MULTIPHASE Catalytic REACTORS

THEORY, DESIGN, MANUFACTURING, AND APPLICATIONS



รษษษษษ

IJ



EDITED BY ZEYNEP ILSEN ÖNSAN AHMET KERIM AVCI

WILEY

T

Multiphase Catalytic Reactors

Multiphase Catalytic Reactors

Theory, Design, Manufacturing, and Applications

Edited by

Zeynep Ilsen Önsan

Department of Chemical Engineering Boğaziçi University Istanbul, Turkey

Ahmet Kerim Avci

Department of Chemical Engineering Boğaziçi University Istanbul, Turkey

WILEY

Copyright © 2016 by John Wiley & Sons, Inc. All rights reserved

Published by John Wiley & Sons, Inc., Hoboken, New Jersey

Published simultaneously in Canada

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at http://www.wiley.com/go/permissions.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data:

Names: Önsan, Zeynep Ilsen, editor. | Avci, Ahmet Kerim, editor.
Title: Multiphase catalytic reactors : theory, design, manufacturing, and applications / edited by Zeynep Ilsen Önsan, Ahmet Kerim Avci.
Description: Hoboken, New Jersey : John Wiley & Sons Inc., [2016] | Includes bibliographical references and index.
Identifiers: LCCN 2016009674 | ISBN 9781118115763 (cloth) | ISBN 9781119248477 (epub) | ISBN 9781119248460 (epdf)
Subjects: LCSH: Phase-transfer catalysis. | Chemical reactors.
Classification: LCC TP159.C3 M85 2016 | DDC 660/.2832–dc23 LC record available at https://lccn.loc.gov/2016009674

Set in 9.5/12pt Minion by SPi Global, Pondicherry, India

Printed in the United States of America

 $10\quad 9\quad 8\quad 7\quad 6\quad 5\quad 4\quad 3\quad 2\quad 1$

Contents

List of Contributors, x

Preface, xii

Part 1 Principles of catalytic reaction engineering

- 1 Catalytic reactor types and their industrial significance, 3 *Zeynep Ilsen 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 Ilsen 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
 - 2.2.1 Kinetic models and mechanisms, 25 2.2.2 Analysis and correlation of rate data, 27
 - 2.3 External (interphase) transport processes, 322.3.1 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 Alírio 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, 613.3.1 Chemical regime, 643.3.2 Diffusional regime, 64
 - 3.4 Dominant fluid-solid mass transfer, 663.4.1 Isothermal axial flow bed, 673.4.2 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

- 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

Nomenclature, 74

- 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 Faïçal 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, 1045.3.1 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, 1085.4.2 Scaling down of trickle-bed reactors, 109
 - 5.4.3 Salient conclusions, 110
- 5.5 Trickle-bed reactor/bioreactor modeling, 1105.5.1 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, 1436.3.1 Lower order models, 1436.3.2 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, 1597.3.1 Operation with enzymes, 1597.3.2 Operation with living cells, 160
- 7.4 Immobilized enzymes and cells, 1647.4.1 Mass transfer effects, 1647.4.2 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 Alírio 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, 2028.3.5 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, 2169.3.1 Microstructured packed beds, 2169.3.2 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 GregoryS. 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, 24110.6.1 TAP experiment design, 24210.6.2 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, 25611.3.1 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, 27612.4.2 Fluidized-bed reactors, 28012.4.3 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, 29613.2.1 Overview, 29613.2.2 Role in petroleum refining, 29713.2.3 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, 30713.4.1 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, 33314.4.1 Fixed-bed reformers, 33614.4.2 Monolithic reformers, 337
 - 14.4.3 Plate heat exchangers and microstructured reformers, 34214.4.4 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, 34814.5.3 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, 35514.7.1 Monolithic fuel processors, 35514.7.2 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 *Teuvo Kilpiö, Päivi Mäki-Arvela, Tapio Salmi and Dmitry Yu. Murzin*
 - 15.1 Introduction, 365
 - 15.2 Experimental data for stearic acid deoxygenation, 366
 - 15.3 Assumptions, 366
 - 15.4 Model equations, 367
 - 15.5 Evaluation of the adsorption parameters, 368
 - 15.6 Particle diffusion study, 369

- 15.7 Parameter sensitivity studies, 369
- 15.8 Parameter identification studies, 370
- 15.9 Studies concerning the deviation from ideal plug flow conditions, 371
- 15.10 Parameter estimation results, 372
- 15.11 Scale-up considerations, 372
- 15.12 Conclusions, 375
- Acknowledgments, 375
- Nomenclature, 375
- Greek letters, 375
- References, 376
- Index, 377

List of contributors

Anton Alvarez-Majmutov

Instituto Mexicano del Petróleo, Management of Products for the Transformation of Crude Oil, Mexico City, Mexico

Jorge Ancheyta Instituto Mexicano del Petróleo, Management of Products for the Transformation of Crude Oil, Mexico City, Mexico

Ahmet Kerim Avci Department of Chemical Engineering, Boğaziçi University, Istanbul, Turkey

Vivek V. Buwa Department of Chemical Engineering, Indian Institute of Technology-Delhi, New Delhi, India

Joaquim M.S. Cabral

Department of Bioengineering and IBB-Institute for Bioengineering and Biosciences, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

Sourav Chatterjee School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, UK

Burtron H. Davis Center for Applied Energy Research, University of Kentucky, Lexington, KY, USA

Pedro Fernandes

Department of Bioengineering and IBB-Institute for Bioengineering and Biosciences, Instituto Superior Técnico, Universidade de Lisboa; Faculdade de Engenharia, Universidade Lusófona de Humanidades e Tecnologias, Lisboa, Portugal

Rebecca R. Fushimi Materials Science & Engineering Department, Idaho National Laboratory, Idaho Falls, ID, USA

John T. Gleaves Department of Energy, Environmental and Chemical Engineering, Washington University, St. Louis, MO, USA

John R. Grace Department of Chemical and Biological Engineering, The University of British Columbia, Vancouver, British Columbia, Canada

Ion Iliuta

Chemical Engineering Department, Laval University, Québec City, Québec, Canada

Gary Jacobs

Center for Applied Energy Research, University of Kentucky, Lexington, KY, USA

Seda Keskin

Department of Chemical and Biological Engineering, Koc University, Istanbul, Turkey

Teuvo Kilpiö

Process Chemistry Centre, Åbo Akademi University, Turku/Åbo, Finland

Gunther Kolb

Fraunhofer ICT-IMM, Decentralized and Mobile Energy Technology Department, Mainz, Germany

Faïçal Larachi

Chemical Engineering Department, Laval University, Québec City, Québec, Canada

Carolina Leyva

Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Unidad Legaria, Instituto Politécnico Nacional, Mexico City, Mexico

João P. Lopes

Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, UK

Päivi Mäki-Arvela

Process Chemistry Centre, Åbo Akademi University, Turku/Åbo, Finland

Dmitry Yu. Murzin

Process Chemistry Centre, Åbo Akademi University, Turku/Åbo, Finland

Zeynep Ilsen Önsan

Department of Chemical Engineering, Boğaziçi University, Istanbul, Turkey

Vivek V. Ranade

Chemical Engineering & Process Development Division, National Chemical Laboratory, Pune, India

Evgeny Rebrov

School of Engineering, University of Warwick, Coventry, UK

Alírio E. Rodrigues

Laboratory of Separation and Reaction Engineering, Associate Laboratory LSRE/LCM, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Porto, Portugal

Shantanu Roy

Department of Chemical Engineering, Indian Institute of Technology-Delhi, New Delhi, India

Tapio Salmi

Process Chemistry Centre, Åbo Akademi University, Turku/Åbo, Finland

Gregory S. Yablonsky

Parks College of Engineering, Aviation and Technology, Saint Louis University, St. Louis, MO, USA

Preface

The single irreplaceable component at the core of a chemical process is the chemical reactor where feed materials are converted into desirable products. Although the essential variables by which chemical processes can be controlled are reaction temperature, pressure, feed composition, and residence time in the reactor, two technological developments of major consequence starting with 1960s have made possible cost-effective operation under less severe conditions; these are the extensive use of efficient catalysts and the introduction of improved or innovative reactor configurations. The impact of heterogeneous catalysis is significant in this respect since petroleum refining, manufacturing of chemicals, and environmental clean-up, which are the three major areas of the world economy today, all require the effective use of solid catalysts. The challenges involved in the design of novel solid catalysts and modification of many existing ones for higher selectivity and stability have also prompted the development of "engineered" catalysts befitting novel reactor configurations, requiring the use of new supports such as monolithic or foam substrates as well as the establishment of new techniques for coating surfaces with diverse catalyst components in order to ensure longevity particularly in cyclic processes.

In industrial practice, the composition and properties of the complex feed mixtures that are processed for producing a range of valuable chemicals generally necessitate the use of heterogeneous catalytic reactors. Numerous chemical and physical rate processes take place in a heterogeneous reactor at different length and time scales and frequently in different phases. The prerequisite for the successful design and operation of catalytic reactors is a thorough microkinetic analysis starting from intrinsic kinetic models of the steady-state chemical activity and leading to global rate expressions obtained by overlaying the effects of physical rate phenomena occurring at the particle scale. Kinetic models of increasing complexity may be required depending on the variety of components and number of reactions involved. The second critical stage in reactor modeling and design is a macrokinetic analysis including the detailed description of physical transport phenomena at the reactor scale and utilizing the global rate expressions of the microkinetic analysis. The final catalytic reactor model which integrates these essential stages can successfully predict the performance and dynamics of plant-scale industrial reactors as well as simulating their start-up, shutdown, and cyclic operation. Taking into account engineered catalysts and new reactor configurations, the modeling and scaling up of reactions conducted at the bench-scale to pilot plant and industrial-scale reactor levels have to be modified in order to include simultaneous multiscale approaches along with the conventional sequential modes.

Multiphase Catalytic Reactors: Theory, Design, Manufacturing, and Applications is a comprehensive up-to-date compilation on multiphase catalytic reactors which will serve as an excellent reference book for graduate students, researchers, and specialists both in academia and in industry. The content of the book is planned to cover topics starting from the first principles involved in macrokinetic analysis of two- and three-phase catalytic reactors to their particular industrial applications. The main objective is to provide definitive accounts on academic aspects of multiphase catalytic reactor modeling and design along with detailed descriptions of some of the most recent industrial applications employing multiphase catalytic reactors, in such a way as to balance the academic and industrial components as much as possible. Accordingly, seven chapters are included in Parts II, III, and IV to review the relevant mathematical models and model equations utilized in the fundamental analysis and macroscopic design of specific reactor types together with some useful approximations for their design and scale-up from a practical standpoint, while the four chapters in Part VI describe specific industrial applications and contain pointers that tie in with the modeling and design approaches presented for the particular multiphase catalytic reactor types discussed in Parts II, III, and IV. Furthermore, the chapters included in Parts I and V of the book contain detailed reviews of the basic principles and essential tools of catalytic reaction engineering that are crucial for the successful design and operation of catalytic reactors. All chapters of the book are contributed by experts distinguished in their respective fields.

