.1 Silicalite and ZSM-5 259
5.2.2 Zeolite A 263
5.2.3 Zeolites X and Y (Faujasites) 265
5.3 Families of Zeolites 268
5.3.1 Pore Sizes and Molecular Sieving 2685.3.2 Aluminum Content and Acidity 269
5.3.2 Aluminum Content and Acidity 269 5.4 Adsorption and Diffusion in Zeolites 272
5.5 The Solventlike Nature of Zeolite Pores 274
5.6 Catalysis by Zeolites 275
5.6.1 Acid-Base Catalysis 275
Cracking 276
Other Reactions of Olefins 283

ง หลงสบดกรบาทยาศาสตรบริการ

References 178

Steric and Transport Effects: Molecular Sieving and	
Shape-selective Catalysis 285	. 4
Influence of Steric and Transport Effects on Catalys Deactivation 293	L
5.6.2 Catalysis by Zeolites Containing Metal Complexes and	
Clusters 295	
Transition Metal Complexes 295	
Metal Clusters and Aggregates 298	
5.6.3 Summary 299	
5.7 Nonzeolite Molecular Sieves 299	
5.8 Clays and Other Layered Materials 300	
References 301	
Further Reading 304	
Problems 304	
1 (Oolems 504	2.7
6 CATALYSIS ON SURFACES	
Introduction 310	_
Surface Structures 312	
6.2.1 Single-Crystal Surfaces of Metals 312	
6.2.2 Experimental Methods of Determining Surface Structure	es
of Single Crystals 313	
6.2.3 High-Surface-Area Amorphous Solids 317	
Macroscopic Structures of Porous Solids 317	
Surface Structures of Metal Oxides 320	
6.3 Adsorption 326	
6.3.1 Adsorption Isotherms 327	
6.3.2 Structures of Adsorbed Species on Single-Crystal Metal	
Surfaces 331	
6.3.3 Adsorption on Complex Surfaces 336	
6.3.4 Functionalized Surfaces 337	
6.4 Surface Catalysis 340	
6.4.1 Catalysis on Functionalized Surfaces: Connections to	
Molecular Catalysis 340	_
Catalysis by Silica-Supported Rh Complexes 340	J
Wacker Oxidation of Ethylene on V ₂ O ₅ Surfaces	
Functionalized with Pd 340	
Olefin Metathesis Catalyzed by Metal-Oxide-	
Supported Metal Complexes 340	
Olefin Polymerization on Surfaces Functionalized	
with Cr Complexes 342 Catalysis by Multicenter Surface Sites 343	
Catalysis by Multicenter Surface Sites 343 6.4.2 Olefin Polymerization Catalysis on Titanium Trichloride	.
Surfaces: Further Links Between Molecular and Surfac	
bullaces. Fulther Links Detween Molecular and Bullac	·

Catalysis

346

6.4.3 Catalysis on Metal Surfaces 351
CO Oxidation on Pd 356
NH ₃ Synthesis on Fe 362
Hydrocarbon Conversion on Pt 369
6.4.4 Catalysis on Metal Oxide Surfaces 371
Alcohol Dehydration on γ-Al ₂ O ₃ 371
Reactions of Olefins on ZnO 373
6.4.5 Catalysis by Supported Metals 378
The Nature of Supported Metals 378
Structure-Insensitive and Structure-Sensitive
Reactions 387
Ethylene Oxidation on Silver 392
Bifunctional Catalysis and the Reforming of Naphtha
Hydrocarbons 396
6.4.6 Catalysis by Mixed Metal Oxides: Ammoxidation of Propylene 403
6.4.7 Catalysis by Metal Sulfides: Hydrodesulfurization and
Related Petroleum Hydroprocessing Reactions 406
References 417
References
Further Reading 422
Problems 422
C1 420
Glossary 430
Reading List 433
Acknowledgments 437
Index 445