

Contents

List of Contributors, x

Preface, xii

Part 1 Principles of catalytic reaction engineering

1 Catalytic reactor types and their industrial significance, 3 *Zeynep Ilse Önsan and Ahmet Kerim Avci*

1.1 Introduction, 3

1.2 Reactors with fixed bed of catalysts, 3

1.2.1 Packed-bed reactors, 3

1.2.2 Monolith reactors, 8

1.2.3 Radial flow reactors, 9

1.2.4 Trickle-bed reactors, 9

1.2.5 Short contact time reactors, 10

1.3 Reactors with moving bed of catalysts, 11

1.3.1 Fluidized-bed reactors, 11

1.3.2 Slurry reactors, 13

1.3.3 Moving-bed reactors, 14

1.4 Reactors without a catalyst bed, 14

1.5 Summary, 16

References, 16

2 Microkinetic analysis of heterogeneous catalytic systems, 17 *Zeynep Ilse Önsan*

2.1 Heterogeneous catalytic systems, 17

2.1.1 Chemical and physical characteristics of solid catalysts, 18

2.1.2 Activity, selectivity, and stability, 21

2.2 Intrinsic kinetics of heterogeneous reactions, 22

2.2.1 Kinetic models and mechanisms, 23

2.2.2 Analysis and correlation of rate data, 27

2.3 External (interphase) transport processes, 32

2.3.1 External mass transfer: Isothermal conditions, 33

2.3.2 External temperature effects, 35

2.3.3 Nonisothermal conditions: Multiple steady states, 36

2.3.4 External effectiveness factors, 38

2.4 Internal (intraparticle) transport processes, 39

2.4.1 Intraparticle mass and heat transfer, 39

2.4.2 Mass transfer with chemical reaction: Isothermal effectiveness, 41

2.4.3 Heat and mass transfer with chemical reaction, 45

2.4.4 Impact of internal transport limitations on kinetic studies, 47

2.5 Combination of external and internal transport effects, 48

2.5.1 Isothermal overall effectiveness, 48

2.5.2 Nonisothermal conditions, 49

2.6 Summary, 50

Nomenclature, 50

Greek letters, 51

References, 51

Part 2 Two-phase catalytic reactors

3 Fixed-bed gas–solid catalytic reactors, 55 *João P. Lopes and Alirio E. Rodrigues*

3.1 Introduction and outline, 55

3.2 Modeling of fixed-bed reactors, 57

3.2.1 Description of transport–reaction phenomena, 57

3.2.2 Mathematical model, 59

3.2.3 Model reduction and selection, 61

3.3 Averaging over the catalyst particle, 61

3.3.1 Chemical regime, 64

3.3.2 Diffusional regime, 64

3.4 Dominant fluid–solid mass transfer, 66

3.4.1 Isothermal axial flow bed, 67

3.4.2 Non-isothermal non-adiabatic axial flow bed, 70

3.5 Dominant fluid–solid mass and heat transfer, 70

3.6 Negligible mass and thermal dispersion, 72

3.7 Conclusions, 73

Nomenclature, 74

Greek letters, 75

References, 75

4 Fluidized-bed catalytic reactors, 80 *John R. Grace*

4.1 Introduction, 80

4.1.1 Advantages and disadvantages of fluidized-bed reactors, 80

4.1.2 Preconditions for successful fluidized-bed processes, 81

- 4.1.3 Industrial catalytic processes employing fluidized-bed reactors, 82
- 4.2 Key hydrodynamic features of gas-fluidized beds, 83
 - 4.2.1 Minimum fluidization velocity, 83
 - 4.2.2 Powder group and minimum bubbling velocity, 84
 - 4.2.3 Flow regimes and transitions, 84
 - 4.2.4 Bubbling fluidized beds, 84
 - 4.2.5 Turbulent fluidization flow regime, 85
 - 4.2.6 Fast fluidization and dense suspension upflow, 85
- 4.3 Key properties affecting reactor performance, 86
 - 4.3.1 Particle mixing, 86
 - 4.3.2 Gas mixing, 87
 - 4.3.3 Heat transfer and temperature uniformity, 87
 - 4.3.4 Mass transfer, 88
 - 4.3.5 Entrainment, 88
 - 4.3.6 Attrition, 89
 - 4.3.7 Wear, 89
 - 4.3.8 Agglomeration and fouling, 89
 - 4.3.9 Electrostatics and other interparticle forces, 89
- 4.4 Reactor modeling, 89
 - 4.4.1 Basis for reactor modeling, 89
 - 4.4.2 Modeling of bubbling and slugging flow regimes, 90
 - 4.4.3 Modeling of reactors operating in high-velocity flow regimes, 91
- 4.5 Scale-up, pilot testing, and practical issues, 91
 - 4.5.1 Scale-up issues, 91
 - 4.5.2 Laboratory and pilot testing, 91
 - 4.5.3 Instrumentation, 92
 - 4.5.4 Other practical issues, 92
- 4.6 Concluding remarks, 92
- Nomenclature, 93
- Greek letters, 93
- References, 93