The total of 15 chapters included in *Multiphase Catalytic Reactors: Theory, Design, Manufacturing, and Applications* are organized in six parts. Part I is an overview of the principles of catalytic reaction engineering, embracing Chapter 1 which is a survey of multiphase catalytic reactor types and their industrial significance as well as Chapter 2 on the microkinetic analysis of heterogeneous catalytic systems which surveys the formulation of intrinsic rate equations describing chemical rate processes and the construction of global rate expressions that include the effects of physical mass and heat transport phenomena occurring at the particle scale. Chapters 3 through 9 in Parts II, III, and IV discuss individual two- and three-phase catalytic reactor types and provide design equations and empirical relationships that characterize different multiphase reactors; mathematical modeling is an integral part of these chapters. In Part II, two-phase catalytic reactors are grouped as fixedbed gas-solid catalytic reactors (Chapter 3) and fluidized-bed catalytic reactors (Chapter 4). Part III deals exclusively with three-phase catalytic reactors and includes Chapter 5 on three-phase fixed-bed reactors as well as Chapter 6 on threephase slurry reactors, both of which find significant industrial applications; moreover, multiphase bioreactors are also included in Part III as Chapter 7. Part IV is devoted to the discussion of the more recent state-of-the-art structured reactors; the theoretical aspects and examples of structured reactors enabling process intensification in multiphase operation are treated in Chapter 8 on monolith reactors and in Chapter 9 on microreactors of different configurations including microstructured packed beds and microchannel reactors. Part V of the book is specifically designed for surveying the essential tools of catalytic reactor modeling and design and comprises two chapters. Chapter 10 discusses the recent developments and experimental techniques involved in lab-scale testing of catalytic reactions, including steady-state and transient flow experiments as well as the microkinetic and TAP approaches to kinetic analysis, while Chapter 11 surveys the numerical solution techniques that are frequently used in catalytic reactor analysis and demonstrates with some case studies. The capstone section of the book, Part VI, contains four chapters devoted to specific industrial applications of multiphase catalytic reactors and includes the

recent developments and practices in Fischer–Tropsch technologies (Chapter 12); a thorough discussion of reactor modeling, simulation, and scale-up approaches involved in the hydrotreating of oil fractions (Chapter 13); a detailed assessment of the performances of various reactor configurations used for fuel processing (Chapter 14); and a comprehensive discussion of catalytic deoxygenation of fatty acids in a packed-bed reactor as case study in production of biofuels (Chapter 15).

It is indeed a pleasure to thank all of the contributors who have made this challenging task achievable. The editors are sincerely grateful for their willingness to devote their valuable time and effort to this project, for their readiness in sharing their vision, knowledge, years of experience, and know-how, and also for their patience in tolerating various expected or unexpected extensions arising from the busy schedules of different contributors. It has definitely been a privilege to work with the authors, coauthors, and reviewers involved in this book. The editors would also like to extend their thanks to Wiley-Blackwell for their commitment to this project and to Michael Leventhal for his organization and management of the publication process.

On a more personal note, the editors would like to take this opportunity to express their sincere gratitude to the late Professor David L. Trimm, who has inspired their research in catalysis and catalytic reaction engineering through many years as supervisor, mentor, colleague, and friend.

> Zeynep Ilsen Önsan, Ahmet Kerim Avci, Istanbul, October 2015

Principles of catalytic reaction engineering

CHAPTER 1 Catalytic reactor types and their industrial significance

Zeynep Ilsen Önsan and Ahmet Kerim Avci

Department of Chemical Engineering, Boğaziçi University, Istanbul, Turkey

Abstract

The present chapter is aimed to provide a simplified overview of the catalytic reactors used in chemical industry. Each reactor type is described in terms of its key geometric properties, operating characteristics, advantages, and drawbacks among its alternatives and typical areas of use. The significance of the reactors is explained in the context of selected industrial examples. Industrial reactors that do not involve the use of solid catalysts are also discussed.

1.1 Introduction

Today's chemical markets involve many different products with diverse physical and chemical properties. These products are produced in chemical plants with different architectures and characteristics. Despite these differences, general structure of a chemical plant can be described by three main groups of unit operations, namely, upstream operations, downstream operations, and the reaction section, as shown in Figure 1.1. Among these groups, the reactor is the most critical section that determines the plant profitability via metrics such as reactant conversion, product selectivity, and yield: high per-pass conversions will reduce the operating expenses involved in product separation and purification steps as well as the recycling costs (Figure 1.1). At this stage selection of the appropriate reactor type and ensuring their efficient operation become critical issues to be addressed.

In almost all reactors running in the chemical industry, the desired product throughput and quality are provided by catalysts, the functional materials that allow chemical synthesis to be carried out at economic scales by increasing the reaction rates. Owing to this critical feature, more than 98% of the today's industrial chemistry is involved with catalysis. Since catalysts have direct impact on reactor performance, they have to be operated at their highest possible effectiveness, which is determined by the degree of internal and external heat and mass transport resistances defined and explained in detail in Chapter 2. At this stage, the function of the reactor is to provide

conditions such that the catalyst particles can deliver the best possible performance (e.g., activity, selectivity, yield) at sufficient stability. For example, for a highly exothermic reaction system such as Fischer-Tropsch (FT) synthesis, heat transport/removal rates within the reactor should be very high to prevent undesired temperature elevations that can negatively affect product distribution and, more importantly, cause thermally induced deactivation of the catalysts. Considering the fact that transport rates are favored by good mixing of the reactive fluid at turbulent conditions, the selected reactor type should allow a wide operating window in terms of pressure drop, which is a limit against the occurrence of well-mixed conditions. The possibility of integration and operation of effective external heat exchange systems should also be taken into account in the selected reactor type. The final selection is carried out in the context of fixed capital investment, operating expenses, and profitability of the technically feasible solutions.

Synthesis of commercial chemical products having different physical and chemical functional properties involves the existence of different combinations of catalytic chemistry, thermodynamic properties, and heat and mass transport conditions (e.g., nature of the catalyst and fluids) within the reactor volume. As a result, several reactor types are being proposed. Classification of the reactors can be carried out based on various criteria such as compatibility with the operating mode (batch vs. continuous reactors) and the number of phases (homogeneous vs. heterogeneous reactors). In this chapter, reactors are classified according to the position of the catalyst bed, that is, whether it is fixed or mobile. In packed-bed, trickle-bed, and structured (i.e., monolith and microchannel) reactors, catalyst bed is fixed, while it is mobile in fluidized-bed, moving-bed, and slurry reactors. The descriptions of these reactor types are summarized in the following sections.

1.2 Reactors with fixed bed of catalysts

1.2.1 Packed-bed reactors

In packed-bed reactors (PBRs), the solid particulate catalyst particles forming the bed are fixed in an enclosed volume. The

Multiphase Catalytic Reactors: Theory, Design, Manufacturing, and Applications, First Edition. Edited by Zeynep Ilsen Önsan and Ahmet Kerim Avci. © 2016 John Wiley & Sons, Inc. Published 2016 by John Wiley & Sons, Inc.



Figure 1.1 Outline of a chemical process.



Figure 1.2 Schematic presentation of a packed-bed reactor. (Source: Onsan and Avci [1]. Reproduced with permission of Elsevier.)

particles are randomly packed, so there is not a regular structure, and, as a result, fluid flow takes place through irregular, random paths. Reactions take place over the active sites that are buried within the pores of the catalyst particles. A simple description of the PBR operation is shown in Figure 1.2 [1]. Owing to their relatively simple configuration and operation, PBRs are widely used in the chemical industry. They are used in high-throughput, continuous operations. Since the catalyst is considered as a separate solid phase and the fluid types are either gas only or gasliquid mixtures, PBRs are classified as heterogeneous reactors. In the case of coexistence of three phases with concurrent downflow of liquid and gas over the solid packing, the reactor is called as a trickle-bed reactor (see Section 1.2.4). The geometry of the catalyst-containing volume, which can be either a tube or a vessel, dictates the type of the PBR. Descriptions of the so-called tubular and vessel-type PBRs are given later.

1.2.1.1 Tubular PBRs

PBRs are known to have inherently weak heat transfer properties due to the presence of voids within the catalyst bed (Figure 1.2 [1]) that act as resistances against the transport of heat along the reactor. The tubular PBR geometry, which involves the location of catalyst-containing tubes in a particular pattern within a shell, is preferred over a regular vessel when high rates of heat input or removal are essential for highly endothermic or exothermic reactions, respectively. This advantage of the tubular configuration, however, comes at the expense of higher pressure drop. It is also worth noting that the process of catalyst packing and unloading in tubular geometry is more difficult than that involved in vessels. Therefore, catalyst lifetime in tubular PBRs should be long enough to minimize the downtimes for and costs associated with catalyst changeover.

The shell/tube configuration of tubular PBRs depends on the nature of the catalytic reaction. For highly endothermic reactions such as catalytic steam reforming, the reactor geometry is similar to that of a fired furnace in which the catalyst-packed tubes are heated by the energy released by the combustion of a fuel on the shell side. Catalytic steam reforming involves the conversion of a hydrocarbon to a hydrogen-rich mixture in the presence of steam:

$$C_m H_n O_k + (m - k) H_2 O = m CO + (m - k + n/2) H_2, (m > k) \qquad \Delta H^{\circ} > 0$$
(1.1)

The process is known as the conventional method of producing hydrogen for meeting the hydrogen demands of the refining and petrochemical industry. The most widely used fuel in steam reforming is natural gas, which is mostly composed of methane:

$$CH_4 + H_2O = CO + 3H_2, \quad \Delta H^\circ = 206 \text{ kJ/mol}$$
 (1.2)

Methane steam reforming is conventionally carried out over Ni-based catalysts. Owing to the high endothermicity and slow kinetics, the process depends strongly on the input of external energy at high rates for ensuring commercially viable throughput of hydrogen. The critical energy demand of the reaction is met in a reactor (also called as the reformer) where multiple Ni-based catalyst-packed tubes are heated mainly via radiative heat generated by homogeneous combustion of a fuel, typically natural gas, in a process furnace. This configuration sets the basis for the development and use of various types of commercial steam reforming reactors described in Figure 1.3 [2], which differ in the positions of heat source and the degree of delivery of the combustion energy to the so-called reformer tubes. A further detailed representation of a tubular reformer is provided in Figure 1.4 [2]. Depending on the capacity of the reactor, the number of tubes can be increased up to 1000, each having outer diameter, wall thickness, and heated length ranges of 10-18 cm, 0.8-2.0 cm and 10-14 m, respectively. The degree of furnace-totube heat transfer affecting the rate of Reaction 1.2 and hydrogen production capacity of the reactor is limited by thermal stability of the tube material which is found to decrease significantly with temperature above ca. 850°C [3]. Therefore special alloys, particularly microalloys, composed of 25Cr 35Ni Nb Ti are used to improve the operating window of the reactor [3].

The multitubular PBR configuration is preferred when convection is not sufficient for delivering the necessary heat flux to sustain the operation. However, in most of the exothermic and endothermic reactions, the temperature of the catalyst bed can be regulated by convective external heat transfer. In



Figure 1.3 Furnace configurations for multitubular packed-bed reformers. (Source: Dybkjaer [2]. Reproduced with permission of Elsevier.)



Figure 1.4 Side-fired tubular reformer design by Haldor-Topsøe. (Source: Dybkjaer [2]. Reproduced with permission of Elsevier.)

such cases, the catalyst-containing tubes are bundled in a shelland-tube heat exchanger like configuration involving circulation of the heat transfer fluid on the shell side. This PBR concept is described in Figure 1.5 [4] in which alternative methods of circulation of the heat transfer fluid around the packed tubes are introduced. In mildly endothermic or exothermic reactions, heat transfer can be realized to provide nearly isothermal conditions in cross-flow and parallel flow configurations shown in Figure 1.5a and b [4], respectively. In such reactors, inside diameters and lengths of the tubes are reported to vary between 2–8 cm and 0.5–15 m, respectively [4]. For endothermic cases, the heating medium can be a gas or a liquid, with the latter

offering better heat transfer rates due to higher convective heat transfer coefficients of liquids. Cooling in exothermic reactions is carried out either by circulation of a heat transfer fluid or by boiling heat transfer. In the former case, fluids such as molten salts are force-circulated around the tube bundle. The heated liquid leaving the reactor is then passed through an external steam generator and cooled for the next cycle. In the case of boiling heat transfer (Figure 1.5c [4]), however, the cooling fluid that is fed from the bottom of the reactor rises up due to natural circulation induced by the decreasing density profile that is caused by continuous heat absorption from the tubes. Partial evaporation of the cooling water is also observed. Vapor bubbles agitate the liquid and increase the convective heat transfer coefficient. The resulting vapor-liquid mixture is then let to settle in a steam drum where steam is separated, and the remaining liquid sent back to the cooling cycle together with some makeup water. Even though this configuration eliminates the need for cooling fluid transportation equipment, the tubes may be overheated if heat generation in the tubes becomes excessive to evaporate cooling water on the shell side. In such a case, the rate of convective heat removal will be less than the rate of catalytic heat generation, and the tubes are subjected to the risk of burning out.

In multitubular PBRs heat management can be improved by increasing the heat transfer area per catalyst volume, which is possible by using tubes with smaller diameters. In this case, definite amounts of catalyst will be packed into a higher number of tubes, which will offer increased external tube surface area for heat transfer. Due to the reduced tube cross-sectional area, smaller tube diameters will also increase the linear flow rate of the reactive mixture and favor well-mixed conditions that increase the heat transport rates. However, these advantages are naturally limited by pressure drop, as higher flow rates will cause increased frictional loss of mechanical energy of the reactive fluid and will require increased pumping/compression costs. Nevertheless, the trade-off between heat transfer rates and pressure drop can be relaxed by the possibility of using different combinations of size, shape, and material of the catalyst pellets [4, 5]. For example, pellet shapes offering higher void fractions and larger hydraulic diameters allow lower pressure drop operations. It is worth noting that the rate of catalytic reactions increases with the surface area of the catalyst bed that necessitates the use of smaller pellets. Therefore pellet size also requires careful optimization.



Figure 1.5 Heat transfer strategies in multitubular packed-bed reactors. (a) Cross-flow, (b) parallel flow, and (c) boiling-water cooling. (Source: Eigenberger [4]. Reproduced with permission of John Wiley & Sons, Inc.)



Figure 1.6 Various configurations of vessel-type packed-bed reactors. (a) Single-bed adiabatic packed-bed reactor, (b) adiabatic reactor with interstage gas injection, and (c) multiple adiabatic beds with interstage heat exchange. (Source: Eigenberger [4]. Reproduced with permission of John Wiley & Sons, Inc.)

The length and diameter of the tube and the particle size (hydraulic diameter) also affect flow distribution within the packed tube. If the ratio of the tube diameter to that of the particle diameter is above 30, radial variations in velocity can be neglected, and plug (piston) flow behavior can be assumed. The ratio of the tube length to particle diameter is also important; if this ratio exceeds 50, axial dispersion and axial heat conduction effects can be ignored. These effects bring notable simplifications into the modeling of PBRs, which are discussed in Chapter 3.

1.2.1.2 Vessel-type PBRs

The design and operational requirements explained for tubular PBRs are also valid for PBRs in which the catalyst bed is packed in one vessel as described schematically in Figure 1.6a [4]. This reactor configuration is preferred when the reaction is carried out at adiabatic conditions. However, as demonstrated in Figure 1.6b and c [4], bed temperature can be changed by heat addition to/removal from the bed for obtaining a temperature

profile as close as possible to that of the optimum. Figure 1.6b [4] is a representation of addition or removal of heat to/from the catalyst bed by direct injection of hot or cold feed to the bed. This heat management strategy can be used where the heats of reactions are low. Successful implementation of this strategy depends on careful consideration of mixing and redistribution of the injected fluid with that of the reactive mixture and of the adiabatic temperature change upon injection, which should be within acceptable limits. A better regulation of the bed temperature is possible by the use of interstage heat exchangers between multiple adiabatic beds (Figure 1.6c [4]). This configuration is more suitable for improving conversions or product selectivities in reactions limited by chemical equilibrium. The possibility of using different heat exchange equipment between the stages helps in handling high reaction enthalpies. For endothermic reactions, interstage heating is usually carried out by means of fired heating, in which the heat transfer fluid is heated in a fired furnace and then circulated between the beds to provide heat to the reactive fluid. Adiabatic heat generated during exothermic reactions is removed by contacting the hot bed effluent with interstage heat exchange tubes in which a coolant, for example, water, is circulated for steam generation purposes.

Multiple adiabatic beds with interstage heat exchange configuration compete with tubular PBR geometry, as both configurations provide regulation of the bed temperature to improve reactant conversion and product selectivity. In this respect, the tubular PBR alternative is better, because it offers continuous control over the bed temperature. However, although temperature regulation is only possible through a stepwise pattern in the multiple adiabatic beds, they do offer several practical advantages such as the possibility of (i) changing the catalyst bed in individual stages at different times, (ii) distributed stagewise feeding of a reactant instead of its total feeding at the inlet, and (iii) drawing a limiting product from an intermediate stage in case of reactions limited by equilibrium [4, 5].

Vessel-type PBRs are widely used in chemical industry. A descriptive example is ammonia synthesis, which is an exothermic equilibrium reaction:

$$N_2 + 3H_2 = 2NH_3, \quad \Delta H^\circ = -92.4 \text{ kJ/mol}$$
 (1.3)

The reaction is carried out in a multistage PBR with interstage cooling (Figure 1.7 [4]) in the 400–500°C range and involves the use of iron-based catalysts. In order to favor ammonia production by shifting the chemical equilibrium to the product side, pressures up to 300 bar are required. As adiabatic temperature rise hinders conversion due to the equilibrium limit, the reactive mixture is cooled down between the beds, and the recovered heat is used for steam generation. The resulting conditions deliver a product mixture including ca. 20% NH₃ which is separated by a series of condensers. Upon separation, unreacted mixture of N₂ and H₂ is combined with fresh makeup feed and recycled to the first stage of the reactor.

Another commercial example involving the use of a vesseltype PBR is autothermal reforming (ATR) of natural gas. It is a key step in gas-to-liquid (GTL) processes and is used to produce synthesis gas (CO + H₂) for FT synthesis in which a mixture of hydrocarbons in the C₁–C₃₀₊ range is synthesized [6]. In ATR, noncatalytic oxidation (Reaction 1.4) and Ni-catalyzed steam reforming of natural gas (Reaction 1.2) are combined, and product distribution is affected by water–gas shift (Reaction 1.5), an important side reaction of steam reforming [3, 7]:

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O, \quad \Delta H^\circ = -519 \text{ kJ/mol}$$
(1.4)

$$CH_4 + H_2O = CO + 3H_2, \quad \Delta H^\circ = 206 \text{ kJ/mol}$$
 (1.2)

$$CO + H_2O = CO_2 + H_2, \quad \Delta H = -41 \text{ kJ/mol}$$
 (1.5)

ATR is carried out in an adiabatic PBR as described in Figure 1.8 [7]. Natural gas, steam, and oxygen (or enriched air) are cofed to a mixer-burner unit for ensuring combustion of the homogeneous mixture of reactants taking place in the combustion chamber. Heat produced in the combustion zone, where temperature can be well above ca. 1500°C, is then transferred to the Ni-based catalyst bed on which Reactions 1.2 and 1.5 take place to produce a mixture of H₂ and CO at molar ratios close to 2 at temperatures above ca. 1000°C and at pressures up to ca. 30 bar [3, 7]. Success of the reactor depends on keeping the exothermic heat within the vessel, that is, operating the reactor adiabatically. For this purpose, the inner wall of the steel pressure vessel is lined with multiple layers of refractory insulation. A special catalyst pellet shape including numerous holes is used to minimize pressure drop along the bed and to avoid bypass of gas through the refractory layer.



Figure 1.7 Packed-bed reactor with multiple adiabatic beds for ammonia synthesis.

(Source: Eigenberger [4]. Reproduced with permission of John Wiley & Sons, Inc.)



Figure 1.8 Packed-bed reactor configuration for autothermal reforming of methane to synthesis gas.

(Source: Aasberg-Petersen et al. [7]. Reproduced with permission of Elsevier.)

1.2.2 Monolith reactors

Monolith reactors are composed of a large number of parallel channels, all of which contain catalyst coated on their inner walls (Figure 1.9 [1]). Depending on the porosity of the monolith structure, active metals can be dispersed directly onto the inner channel walls, or the catalyst can be washcoated as a separate layer with a definite thickness. In this respect, monolith reactors can be classified among PBR types. However, their characteristic properties are notably different from those of the PBRs presented in Section 1.2.1. Monolith reactors offer structured, well-defined flow paths for the reactive flow, which occurs through random paths in PBRs. In other words, the residence time of the reactive flow is predictable, and the residence time distribution is narrow in monoliths, whereas in a PBR, different elements of the reactive mixture can pass through the bed at different rates, resulting in a wider distribution of residence times. This is a situation that is crucial for reactions where an intermediate species is the desired product and has to be removed from the reactor before it is converted into an undesired species.

Hydraulic diameters of monolithic channels range between ca. 3×10^{-4} m and 6×10^{-3} m [8]. Combination of such small diameter channels leads to surface areas per reactor volume in the order of $\sim 10^4$ m²/m³ (which is $\sim 10^3$ m²/m³ for PBRs) and void fractions up to $\sim 75\%$ (which is $\sim 40\%$ for PBRs). As shown in Figure 1.10 [9], these design properties allow monolith reactors to operate with pressure drops that are up to three orders of magnitude less than those observed in PBRs.



Figure 1.9 Schematic presentation of a monolith reactor. (Source: Onsan and Avci [1]. Reproduced with permission of Elsevier.)

Monolith reactors differ from PBRs in terms of transport properties. Owing to the small channel diameters, the flow regime is laminar. In this case, channel shape and diameter dictate the values of heat and mass transfer coefficients according to the definitions of the Nusselt ($Nu = h_f d_h / \lambda_f$) and Sherwood ($Sh = k_g d_h / D_{AB}$) numbers, respectively. Assuming that the flow is fully developed, values of Nu and Sh are constant for a given channel shape [10]. However, in the case of PBRs, where turbulent flow conditions are valid, transport coefficients improve with the degree of turbulence and mixing within the reactor. It is worth noting that transport coefficients in monolith channels can be slightly affected by the flow rate if the surface of the channel is tortuous. The reader is directed to Chapter 8 for a detailed analysis and discussion of monolith reactors.

Heat management in monolith reactors via external heating or cooling is not as effective as in PBRs due to lack of convective heat transport in the radial direction. At this point, the material of construction of the monolithic structure affects the overall performance. Monolith reactors can be made of metals or ceramics. In case of nonadiabatic reactions, metallic monoliths are preferred due to their higher thermal conductivity which partially eliminates the lacking convective contribution. Ceramic monoliths, on the other hand, have very low thermal conductivities (e.g., 3 W/m.K for cordierite [11]) and are suitable for use in adiabatic operations.

Despite their notable advantages in terms of residence time distribution and pressure drop, the operating windows of monolith reactors are narrower than those of PBRs. As the catalyst is integrated to the monolithic structure, replacement of the catalyst bed in case of its irreversible deactivation becomes a serious issue. Moreover, small channels are subject to the risk of plugging either by the dirt and scale that can come together with the feed stream or by phenomena such as coking that may occur during reactions involving hydrocarbons conducted at high temperatures. In such as case, flow distribution and residence time in the channels will be disturbed, and product distribution will be adversely affected. Prevention of these risks is possible by careful selection and control of the operating conditions, which in turn put some limitations on the versatility of using monolith reactors.