Part 3 Three-phase catalytic reactors

5 Three-phase fixed-bed reactors, 97

Ion Iliuta and Faiçal Larachi

- 5.1 Introduction, 97
- 5.2 Hydrodynamic aspects of three-phase fixed-bed reactors, 98
 - 5.2.1 General aspects: Flow regimes, liquid holdup, two-phase pressure drop, and wetting efficiency, 98
 - 5.2.2 Standard two-fluid models for two-phase downflow and upflow in three-phase fixed-bed reactors, 100
 - 5.2.3 Nonequilibrium thermomechanical models for two-phase flow in three-phase fixed-bed reactors, 102

- 5.3 Mass and heat transfer in three-phase fixed-bed reactors, 104
 - 5.3.1 Gas-liquid mass transfer, 105
 - 5.3.2 Liquid-solid mass transfer, 105
 - 5.3.3 Heat transfer, 106
- 5.4 Scale-up and scale-down of trickle-bed reactors, 108
 - 5.4.1 Scaling up of trickle-bed reactors, 108
 - 5.4.2 Scaling down of trickle-bed reactors, 109
 - 5.4.3 Salient conclusions, 110
- 5.5 Trickle-bed reactor/bioreactor modeling, 110
 - 5.5.1 Catalytic hydrodesulfurization and bed clogging in hydrotreating trickle-bed reactors, 110
 - 5.5.2 Biomass accumulation and clogging in trickle-bed bioreactors for phenol biodegradation, 115
 - 5.5.3 Integrated aqueous-phase glycerol reforming and dimethyl ether synthesis into an allothermal dual-bed reactor, 121

Nomenclature, 126

Greek letters, 127

Subscripts, 128

Superscripts, 128

Abbreviations, 128

References, 128

6 Three-phase slurry reactors, 132

Vivek V. Buwa, Shantanu Roy and Vivek V. Ranade

- 6.1 Introduction, 132
- 6.2 Reactor design, scale-up methodology, and reactor selection, 134
 - 6.2.1 Practical aspects of reactor design and scale-up, 134
 - 6.2.2 Transport effects at particle level, 139
- 6.3 Reactor models for design and scale-up, 143
 - 6.3.1 Lower order models, 143
 - 6.3.2 Tank-in-series/mixing cell models, 144
- 6.4 Estimation of transport and hydrodynamic parameters, 145
 - 6.4.1 Estimation of transport parameters, 145
 - 6.4.2 Estimation of hydrodynamic parameters, 146
- 6.5 Advanced computational fluid dynamics (CFD)-based models, 147
- 6.6 Summary and closing remarks, 149
- Acknowledgments, 152
- Nomenclature, 152
- Greek letters, 153
- Subscripts, 153
- References, 153

7 Bioreactors, 156*Pedro Fernandes and Joaquim M.S. Cabral*

- 7.1 Introduction, 156
- 7.2 Basic concepts, configurations, and modes of operation, 156
 - 7.2.1 Basic concepts, 156
 - 7.2.2 Reactor configurations and modes of operation, 157
- 7.3 Mass balances and reactor equations, 159
 - 7.3.1 Operation with enzymes, 159
 - 7.3.2 Operation with living cells, 160
- 7.4 Immobilized enzymes and cells, 164
 - 7.4.1 Mass transfer effects, 164
 - 7.4.2 Deactivation effects, 166
- 7.5 Aeration, 166
- 7.6 Mixing, 166
- 7.7 Heat transfer, 167
- 7.8 Scale-up, 167
- 7.9 Bioreactors for animal cell cultures, 167
- 7.10 Monitoring and control of bioreactors, 168
- Nomenclature, 168
- Greek letters, 169
- Subscripts, 169
- References, 169