The capability of offering high surface area-to-volume ratios together with low pressure drop makes monolith reactors the



unique choice for use as three-way catalytic converters in vehicles to regulate the emission levels. The compact nature of the monolithic catalytic converters allows their integration into the exhaust gas aftertreatment zone of the vehicles. These converters involve washcoated layers of precious metal catalysts that are capable of reducing the NO_x, CO, and unburned hydrocarbon content of the exhaust gas below the legislative limits. Apart from vehicular use, monolith reactors are also used in NO_x removal from flue gases in power stations because of their capability of providing adiabatic conditions with low pressure drop. It is worth noting that monolith reactors are not limited for use only in gas-phase reactions and can also be used for handling gas–liquid-type reactive mixtures [10].

1.2.3 Radial flow reactors

In addition to monolith reactors, pressure drop in fixed-bed operation can be reduced by employing radial flow reactors. These units are essentially packed-bed type, with gaseous reactive flow being in the radial direction, that is, perpendicular to the catalyst bed, instead of being in the axial direction (Figure 1.11 [4]). The radial flow pattern is achieved by directing the flow to the catalyst pellets that are packed between two perforated cylinders or concentric screens. The flow orientation is flexible, that is, can be either from outside cylinder to inside cylinder or vice versa. In this design, radial flow distance along the catalyst bed is constant and is independent of the amount of catalyst packed. This unique feature makes radial flow reactors suitable for use in cases where large catalyst volumes are needed in high-pressure operations with strict pressure drop limitations. During operation, however, the catalyst bed settles down and causes a gap for bypassing of the fresh feed through the upper



Figure 1.11 Radial flow reactor concept. (Source: Eigenberger [4]. Reproduced with permission of John Wiley & Sons, Inc.)

part of the perforated cylinder. This issue can be addressed by refining the design of the upper closure [4]. Radial flow reactors are used in such applications as the synthesis of ammonia (Figure 1.12 [12]) and methanol.

1.2.4 Trickle-bed reactors

Trickle-bed reactors are similar to the PBR geometry described in Section 1.2.1.2, with the main difference being the coexistence



Figure 1.12 Radial flow ammonia synthesis converter by Haldor-Topsøe. (Source: Couper et al. [12]. Reproduced with permission of Elsevier.)

of gas and liquid phases in the reactive mixture and putting trickle-bed reactors among those classified as three-phase (gas-liquid-solid) reactors. In gas-solid PBRs described in Section 1.2.1.2, headspace above the catalyst bed is usually filled with inert ceramic balls to ensure uniform distribution of the gaseous feed over the entire bed. Cocurrent feeding of gas and liquid phases, however, calls for using a more sophisticated distributor design that is expected to mix the two phases and then distribute them uniformly across the catalyst bed to ensure sufficient wetting of the catalyst pellets and to prevent channeling of the gas and liquid components in the feed. The requirement of sophisticated distributors such as bubble cap trays is another factor that differentiates trickle-bed reactors from gas-solid PBRs. Status of feed mixture distribution to the catalyst bed dictates the diameter of the reactor, which is usually under 5 m. Height-to-diameter ratio is usually in the range of 5 and 25 [13]. Typical sizes of the catalyst pellets, which can be cylinder, sphere, extrudate, needle, or bead in shape, range between 1 and 5×10^{-3} m and give bed void fractions between ~0.35 and 0.40 [13]. Details on the design, analysis, and operation of trickle-bed reactors are provided in Chapters 5 and 13.

Trickle-bed reactors are mainly used in key petroleum refining applications such as hydrocracking, hydrodesulfurization, and hydroisomerization. The process involves the combination of hydrogenation/hydrotreating and cracking of vacuum gas oil and residues (liquid phase) to produce lighter hydrocarbons such as gasoline in the presence of hydrogen (gas phase) over a catalyst (solid phase) in the 300-600°C range and at pressures up to ~150 atm to ensure high solubility of the gaseous phase in the liquid. Conventional hydrocraking catalysts, such as Pt on aluminosilicates or zeolites, involve two components, namely, an acidic component for cracking and isomerization reactions and a noble metal component for the hydrogenation reactions [14]. The trickle-bed reactor involves the presence of up to six successive catalyst beds. Since hydrocracking reactions are exothermic, adiabatic temperature rise in each bed is regulated by interstage cooling enabled by the injection of cold hydrogen quenches; the gas-liquid mixture is remixed and redistributed prior to its entrance to the succeeding bed. In hydrodesulfurization, which is an important operation in crude oil refining, the organic sulfur components, that is, sulfides, disulfides, thiols, and thiophenes existing in crude oil (liquid phase), are converted to hydrogen sulfide in the presence of hydrogen (gas phase) over alumina-supported Co-Mo or Ni-Mo catalysts (solid phase) in the 350–400°C range. The resulting H_2S is then removed by processing over beds of ZnO. In hydroisomerization, on the other hand, the light alkanes in the C_4 - C_6 range are converted to branched-chain isomers in the presence of hydrogen for producing high-octane component additives for being blended into gasoline. The process, carried out in trickle-bed reactors, involves the use of catalysts such as Pt supported on chlorinated alumina or on acidic zeolites. In contrast with hydrocrackers, interstage heat exchange is not used in hydroisomerization reactors which involve milder conditions, with temperatures and pressures ranging between ca. 110-180°C and 20-70 atm, respectively. As exothermic equilibrium reactions are involved in hydroisomerization, the catalyst should be able to operate at low temperatures to favor the desired conversions.

1.2.5 Short contact time reactors

Pressure drop in fixed beds can be reduced by minimizing the amount of catalyst used, which leads to the existence of short contact times. In addition to reduction of pressure drop, these reactors are ideal for carrying out reactions whose extent and product distribution depend strongly on the contact time (e.g., direct partial oxidation of hydrocarbons to synthesis gas). A typical concept of such a reactor, called the disk reactor, is shown in Figure 1.13 [4]. The reactor involves a thin layer of catalyst in the form of wire gauzes or pellets, whose height and diameter are in the orders of centimeters and meters, respectively. Quenching at the downstream of the catalyst bed helps in halting further conversion of the products into other unwanted species.

In addition to the disk reactor, short contact times can also be achieved in monolith reactors (Section 1.2.2) and in microchannel reactors (Section 1.2.5), the latter involving fluid mechanical



Figure 1.13 Disk reactor concept. (Source: Eigenberger [4]. Reproduced with permission of John Wiley & Sons, Inc.)

properties and architectures similar to those of monoliths, where the existence of thin layers of washcoated porous catalysts together with high fraction of void space allows fast fluid flow almost without compromise from pressure drop (Figure 1.14 [1]). These factors lead to the occurrence of contact times in the order of milliseconds, whereas it is in the order of seconds in PBRs. Like in the case of monoliths, the existence of a structured flow pattern in microchannel units leads to precise control of residence times that promotes selective productions. Even though such similarities exist between monolith and microchannel reactors, they differ in certain aspects. Microchannel units have channel diameters in the submillimeter range, whereas larger diameter channels up to 6×10^{-3} m are used in monoliths. Owing to the constant Nu and Sh numbers per cross-sectional channel shape, higher heat and mass transport coefficients can be obtained in microchannels as a result of the smaller hydraulic diameters which also lead to higher surface area-to-volume ratios (i.e., up to $\sim 5 \times 10^4 \text{ m}^2/\text{m}^3$) than those of monoliths. These factors favor precise regulation of reaction temperature, an important benefit for strongly exothermic reactions. Due to their special manufacturing techniques involving micromachining and bonding of the plates (Figure 1.14 [1]), various nonlinear patterns (e.g., wavy shapes) along the channel length, which induce static mixing and improve heat transport, can be implemented in microchannels [15]. On the other hand, in monoliths, channels are limited to have straight axial patterns. Finally, the range of materials of construction is versatile (e.g., various metals and ceramics, polymers, silicon) in microchannels, whereas monoliths can be made of ceramics and metals only.

In addition to their advantages stated earlier, compact dimensions of the microchannel reactors allow inherently safe productions, as the risks associated with reactions (e.g., thermal runaway) are not significant due to the small quantities in the



Figure 1.14 Schematic presentation of a microchannel reactor. (a) Machined plates with microchannels, (b) microchannel reactor block obtained after bonding the plates, and (c) characteristic section of the multichannel reactor. (Source: Onsan and Avci [1]. Reproduced with permission of Elsevier.)

order of microliters processed in each channel. Even though small throughput is a disadvantage of short contact time reactors, the capacity of the microchannel reactors can be rapidly increased through the so-called numbering-up approach, which is much simpler than the traditional scaling-up approach. The resulting capacities are expected to be suitable for small-scale throughput industries such as pharmaceuticals and fine chemical productions. Applications of microchannel reactors in these industries are provided by Hessel et al. [16]. Nevertheless, production capacities of the microchannel units and other short contact time reactors are far from being able to compete with those of the continuously operating commercial reactors involved in the petroleum and petrochemical industries. The reader is directed to Chapters 9 and 14 for more detailed information about the microchannel reactors.

1.3 Reactors with moving bed of catalysts

1.3.1 Fluidized-bed reactors

Fluidized-bed reactors (FBRs) are continuously operating units of the gas-solid type, involving a catalyst bed which is fluidized when the volumetric flow rate of the gaseous feed stream exceeds a limiting value called the *minimum fluidization* flow rate. The resulting degree of mixing between the gas and solid phases in the FBR brings several operational advantages over a gas-solid PBR (Section 1.2.1). FBRs offer uniform temperature distribution due to intensive mixing, which minimizes the chance of hot spot formation in exothermic reactions. Heat management in FBRs is conventionally carried out by the heat transfer surfaces that are immersed into the reactor vessel. In this respect, fluidization favors heat transfer coefficients and subsequent fast heat exchange between the bed and immersed heat transfer surfaces. Mobility of the catalyst phase widens the operating window for allowable pressure drop. Therefore, pellet sizes smaller than those involved in PBRs can be used in FBRs, and higher reaction rates can be obtained due to increased catalytic surface area per unit bed volume. Even though higher heats of reactions evolve with increased rates, the possibility of fast heat exchange helps in effective regulation of the bed temperature. FBRs also allow constant catalytic activity either by online addition of fresh catalyst or by its continuous regeneration in a separate zone, like in the case of the fluidized catalytic cracking (FCC) operation described later. Modeling and design aspects of FBRs are explained in detail in Chapter 4.

The advantages listed previously for FBRs, however, have to be considered together with several operational limitations. Fluidization of the catalyst pellets at high velocities can cause unavoidable acceleration of the erosion of both reactor vessel and heat exchange surfaces, and their undesirable breakdown into smaller particle sizes eventually calls for the need of cost-intensive catalyst separation/gas purification equipment. In contrast with breakdown, the pellets can also merge into each other, and the resulting increase in particle weights can cause defluidization, which can seriously disturb the reactor operation. Moreover, residence time distribution is not narrow in FBRs due to the chaotic movement of reactive fluid inside the vessel. Another operational drawback of FBRs is linked with their high sensitivity against the presence of sulfur in the gaseous feed mixture. Once they enter the reactor, sulfur-containing molecules can immediately poison the entire bed due to intense mixing of the phases and the highly exposed surface area of small catalyst particles and can eventually cause a sudden drop in pressure. This serious drawback, however, is less serious in gas-solid PBRs as sulfur poisoning moves like a wave front. In other words, at the beginning of the operation, only the section of the packed bed near the inlet will be poisoned, while pellets at the downstream will remain active until the ones at the upstream are saturated with sulfur.

Apart from the operational drawbacks stated earlier, capital and operating expenses involved in an FBR exceed those of a PBR of equivalent capacity due to requirements of larger vessel volume for handling fluidization and of installing gas purification and solid circulation components. Chaotic nature of the operation also calls for a tedious preliminary study of the process of interest at the pilot scale that should be followed by a labor and cost-intensive scaling-up stage, all of which eventually increase the capital cost of the commercial FBR unit.

Although not as widely used as a gas-solid PBR, FBR remains as the only choice for processes such as FCC and hightemperature Fischer–Tropsch (HTFT) synthesis, both of which have key roles in the petroleum processing and petrochemical industries. FCC is a critical step in petroleum refining and involves catalytic breakdown of heavy gas oil molecules into



Figure 1.15 Riser cracking process by UOP. (a) Reactor, (b) stripper, (c) riser, (d) slide valve, (e) air grid, and (f) regenerator. (Source: Werther [17]. Reproduced with permission of John Wiley & Sons, Inc.)

commercially valuable products such as gasoline, diesel, and olefins. The FBR reactor, shown in Figure 1.15 [17], is composed of a riser and a regenerator between which the catalyst is circulated continuously at rates that can exceed 100 tons/min. Endothermic cracking reactions that take place in the riser at temperatures of 500-550°C unavoidably deposit coke on the surface of the zeolite-based catalyst pellets [17]. Spent catalysts are continuously transported to the regenerator in which coke is burned off with hot air at ca. 730°C for the restoration of the catalytic activity. The cycle is completed when the regenerated catalysts are conveyed back to the riser unit. Heat needed to drive the endothermic cracking reactions is supplied by the hot catalysts that come from the regenerator. HTFT synthesis, on the other hand, involves catalytic conversion of synthesis gas into a hydrocarbon mixture rich in olefins and gasoline. The process is carried out at 340°C and 20 atm over iron-based catalysts. As FT synthesis is strongly exothermic and the product distribution is a strong function of temperature, the catalyst bed should be maintained at isothermal conditions. This requirement is met by the circulating fluidized-bed (CFB) reactor, known as the Sasol Synthol reactor, shown in Figure 1.16a [12], in which heat released during reactions is absorbed by the cooling coils immersed into the reactor vessel to produce steam [18, 19]. These reactors can operate with capacities up to 8×10^3 barrels/day $(3.3 \times 10^{\circ} \text{ tons/year})$. CFB reactors are then replaced by turbulent FBRs, known as Sasol Advanced Synthol reactors (Figure 1.16b [19]), due to their smaller size, lower capital expense requirements and maintenance costs, and their ability to operate at higher conversions and capacities up to 2×10^4



Figure 1.16 High-temperature Fischer–Tropsch synthesis reactors. (a) Sasol Synthol circulating fluidized-bed reactor. (Source: Couper et al. [12]. Reproduced with permission of Elsevier.) (b) Sasol Advanced Synthol turbulent fluidized-bed reactor. (Source: Steynberg et al. [19]. Reproduced with permission of Elsevier.)

barrels/day $(8.5 \times 10^5 \text{ tons/year})$ with lower pressure drop [18, 19]. The use of FBRs in HTFT is extensively discussed in Chapter 12.

1.3.2 Slurry reactors

Slurry reactors involve the coexistence and intense mixing of gas, liquid, and solid phases in the same volume. The possibility to run slurry reactors in the batch, semibatch, or continuous modes differentiates these reactors from others in terms of operational flexibility. In slurry reactors, the roles of the three phases can be different, that is, liquid can be a reactant, a product, or an inert that serves as a contacting medium for gas and solids. Similarly, dissolved gas can either be a reactant or an inert for inducing mixing of liquid and solids via bubbling. The solid phase usually corresponds to the finely dispersed catalyst particles with diameters lower than 5×10^{-3} m [20].

Slurry reactors are typically used for highly exothermic reactions. Heat removal from the reaction mixture is provided by cooling coils immersed into the reactor vessel. Intense mixing, which is enabled either by gas bubbling or by a mechanical agitator, increases the heat transfer coefficient between the reaction mixture and coils and improves the rate of heat removal. High heat capacity and heat transfer coefficients of the slurries are other factors that further promote heat transport and temperature control. Excellent heat management capabilities of slurry reactors make them promising candidates for several processes, with the most popular one being the low-temperature Fischer– Tropsch (LTFT) synthesis that involves conversion of syngas into a hydrocarbon mixture heavier than that synthesized in HTFT. LTFT is carried out in the ~190–250°C range and at pressures between 20 and 40 atm over Co-based catalysts [6, 18]. As Co is more active than the Fe catalyst of HTFT [21], exothermic heat generation is higher, and the demand for fast heat removal becomes more critical. The reaction starts in the gas-solid mode, where the synthesis gas with a molar $H_2/$ CO ratio of ~2 contacts the Co-based catalyst pellets. In the course of reaction, the liquid phase, called wax, is produced first in the pores of the pellets and then in the entire reactor. These conditions can be handled in a slurry bubble column reactor (SBCR), a special version of the slurry reactor, described in Figure 1.17 [21]. The same process can also be carried out in a multitubular PBR involving trickle flow. However, the slurry bubble column offers several advantages such as lower pressure drop (ca. 1 atm in SBCR vs. 4 atm in PBR), higher intrinsic catalytic activity due to the possibility of using small particle sizes that minimize intraparticle diffusion limitations, higher mass transfer coefficients due to well mixing, longer runs due to possibility of online addition/removal of the catalyst, better temperature control improving reactant conversion and product selectivity, and lower capital expenditure requirements [21]. Nevertheless, the drawbacks brought by the mobility of the catalyst phase, that is, the need for catalyst-wax separation and the risk of immediate catalyst poisoning, should not be underestimated in SBCR operation. Apart from LTFT synthesis, slurry reactors are used in other applications such as oxidation and hydroformylation of olefins, methanation and polymerization reactions, and ethynylation of aldehydes [20]. Further information regarding the modeling and design of the slurry reactors is presented in Chapter 6. The reader is also directed to Chapter 12 for a detailed discussion about the use of slurry reactors in LTFT.



Figure 1.17 Slurry bubble column reactor for low-temperature Fischer–Tropsch synthesis.

(Source: Espinoza et al. [21]. Reproduced with permission of Elsevier.)

1.3.3 Moving-bed reactors

Moving-bed reactors are preferred when there is a need for continuous catalyst regeneration. In this operation, fresh catalyst is fed from the top of the reactor, and it moves in the downflow direction by gravitational forces. Spent catalyst leaving the reactor at the bottom is usually replaced in the continuous mode. While the catalyst movement is downward, reactive mixture flow can be cocurrent or countercurrent to that of the catalyst flow.

Moving-bed reactors do not involve intense mixing of the catalyst bed with the reaction mixture. In this respect, heat management within the bed is not as efficient as that involved in FBRs or in slurry reactors. High heat capacity of the circulating catalyst pellets dictates the heat transport in the moving-bed reactors. As described in Chapter 13, these reactors are used in catalytic hydrotreating of heavy oils, in which the moving bed ensures steady conditions for the catalyst and therefore minimizes the need for periodic shutdowns.

1.4 Reactors without a catalyst bed

The reactor types introduced in Sections 1.2 and 1.3 depend on the existence of a catalyst bed, either fixed or moving, for the operation. However, there are multiphase reactions, such as the gas–liquid type, which do not involve the use of a solid catalyst. Gas cleaning/purification applications, such as removal of CO₂ or H₂S from gas streams via mono-/diethanolamine or di-/triethylene glycol solutions and removal of nitrogen oxides by water; liquid-phase processes of oxidation, nitration, alkylation, hydrogenation, or manufacturing of products such as sulfuric acid, nitric acid, and adipic acid; and biochemical processes such as fermentation and oxidation of wastewater are examples of industrial applications of gas-liquid reactions [22]. Depending on factors such as residence time distribution of the phases, throughput demand of the process, and heat transfer requirements, gas and liquid phases can be contacted in various configurations; that is, gas can be distributed into the bulk liquid in the form of bubbles (bubble columns, plate columns), liquid can be sprayed to the bulk gas in the form of droplets (spray columns), or both phases can be contacted as thin films over an inert packing or on the reactor wall (packed columns, wetted wall columns). The common direction for liquid flow is from the top to the bottom of the reactor, and gas flow is usually in the opposite direction. Column-type reactors presented here involve a vessel and the particular components required to introduce or contact the phases (e.g., spargers for gas bubbling, spraying equipments for showering down the liquid, packing materials for contacting gas and liquid films, liquid distributors for ensuring uniform wetting of the packings, sieve plates for directing the liquid flow and for providing crosscontact with the rising gas). In general, reactor performance is affected by the gas solubility, which is expected to be high for improved rates. Operating temperature should be low, while pressure should be high for increasing gas solubility in the reactor. Depending on the heat of reaction, heat transfer equipment can be integrated to the reactor structure for regulating the temperature in the desired limits.

In some gas-liquid reactions, a mechanical agitator can be integrated into the reactor for improving mixing and mass transfer between the phases. In this case, the reactor is called as a stirred-tank reactor (Figure 1.18 [12]). The agitator is composed of an impeller that is mounted on a mechanically rotated shaft. Rotation and desired level of fluid mixing are provided by a variable speed electric motor that is placed on the reactor vessel. Gas-liquid stirred-tank reactors are also equipped by spargers for dispersing the gas bubbles into the liquid and by baffles to minimize swirl and vortex formations. In general, four baffles, each of which is one-tenth of the vessel diameter, are placed into the inner perimeter of the vessel. Aspect ratio, which is defined as the ratio of the liquid height in the tank to the tank diameter, is usually set up to be ~3 for increasing the residence time of the gas and improving the extent of reaction between phases. In such configurations, mixing is provided by multiple impellers mounted on the same shaft with distances up to one tank diameter [23].

In stirred-tank reactors, the possibility of regulating the agitation speed and the selection of various impeller types and diameters allow control over the degree of mixing of different fluids, which is quantified by the impeller Reynolds number ($Re = D^2 S\rho/\mu$; D, impeller diameter; S, speed of agitation; ρ , fluid density; μ , fluid viscosity). The impeller types not only affect the mixing characteristics but also the power consumption determined by the dimensionless power number ($Po = P/\rho S^3 D^5$; *P*: power consumption). Plots of *Po* versus *Re* define the power



Figure 1.18 Stirred-tank reactor with typical dimensions. (Source: Couper et al. [12]. Reproduced with permission of Elsevier.)

characteristics of the impeller which is affected by factors such as its position in the tank and its diameter. In the laminar regime, characterized by Re < 10, Po decreases linearly with Re, whereas in the turbulent regime ($Re > 10^4$), Po remains constant and reaches an asymptotic value which is a function of the impeller type [23].

Heat transfer into/from the stirred-tank reactors is made possible by various configurations (Figure 1.19 [12]). Low heat duties can be realized by the heat transfer fluid flowing in a jacket surrounding the vessel (Figure 1.19a). For higher heat duties coils (Figure 1.19b) or internal tubes (Figure 1.19c) are immersed into the vessel for heat transfer fluid circulation. Heating/cooling of the reactive mixture in an external heat exchanger via a circulating loop (Figure 1.19d) is also possible. Other possible heat transfer configurations are shown in Figure 1.19e and f. In all cases, heat transfer coefficient on the reactor side is known to increase with the degree of mixing.

In addition to processes involving gas–liquid reactions, stirred-tank reactors can also be used for single (liquid)-phase reactions. Moreover, their operation is not limited to the continuous mode, and they can be easily adapted for use in semibatch and batch modes. The absence of a gas phase does not pose important structural and operational differences from those stated earlier for multiphase systems. However, in the case of single-phase operation, the aspect ratio is usually kept lower (~1) to ensure well mixing of the reactive liquid. Regardless of the number of phases involved, stirred-tank reactors can approach their ideal states if perfect mixing is established. Under such conditions, it is assumed that reaction takes place immediately just



Figure 1.19 Heat transfer strategies in stirred-tank reactors. (a) Jacket, (b) internal coils, (c) internal tubes, (d) external heat exchanger, (e) external reflux condenser, and (f) fired heater.

(Source: Couper et al. [12]. Reproduced with permission of Elsevier.)

after the entrance of the reactants, and the properties of the exit stream are the same with those of the reactive mixture. Nevertheless, depending on the fluid properties and the specific internal geometry of the vessel, poorly mixed zones causing selectivity issues may develop in real operations.