Part 4 Structured reactors**8 Monolith reactors, 173***João P. Lopes and Alirio E. Rodrigues*

- 8.1 Introduction, 173
 - 8.1.1 Design concepts, 174
 - 8.1.2 Applications, 178
- 8.2 Design of wall-coated monolith channels, 179
 - 8.2.1 Flow in monolithic channels, 179
 - 8.2.2 Mass transfer and wall reaction, 182
 - 8.2.3 Reaction and diffusion in the catalytic washcoat, 190
 - 8.2.4 Nonisothermal operation, 194
- 8.3 Mapping and evaluation of operating regimes, 197
 - 8.3.1 Diversity in the operation of a monolith reactor, 197
 - 8.3.2 Definition of operating regimes, 199
 - 8.3.3 Operating diagrams for linear kinetics, 201
 - 8.3.4 Influence of nonlinear reaction kinetics, 202
 - 8.3.5 Performance evaluation, 203
- 8.4 Three-phase processes, 204
- 8.5 Conclusions, 207
- Nomenclature, 207

Greek letters, 208

Superscripts, 208

Subscripts, 208

References, 209

9 Microreactors for catalytic reactions, 213*Evgeny Rebrov and Sourav Chatterjee*

- 9.1 Introduction, 213
- 9.2 Single-phase catalytic microreactors, 213
 - 9.2.1 Residence time distribution, 213
 - 9.2.2 Effect of flow maldistribution, 214
 - 9.2.3 Mass transfer, 215
 - 9.2.4 Heat transfer, 215
- 9.3 Multiphase microreactors, 216
 - 9.3.1 Microstructured packed beds, 216
 - 9.3.2 Microchannel reactors, 218
- 9.4 Conclusions and outlook, 225
- Nomenclature, 226
- Greek letters, 227
- Subscripts, 227
- References, 228

Part 5 Essential tools of reactor modeling and design**10 Experimental methods for the determination of parameters, 233***Rebecca R. Fushimi, John T. Gleaves and Gregory S. Yablonsky*

- 10.1 Introduction, 233
- 10.2 Consideration of kinetic objectives, 234
- 10.3 Criteria for collecting kinetic data, 234
- 10.4 Experimental methods, 234
 - 10.4.1 Steady-state flow experiments, 235
 - 10.4.2 Transient flow experiments, 237
 - 10.4.3 Surface science experiments, 238
- 10.5 Microkinetic approach to kinetic analysis, 241
- 10.6 TAP approach to kinetic analysis, 241
 - 10.6.1 TAP experiment design, 242
 - 10.6.2 TAP experimental results, 244
- 10.7 Conclusions, 248
- References, 249

11 Numerical solution techniques, 253*Ahmet Kerim Avci and Seda Keskin*

- 11.1 Techniques for the numerical solution of ordinary differential equations, 253
 - 11.1.1 Explicit techniques, 253
 - 11.1.2 Implicit techniques, 254
- 11.2 Techniques for the numerical solution of partial differential equations, 255

- 11.3 Computational fluid dynamics techniques, 256
 - 11.3.1 Methodology of computational fluid dynamics, 256
 - 11.3.2 Finite element method, 256
 - 11.3.3 Finite volume method, 258
- 11.4 Case studies, 259
 - 11.4.1 Indirect partial oxidation of methane in a catalytic tubular reactor, 259
 - 11.4.2 Hydrocarbon steam reforming in spatially segregated microchannel reactors, 261
- 11.5 Summary, 265
- Nomenclature, 266
- Greek letters, 267
- Subscripts/superscripts, 267
- References, 267