1.5 Summary

Catalytic reactors are critical processing units of industrial chemistry. The complex combination of several factors such as conditions of the key reactions, requirements, and limitations of the catalytic chemistry and the demand for meeting the commercial targets for conversion and yield have led to the evolution of numerous catalytic reactor types. Besides technical requirements, fixed and operating capital expenses of the reactors determine the final decision for the selection of the appropriate reactor type. This chapter aims to provide an overview of all the factors involved that may help readers in understanding the key features of these complex reactors and their significance in chemical industry. The contents of this chapter are prepared to set the basis for the following chapters, each of which provides detailed information about the analysis, design, and modeling of the multiphase reactors covered in this book.

References

- Onsan ZI, Avci AK. Reactor design for fuel processing. In: Shekhawat D, Spivey JJ, Berry DA, editors. Fuel cells: technologies for fuel processing. Amsterdam: Elsevier Science; 2011. p. 451–516.
- 2 Dybkjaer I. Tubular reforming and autothermal reforming of natural gas – an overview of available processes. Fuel Processing Technology 1995;42:85–107.
- 3 Aasberg-Petersen K, Christensen TS, Dybkjaer I, Sehested J, Ostberg M, Coertzen RM, Keyser MJ, Steynberg AP. Synthesis gas production for FT synthesis. In: Steynberg AP, Dry ME, editors. Fischer-Tropsch technology. Amsterdam: Elsevier; 2004. p. 258–405.
- 4 Eigenberger G. Catalytic fixed-bed reactors. In: Ertl G, Knözinger H, Schüth F, Weitkamp J, editors. Handbook of heterogeneous catalysis. Weinheim: Wiley-VCH; 2008. p. 2075–2106.
- 5 Eigenberger G. Fixed-bed reactors. In: Ullmann's processes and process engineering. Weinheim: Wiley VCH; 2004. p. 1983–2023.
- 6 Dry ME. The Fischer-Tropsch process: 1950–2000. Catalysis Today 2002;71:227–241.
- 7 Aasberg-Petersen K, Christensen TS, Nielsen CS, Dybkjaer I. Recent developments in autothermal reforming and pre-reforming for synthesis gas production in GTL applications. Fuel Processing Technology 2003;83:253–261.

- 8 Cybulski A, Moulijn JA. The present and the future of structured catalysts: an overview. In: Cybulski A, Moulijn JA, editors. Structured catalysts and reactors. Boca Raton, FL: CRC Press; 2006. p. 1–17.
- 9 Boger T, Heibel AK, Sorensen CM. Monolithic catalysts for the chemical industry. Industrial & Engineering Chemistry Research 2004;43:4602–4611.
- 10 Shah RK, London AL. Laminar flow forced convection in ducts. Advances in heat transfer, Supplement 1. New York: Academic Press; 1978.
- 11 Lide DR, editor. CRC handbook of chemistry and physics. Boca Raton, FL: CRC Press; 2003.
- 12 Couper JR, Penney WR, Fair JR, Walas SM. Chemical process equipment: selection and design. Boston: Butterworth-Heinemann; 2010.
- Westerterp KR, Wammes WJA. Three-phase trickle-bed reactors. In: Ullmann's reaction engineering. Weinheim: Wiley-VCH; 2013. p. 651–663.
- 14 Dingerdissen U, Martin A, Herein D, Wernicke HJ. The development of industrial heterogeneous catalysis. In: Ertl G, Knözinger H, Schüth F, Weitkamp J, editors. Handbook of heterogeneous catalysis. Weinheim: Wiley-VCH; 2008. p. 37–56.
- 15 Hardt S, Ehrfeld W, Hessel V, Vanden Bussche KM. Strategies for size reduction of microreactors by heat transfer enhancement effects. Chemical Engineering Communications 2003;190:540–559.
- 16 Hessel V, Löb P, Löwe H. Industrial microreactor process development up to production. In: Hessel V, Renken A, Schouten JC, Yoshida J, editors. Micro process engineering, Vol. 3: System, process and plant engineering. Weinheim: Wiley-VCH; 2009. p. 183–247.
- 17 Werther J. Fluidized-bed reactors. In: Ertl G, Knözinger H, Schüth F, Weitkamp J, editors. Handbook of heterogeneous catalysis. Weinheim: Wiley-VCH; 2008. p. 2106–2132.
- 18 Steynberg AP, Dry ME, Davis BH, Breman BB. Fischer-Tropsch reactors. In: Steynberg AP, Dry ME, editors. Fischer-Tropsch technology. Amsterdam: Elsevier; 2004. p. 64–195.
- 19 Steynberg AP, Espinoza RL, Jager B, Vosloo AC. High temperature Fischer-Tropsch synthesis in commercial practice. Applied Catalysis A: General 1999;186:41–54.
- 20 Nedeltchev S, Schumpe A. Slurry reactors. In: Ertl G, Knözinger H, Schüth F, Weitkamp J, editors. Handbook of heterogeneous catalysis. Weinheim: Wiley-VCH; 2008. p. 2132–2156.
- 21 Espinoza RL, Steynberg AP, Jager B, Vosloo AC. Low temperature Fischer-Tropsch synthesis from a Sasol perspective. Applied Catalysis A: General 1999;186:13–26.
- 22 Walas SM. Chemical reactors. In: Perry RH, Green DW, Maloney JO, editors. Perry's chemical engineers' handbook. New York: McGraw-Hill; 1999. p. 23-1–23-61.
- 23 Nienow AW. Stirred tank reactors. In: Ullmann's reaction engineering. Weinheim: Wiley-VCH; 2013. p. 623–640.

CHAPTER 2 Microkinetic analysis of heterogeneous catalytic systems

Zeynep Ilsen Önsan

Department of Chemical Engineering, Boğaziçi University, Istanbul, Turkey

Abstract

This chapter deals with the microkinetics of gas-solid catalytic reaction systems. An applied approach is adopted in the discussion, which starts with the formulation of *intrinsic* rate equations that account for chemical processes of adsorption and surface reaction on solid catalysts and then proceeds with the construction of global rate expressions that include the individual and simultaneous effects of physical external and internal mass and heat transport phenomena occurring at the particle scale.

2.1 Heterogeneous catalytic systems

The task of the chemical reaction engineer is generally completed in two consecutive phases: (i) measurement and evaluation of the chemical kinetic behavior of a reaction system (microkinetic analysis and modeling) and (ii) use of this information in the design of equipment in which the reaction will be conducted (macrokinetic analysis and reactor design). Without underestimating the importance and complexity of the second phase, it can be said that the first phase of the task is by far the more critical, since it has to be completed correctly before the second phase is tackled. Chemical kinetic models, which are essential for efficient reactor design and scale-up, need to be based on experimental data that reflect steady-state chemical activity, that is, chemical events only. In solid-catalyzed heterogeneous systems, physical processes such as mass and energy transport at the particle scale may interfere with chemical (intrinsic) rates to modify the overall (global) reaction rates observed. These physical transport phenomena are analyzed depending on the characteristics of the particular catalyst/reactor system used and are then superimposed on the chemical kinetic model.

Accordingly, in order to arrive at the rate equation(s) appropriate for macrokinetic analysis at the reactor scale, microkinetic analysis has to take into account several chemical and physical rate processes at the particle scale:

- 1 Transfer of reactant(s) from the bulk gas stream to the exterior catalyst surface
- 2 Diffusion of reactant(s) from the exterior surface into the interior surface
- 3 Chemisorption of reactant(s) on the inner surface of the pores
- **4** Surface chemical reaction to form product(s)
- **5** Desorption of product(s) from the surface of the pores
- **6** Diffusion of product(s) from the pores to the exterior catalyst surface
- 7 Transfer of product(s) from the exterior catalyst surface to the bulk gas stream

In this sequence, steps 3–5 are the chemical rate processes; laboratory analysis of these steps in the absence of physical effects yields the intrinsic reaction rate. Steps 1 and 7 are external physical rate processes separated from and in series with the chemical rate processes, while steps 2 and 6 are internal physical rate processes occurring simultaneously with chemical rate processes. The external and internal physical transport effects existing in a particular system are superimposed on the intrinsic reaction rate to obtain the global reaction rate, which is used in the macroscopic mass and energy transport equations required for reactor design.

In the intrinsic heterogeneous catalytic cycle, the reactants are adsorbed on the catalyst surface at specific locations called active sites, and they are activated by chemical interaction with these sites to form the catalyst–reactant complex, thus rapidly transforming on the active site to adsorbed products which subsequently desorb from these sites allowing them to momentarily return to their original state until other reactant molecules adsorb. The simple hypothesis initiating from Langmuir's work on chemisorption [1, 2] forms the basis of the modern theory used in the interpretation of the kinetics of reactions at the catalyst surface:

This postulation has been useful in correlating a wide variety of kinetic results as well as in predicting the effects of new

Multiphase Catalytic Reactors: Theory, Design, Manufacturing, and Applications, First Edition. Edited by Zeynep Ilsen Önsan and Ahmet Kerim Avci. © 2016 John Wiley & Sons, Inc. Published 2016 by John Wiley & Sons, Inc.

conditions imposed on reacting systems. There are, however, some conceptual difficulties arising from experimental results which suggest that only a small fraction of the surface is active and that active sites for chemisorption are not the same for all species. The simple physical model of the catalyst surface proposed later by Taylor [3] has the following features: (i) the catalyst surface can offer a variety of sites where molecules can adsorb with various bond strengths, (ii) the structure of the adsorbed species depends on bond strength, (iii) for a particular surface reaction to happen, bond strengths must be within specific limits, and (iv) sites that meet these bond energy requirements are called the active sites for the reaction. In short, there are a "fixed number of active sites" that account for the catalytic activity of a solid catalyst.

While the basic variables by which chemical processes can be controlled are temperature, pressure, inlet reactant concentrations, and residence time in the reactor, two technological developments of major consequence starting with 1960s have made possible cost-effective operation under less severe conditions: the prevalent use of efficient catalysts and improved reactor configurations. The impact of heterogeneous catalysis is significant, since three major areas of the world economy, namely, petroleum refining, chemicals manufacturing, and environmental cleanup, all require the use of efficient solid catalysts.

The general definition of a catalyst is common to homogeneous, heterogeneous, and enzyme catalysis. A catalyst is a substance that increases the rate at which a chemical reaction approaches equilibrium without itself suffering permanent chemical change. This description indicates that a catalyst gets temporarily involved in the chemical reaction, changes chemical reaction rates, but does not disturb chemical reaction equilibrium. Catalysts can only accelerate reactions that are thermodynamically feasible, that is, only those with negative Gibbs free energy change, $\Delta G^{\circ} < 0$, at a specified temperature. For a given reaction, the chemical equilibrium reached in the absence and presence of a catalyst is the same equilibrium:

$$\Delta G^{\circ} = -R_{\sigma} T \ln K \tag{2.1}$$

Since the overall reaction equilibrium constant *K* is also equal to the quotient of the velocity constants for the forward and reverse reactions ($K = k_f/k_r$), both reactions are accelerated by the same factor. This does not, however, suggest that all the reactions in a multiple reaction system are accelerated to the same extent; quite the reverse, the merit of a successful catalyst is to accelerate only the desirable reaction(s).

In solid-catalyzed reactions, the reactant binds to an active site on the catalyst surface where an intermediate catalyst– reactant complex is formed, and reaction occurs on the active site to form products which are then released into the gas. Transformation of the reactant into product is expedited, because the role of the catalyst is to convert reactant(s) into a form in which conversion to product(s) is easier, and by this means, the catalyst provides a new reaction path that is energetically more beneficial than the uncatalyzed path (Figure 2.1).



Figure 2.1 Potential energy curves representing the action of a solid catalyst. (Source: Davis [4]. Reproduced with permission of John Wiley & Sons.)

Chemical reactions, catalyzed or uncatalyzed, take place in accordance with the Arrhenius equation:

$$k = A \exp\left(-\frac{E_A}{R_g T}\right) \tag{2.2}$$

The preexponential or the frequency factor A is catalyst dependent, that is, it varies with the extent of surface and has the same units as the rate constant k. On the basis of the collision theory, it can be estimated that the frequency factor of a unimolecular heterogeneous reaction is smaller than that of its homogeneous counterpart by a factor of 10^{12} . It follows that, for efficient catalysis, the activation energy E_A of the catalyzed reaction should be at least 80 kJ/mol lower than that of the uncatalyzed one at 298 K. At higher reaction temperatures, the difference in E_A must also be higher in order to keep the advantage of the catalyzed reaction rate. E_A and A usually tend to compensate the change in one another; hence, the compensation (or theta) effect between A and E_A has to be taken into account [4].

2.1.1 Chemical and physical characteristics of solid catalysts

In heterogeneous catalysis, the reaction takes place at the interface between the catalyst and the less dense phase. Adsorption is defined as the preferential concentration of gas molecules at a fresh solid surface, caused by the existence of a field force that attracts molecules of the contacting fluid. Two major types of adsorption have been recognized, namely, physical adsorption and chemisorption [5, 6].



Figure 2.2 Effect of temperature on amount of gas adsorbed for simultaneous physical adsorption and activated chemisorption. (Source: Hill [7]. Reproduced with permission of John Wiley & Sons.)

Physical adsorption, which is similar to the condensation of vapor molecules onto a liquid surface of the same composition, (i) is due to weak attractive forces of the van der Waals type, (ii) is multilayer and nonspecific, (iii) occurs at temperatures close to the boiling point of the adsorbate, and (iv) has low heats of adsorption close to the heats of condensation of the adsorbate involved.

Chemical adsorption (chemisorption), on the other hand, is similar to a chemical reaction resulting in the formation of an intermediate compound restricted to the surface layer of the adsorbent and, unlike physical adsorption, it (i) involves chemical bonding and exchange of electrons between the adsorbate and the partially uncoordinated active sites of the adsorbent, (ii) is monolayer and highly specific, (iii) occurs at temperatures well above the boiling point of the adsorbate, and (iv) has much higher heats of adsorption close to the heats of chemical reactions. Conditions required for catalysis designate chemisorption as the essential precursor to surface reaction. Physical adsorption may, nonetheless, facilitate the transition of reactants from the gaseous to the chemisorbed state (Figure 2.2).

2.1.1.1 Quantitative treatment of chemisorption

The key concept in the quantitative treatment of chemical adsorption is due to Langmuir [1, 2] in his pioneering work aiming to find "a relation between the quantity of gas adsorbed by a solid and the pressure of the gas over the solid when equilibrium is reached." His original derivation was a kinetic one, with the implicit assumptions of (i) monolayer adsorption, taking place through the collision of gaseous adsorbate molecules with vacant active sites on the surface, (ii) one site–one entity interaction, with each surface site accommodating only one entity (i.e., one atom or one molecule), and (iii) energetic uniformity of the entire active surface.

Langmuir used fractional surface coverage by the adsorbate gas, θ_A , as a measure of the amount of gas adsorbed and

envisaged a dynamic equilibrium between the adsorption and desorption rates of the adsorbate, $R_{ads} = R_{des}$. The original form of the Langmuir isotherm for molecular adsorption of the adsorbate gas, $A + S \leftrightarrow A - S$, was obtained as

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A}$$
(2.3)
$$K_A = \frac{k_{ads}}{1 + k_A P_A} = 2 A_{ads} + 2 A_{$$

 $K_A = \frac{a_{ads}}{k_{des}}$ = adsorption equilibrium coefficient $R_{ads} = k_{ads}P_A(1 - \theta_A)$ and $R_{des} = k_{des}\theta_A$

For dissociative adsorption, $A_2 + 2S \leftrightarrow 2A - S$, the Langmuir isotherm becomes

$$\theta_A = \frac{(K_A P_A)^{\frac{1}{2}}}{1 + (K_A P_A)^{\frac{1}{2}}}$$
(2.4)

For multicomponent adsorption on similar sites, $A + S \leftrightarrow A - S$ and $B + S \leftrightarrow B - S$,

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B}$$

$$\theta_A = \frac{K_A P_A}{1 + \sum K_i P_i} \text{ for } i \text{ number of components}$$
(2.5)

The monolayer assumption of the Langmuir treatment is valid since exchange of electrons and chemical bonding are involved in chemisorption, and the usual range of chemical bond distances would indicate the formation of only a monolayer restricted to the surface. The second one site-one entity assumption is not always true, since chemisorption of more molecules on one site or one molecule on two or more sites is possible depending on the coordination between active sites and adsorbate molecules. The third assumption regarding energetic equivalence of the active surface contains an important weak point; experimental observations clearly indicate decreasing heats of adsorption ΔH_{ads} with increasing surface coverage θ . The major reasons for the decline in ΔH_{ads} are listed as surface heterogeneity and lateral interaction between adjacent species; that is, highly active sites are covered first and adsorption on neighboring sites increases surface repulsions.

The early work of Beeck in 1950 shows isosteric heats of adsorption for hydrogen as a function of surface coverage on several metal films, exhibiting their dependence on surface coverage [8, 9]. These data also indicate that there is a common region corresponding to intermediate surface coverages ($0.2 < \theta < 0.8$) that are essential for efficient catalysis, where the decline in the heats of adsorption is linear and an average ΔH_{ads} value may be used with some approximation if the fall is not appreciable. The distinct advantage of the Langmuir isotherm is that it readily describes multicomponent chemisorption in all partial pressure ranges and also predicts the two limiting conditions of $\theta_A \rightarrow 0$ when $P_A \rightarrow 0$ and $\theta_A \rightarrow 1$ when $P_A \rightarrow \infty$; as a result, it forms the basis of the modern treatment of heterogeneous reaction kinetics in the formulation of rate equations.

Two other well-known isotherms that do not involve an assumption regarding energetic equivalence of the active surface

are the Temkin isotherm and the Freundlich isotherm [6]. The Temkin isotherm takes into account a linear fall in ΔH_{ads} with increasing θ and permits its interpretation in terms of surface heterogeneity as well as lateral repulsion between adsorbed species:

$$\theta_A = k_1 \ln(k_2 P_A) \tag{2.6}$$

This isotherm may be derived from kinetic considerations for intermediate surface coverages ($0.2 < \theta < 0.8$), but it does not lend itself to multicomponent adsorption and also fails to predict the limiting conditions of $\theta_A \rightarrow 0$ when $P_A \rightarrow 0$ and $\theta_A \rightarrow 1$ when $P_A \rightarrow \infty$. Even though it was used for correlating the kinetics of ammonia synthesis, the Temkin isotherm has not found much use in the kinetic analysis of solid-catalyzed gas-phase reactions.

Originally postulated as an empirical equation, the Freundlich isotherm with two constants, *k* and *n*, can be derived from thermodynamic or statistical considerations with the assumptions that ΔH_{ads} decreases exponentially with increasing surface coverage and that this decrease is due to surface heterogeneity:

$$\theta_A = k(P_A)^{\frac{1}{n}}; \quad n > 1 \tag{2.7}$$

The statistical derivation shows that the Freundlich isotherm is expected to be valid at low surface coverages; in fact, the isotherm successfully predicts that $\theta_A \rightarrow 0$ when $P_A \rightarrow 0$ but fails to predict $\theta_A \rightarrow 1$ when $P_A \rightarrow \infty$. The Freundlich isotherm can handle multicomponent adsorption to some extent, and in some cases, the Langmuir isotherm can be reduced to the power function form of the Freundlich isotherm.

2.1.1.2 BET treatment of physical adsorption

The Langmuir approach was extended to multilayer adsorption by Brunauer, Emmett, and Teller in the form of the BET equation with two constants. The linearized form of the BET equation is important in the measurement of total surface areas of porous solid catalysts [5]:

$$\frac{P}{V_{ads}(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C P_0} P_0$$
(2.8)

Here, *P* is the pressure of adsorbate (N₂), in mmHg; P_0 is the saturation or vapor pressure of adsorbate, in mmHg; V_{ads} is the volume of adsorbed gas, in cm³; V_m is the volume of monolayer, also in cm³; and *C* is a constant for the particular gas–solid system used and temperature. Utilizing the *P* versus V_{ads} data obtained on a constant-volume or constant-pressure BET equipment, the volume of the monolayer is easily calculated from the slope and intercept of the BET equation. The specific surface area S_g of the catalyst is then calculated in a simple sequence of steps using the ideal gas law, Avogadro's number N_0 , and the cross-sectional area A_m of one molecule of the adsorbate:

 $S_g(m^2/g)$ = total surface area per unit weight of catalyst sample

 $V_m = \text{monolayer volume} (\text{cm}^3)$

$$\frac{V_m}{22414} = \frac{\text{cm}^3}{\text{cm}^3/\text{mol at STP}} = \text{moles of gas in monolayer}$$
$$\left(\frac{V_m}{22414}\right) \left(6.02 \times 10^{23} \frac{\text{molecules}}{\text{mol}}\right) = \text{number of molecules in monolayer}$$

 $\left(\frac{V_m}{22414}\right)$ $(6.02 \times 10^{23})(A_m)$ = area covered by the molecules in monolayer

 A_m = cross-sectional area of one molecule = 16.2Å² for N₂

$$S_g(\mathbf{m}^2/\mathbf{g}) = \left(\frac{V_m}{22414}\right) \left(6.02 \times 10^{23}\right) (A_m) \left(\frac{1}{w_{cat}}\right) \left(10^{-20}\right) \quad (2.9)$$

including the conversion of $(\text{\AA})^2$ to m^2 as well as the weight of the solid catalyst sample.

2.1.1.3 Catalyst physical properties

The physical properties of solid catalysts have a pronounced effect on their catalytic performance and are also used in geometric models of catalyst particles as well as in expressing effectiveness factors. The more frequently used properties are listed in the following.

 S_g (m²/g), total surface area per gram of catalyst, or specific surface area, is a measure of the extent of surface available for adsorption and determines the amount of gas adsorbed.

 V_g (cm³/g), void volume or pore volume per gram of catalyst particle, is a measure of the effectiveness of the internal surface and is calculated from

$$V_g(\text{cm}^3/\text{g}) = \frac{V_{\text{Hg}} - V_{\text{He}}}{m_p}$$
 (2.10)

Here, V_{Hg} and V_{He} (both in cm³) are the volumes of Hg and He displaced by the particle as measured by pycnometry, respectively, and m_P is the mass of the catalyst sample.

 \bar{a} (Å), mean pore radius, is roughly estimated by assuming all pores are cylindrical, straight, and parallel with the same radius and length:

$$\bar{a}\left(\mathring{A}\right) = \frac{2V_g}{S_g} \tag{2.11}$$

 $\rho_{\rm S}$ (g/cm³), density of the solid phase in the particles, is calculated using $V_{\rm He}$:

$$\rho_{S}(g/cm^{3}) = \frac{m_{P}}{V_{He}}$$
(2.12)

 ρ_P (g/cm³), density of the porous particles, is calculated using V_{Hg} :

$$\rho_P(g/cm^3) = \frac{m_P}{V_{Hg}}$$
(2.13)

 \mathcal{E}_P , void fraction or porosity of the particles, is calculated using the difference between V_{Hg} and V_{He} or from $(V_g \rho_P)$; voidage of most industrial catalysts is in the range of 0.40–0.60:

$$\epsilon_P = \frac{V_{\rm Hg} - V_{\rm He}}{V_{\rm Hg}} \quad \text{or} \ V_g \rho_P \tag{2.14}$$

Pore-volume distribution, distribution of void volume according to pore size or radius of pore mouth, is measured by N_2 adsorption–desorption experiments [5, 8].