Part 6 Industrial applications of multiphase reactors

- 12 Reactor approaches for Fischer–Tropsch synthesis, 271
Gary Jacobs and Burtron H. Davis
 - 12.1 Introduction, 271
 - 12.2 Reactors to 1950, 272
 - 12.3 1950–1985 period, 274
 - 12.4 1985 to present, 276
 - 12.4.1 Fixed-bed reactors, 276
 - 12.4.2 Fluidized-bed reactors, 280
 - 12.4.3 Slurry bubble column reactors, 281
 - 12.4.4 Structured packings, 286
 - 12.4.5 Operation at supercritical conditions (SCF), 288
 - 12.5 The future?, 288
 - References, 291
- 13 Hydrotreating of oil fractions, 295
Jorge Ancheyta, Anton Alvarez-Majmutov and Carolina Leyva
 - 13.1 Introduction, 295
 - 13.2 The HDT process, 296
 - 13.2.1 Overview, 296
 - 13.2.2 Role in petroleum refining, 297
 - 13.2.3 World outlook and the situation of Mexico, 298
 - 13.3 Fundamentals of HDT, 300
 - 13.3.1 Chemistry, 300
 - 13.3.2 Reaction kinetics, 303
 - 13.3.3 Thermodynamics, 305
 - 13.3.4 Catalysts, 306
 - 13.4 Process aspects of HDT, 307
 - 13.4.1 Process variables, 307

- 13.4.2 Reactors for hydroprocessing, 310
- 13.4.3 Catalyst activation in commercial hydrotreaters, 316
- 13.5 Reactor modeling and simulation, 317
 - 13.5.1 Process description, 317
 - 13.5.2 Summary of experiments, 317
 - 13.5.3 Modeling approach, 319
 - 13.5.4 Simulation of the bench-scale unit, 320
 - 13.5.5 Scale-up of bench-unit data, 323
 - 13.5.6 Simulation of the commercial unit, 324
- Nomenclature, 326
- Greek letters, 327
- Subscripts, 327
- Non-SI units, 327
- References, 327

- 14 Catalytic reactors for fuel processing, 330
Gunther Kolb
 - 14.1 Introduction—The basic reactions of fuel processing, 330
 - 14.2 Theoretical aspects, advantages, and drawbacks of fixed beds versus monoliths, microreactors, and membrane reactors, 331
 - 14.3 Reactor design and fabrication, 332
 - 14.3.1 Fixed-bed reactors, 332
 - 14.3.2 Monolithic reactors, 332
 - 14.3.3 Microreactors, 332
 - 14.3.4 Membrane reactors, 333
 - 14.4 Reformers, 333
 - 14.4.1 Fixed-bed reformers, 336
 - 14.4.2 Monolithic reformers, 337
 - 14.4.3 Plate heat exchangers and microstructured reformers, 342
 - 14.4.4 Membrane reformers, 344
 - 14.5 Water-gas shift reactors, 348
 - 14.5.1 Monolithic reactors, 348
 - 14.5.2 Plate heat exchangers and microstructured water-gas shift reactors, 348
 - 14.5.3 Water-gas shift in membrane reactors, 350
 - 14.6 Carbon monoxide fine cleanup: Preferential oxidation and selective methanation, 350
 - 14.6.1 Fixed-bed reactors, 352
 - 14.6.2 Monolithic reactors, 352
 - 14.6.3 Plate heat exchangers and microstructured reactors, 353
 - 14.7 Examples of complete fuel processors, 355
 - 14.7.1 Monolithic fuel processors, 355
 - 14.7.2 Plate heat exchanger fuel processors on the meso- and microscale, 357

Nomenclature, 359	
References, 359	
15 Modeling of the catalytic deoxygenation of fatty acids in a packed bed reactor, 365	
<i>Teuvo Kilpiö, Päivi Mäki-Arvela, Tapio Salmi and Dmitry Yu. Murzin</i>	
15.1 Introduction, 365	15.7 Parameter sensitivity studies, 369
15.2 Experimental data for stearic acid deoxygenation, 366	15.8 Parameter identification studies, 370
15.3 Assumptions, 366	15.9 Studies concerning the deviation from ideal plug flow conditions, 371
15.4 Model equations, 367	15.10 Parameter estimation results, 372
15.5 Evaluation of the adsorption parameters, 368	15.11 Scale-up considerations, 372
15.6 Particle diffusion study, 369	15.12 Conclusions, 375
	Acknowledgments, 375
	Nomenclature, 375
	Greek letters, 375
	References, 376
	Index, 377