2.1.2 Activity, selectivity, and stability

The three fundamental properties inherent in the actual definition of a catalyst are activity, selectivity, and stability. Moreover, for successful industrial applications, catalysts must be regenerable, reproducible, mechanically and thermally stable with suitable morphological characteristics, and also economical.

2.1.2.1 Catalyst activity

Activity is a measure of the rate at which the catalyst causes the chemical reaction to arrive at equilibrium. In terms of kinetics, the reaction rate defines catalyst activity as the quantity of reactant consumed per unit time per unit volume or mass of catalyst:

 $(-R_A)_V = \text{mol}/\text{L/h}$ or $(-R_A)_P = \text{mol}/\text{kg/h}$

In industrial practice, it is more practical to use readily measured parameters such as

$$STY =$$
 space-time yield = mol/L/h or $(R_B)_V =$ mol/L/h

Space-time yield is the quantity of product formed per unit time per unit volume of reactor or catalyst, since reactor volume is taken as the catalyst-packed volume.

Space time is defined as the time required for processing one reactor volume of feed and is calculated by dividing the reactor volume by the volumetric flow rate of feed. The reciprocal of space time is defined as space velocity, with units of reciprocal time, and signifies the number of reactor volumes of feed processed per unit time. The phase and the conditions at which the volumetric flow rate of feed is measured have to be specified.

High activity is reflected in either high space-time yield from comparatively small catalyst volumes or mild operating conditions that enhance selectivity and stability. Catalyst activity defined as $(-R_A)_V$ or $(R_B)_V$ depends on pressure, temperature, and reactant concentrations.

In the screening of a range of solid catalysts in order to select the best candidate(s), a correct comparison of their catalytic activity is possible by determining one of the following, under otherwise similar reaction conditions [10, 11]: (i) their conversion levels, x, (ii) the space velocity required in each case for achieving a given constant conversion level, x, (iii) the spacetime yield, or (iv) the temperature necessary for reaching a given conversion level, x.

2.1.2.2 Catalyst selectivity

In complex reaction systems, several stable products are produced by more than one reaction, and some of the products are not desirable. Selectivity is a measure of the extent to which the catalyst accelerates the formation of desired product(s) and is usually a function of the degree of conversion of reactant and reaction conditions, particularly temperature. A number of different definitions of selectivity are used according to purpose.

The basic concept is overall selectivity, defined as the ratio of the quantity of desired product to the quantity of reactant converted, (mol/mol) or (mol%). For parallel (competing) reactions, rate selectivity is defined as the ratio of the rate of formation of desirable product *B* to the rate of formation of another product *C*, $(R_B)_V/(R_C)_V$, as in the case of the simultaneous reactions, $A \rightarrow B$ and $A \rightarrow C$.

2.1.2.3 Turnover frequency and turnover number

Turnover frequency (*TOF*) quantifies the number of molecules converted or formed per catalytic site per second at specified conditions of temperature, pressure, and conversion:

$$TOF = \frac{(-R_A)_V}{\left(\frac{\text{number of centers}}{\text{volume}}\right)}; \quad \frac{\text{mol/L/s}}{\text{mol/L}} = s^{-1}$$

For most relevant industrial applications, *TOF* values in the range of 10^{-2} – 10^3 s⁻¹ have been observed. For enzyme-catalyzed reactions, *TOF* levels are much higher at 10^3 – 10^7 s⁻¹. TOF is limited by the difficulty in determining the number of active centers for multimetallic, nonmetallic, and mixed oxide catalysts used more frequently in large-scale operations.

Turnover number (*TON*) specifies the number of catalytic cycles for which the catalyst is effective up to the decline in activity. For most industrial applications, *TON* values are in the range of 10^{6} – 10^{8} .

2.1.2.4 Catalyst stability

The stability of a catalyst is determined by its ability to withstand changes in physical and chemical properties that take place during use, leading to catalyst deactivation. Chemical, thermal, and mechanical stability of a catalyst determines its lifetime in industrial reactors. Total catalyst lifetime is usually crucial for the economics of a catalytic process.

A catalyst with good stability will change only very slowly over the course of time under conditions of use and regeneration. Catalyst stability is influenced by numerous factors, including decomposition, coke formation, poisoning, and sintering. The priority of target properties in catalyst design and development for industrial applications is commonly given in the following order: selectivity > stability > activity.

2.1.2.5 Catalyst deactivation

It is misleading to say that a catalyst is totally unchanged by the reaction it catalyzes. Gradual physical and chemical alterations may take place during catalysis or with usage. Industrial catalysts are slowly deactivated by phenomena that accompany the main catalytic process. Catalyst aging, or deactivation, is indicated by the decrease in catalyst activity with time. It introduces additional complexity to the determination of rate parameters and has to be considered in macrokinetic analysis, that is, in catalytic reactor design.

The most common causes of catalyst deactivation are [12] (i) poisoning by strong chemisorption of impurity chemicals on active sites, (ii) fouling or coking by the deposition of carbon on active sites, (iii) sintering due to loss of active surface by the agglomeration of metals, narrowing or closing of pores of the solid support, (iv) chemical decomposition due to loss of active components by vapor transport, and (v) mechanical failure caused by the attrition and crushing of catalysts.

Poisoning is a chemical effect, and catalyst poisons are extraneous materials forming strong adsorptive bonds with the active sites on the catalyst surface. Adsorbed poisons physically block adsorption sites and may also induce changes in the electronic or geometric structure of active surfaces. For instance, sulfur adsorbs strongly on metals such as Ni and prevents or modifies the adsorption of reactant molecules; its presence causes substantial or complete loss of activity. Sulfur poisoning is a major problem in the industrial processes of steam reforming, hydrogenation, methanation, and Fischer–Tropsch synthesis. The order of decreasing toxicity for sulfur is given as $H_2S > SO_2 >$ SO_4^{2-} , which results from the increased shielding by oxygen.

Frequently, reaction products may adsorb more strongly than reactants; reaction products that desorb slowly from the active sites and thereby reduce reaction rates are generally termed as inhibitors, not as poisons, and are taken into account in reaction rate equations.

Fouling, coking, and carbon formation are used interchangeably and refer to the physical deposition of species from the fluid phase onto the catalyst surface, resulting in activity loss due to blockage of sites and/or pores. Coke-forming processes may also be accompanied by the chemisorption of condensed hydrocarbons which act as poisons.

On nonmetallic catalysts, coke formation is a result of cracking reactions involving alkenes and aromatics. On metallic catalysts, depending on temperature, carbon deposits may contain little or no hydrogen. Carbon is formed either as graphite or as filaments growing out from metal surfaces, causing metal dispersion and deterioration. Coke formation processes can be attributed to the following reactions:

$$2CO \rightarrow C + CO_2; CH_4 \rightarrow C + 2H_2; 2H_2 + CO_2 \rightarrow C + H_2O_2$$

Thermally induced catalyst deactivation may result from (i) loss of catalytic surface due to metal crystallite growth, that is, metal(s) present in the form of separate dispersed atoms or small clusters rearrange to form larger crystallites, (ii) loss of support area due to support collapse or pore collapse on metal crystallites, resulting in pore closure and encapsulation of metals, or (iii) transformation of catalytic phases to noncatalytic phases, as in the solid-state reaction of NiO with Al₂O₃ to form a stable but inactive NiAl₂O₄ under steam-containing or oxidizing conditions at temperatures above 400–500 °C. The first two processes described in (i) and (ii) here are typically called sintering.

2.1.2.6 Measures against catalyst deactivation

A brief synopsis of commonly used measures is given here to emphasize their significance both in catalyst development and in processing strategies [12, 13]. Poisoning of metal catalysts can be avoided by the incorporation of suitable promoters in catalyst formulations as well as pretreatment of feed mixtures to remove impurities. A good example of increasing the sulfur resistance of Ni or Co catalysts is the addition of Mo in the hydrogenation of CO_x or in hydrotreatment processes. Coke formation can be reduced substantially by increasing the hydrogen partial pressure, by partial neutralization of acid sites with promoters, and by additives such as SiO₂, Al₂O₃, TiO₂, MoO₃, or WO₃ to prevent filamentous carbon in the case of Ni-Fe catalysts. In steam reforming processes, the steam to carbon ratio is increased to inhibit carbon formation and/or to gasify the carbon deposited on the surface. Coke already formed is removed by periodic regeneration of the catalyst by combustion (burning off) of the deposited carbon layer in a controlled manner to avoid local sintering of the active phase or carrier. In sintering, catalyst stabilization is increased by using particles with lower densities and narrow pore-size distributions. For a given reactant, the stability of active metals against sintering increases as follows, with Re being the most stable:

Ag < Cu < Au < Pd < Ni < Co < Pt < Rh < Ru < Ir < Os < Re

Addition of higher melting noble metals like Rh and Ru to base metals such as Ni also improves thermal stability.

Considering some of the commonly used support materials, the stability against sintering increases in the following order:

 $TiO_2 < SiO_2 < Al_2O_3 < MgO$

 TiO_2 is an exception, since it is the typical support for strong metal–support interactions (SMSI). Addition of Ba, Zn, La, Si, and Mn promoters improves the thermal stability of Al_2O_3 supports and hinders loss of total surface through extended use at relatively high temperatures.

2.2 Intrinsic kinetics of heterogeneous reactions

The intrinsic catalytic cycle contains only the chemical steps 3–4–5 of the 7-step sequence listed in the so-called continuous reaction model. It is necessary to make the assumption of zero gradients with respect to heat and mass transport both outside and within the catalyst particle. Therefore, experimental conditions in the laboratory have to be adjusted to ensure that (i) external transport processes (steps 1 and 7 of the sequence) are very rapid compared to chemical steps and (ii) internal transport processes (steps 2 and 6 of the sequence) are negligible, that is, particle sizes are small enough to ignore pore structure. In Figure 2.3, the reactant concentration profile labeled as IV represents the case for intrinsic kinetics.

In the interpretation of the intrinsic kinetics of catalytic reactions, the simple scheme based on Langmuir's work including chemisorption of reactants, surface chemical reaction, and desorption of products provides the framework together with Taylor's physical surface model postulating a fixed number of active surface sites. This analysis has been successful in correlating a wide range of kinetic results and also in predicting possible effects of new reaction conditions.



Figure 2.3 Reactant concentration profiles in different global rate regimes: I, external mass transfer limitation; II, pore diffusion limitation; III, both external and internal mass transfer limitations; IV, no mass transfer limitations on the intrinsic rate.

(Source: Hill [7]. Reproduced with permission of John Wiley & Sons.)

The three key principles used in the formulation of intrinsic rate equations originate from these surface model concepts [14]:

- 1 Constancy of the total number of active sites, which is *a priori* assumption based on the physical surface model
- 2 Quasi- or pseudo-steady-state approximation, which assumes that concentrations of intermediate complexes formed on the surface are small and time invariant
- **3** Presence of rate-controlling or slow step(s) in the reaction mechanism comprising adsorption, reaction, and desorption steps, which establishes the final functional form of the intrinsic rate equation.

2.2.1 Kinetic models and mechanisms

Consider a single reaction of the form

 $A \leftrightarrow B$

Since the reaction is solid catalyzed, it is clear that it does not take place as written by the stoichiometric equation. Postulating a possible reaction mechanism in terms of elementary reaction steps and intermediate complexes of the type described by Langmuir,

 $A + S \leftrightarrow A - S$ adsorption; k_1 , k_{-1} $A - S \leftrightarrow B - S$ surface reaction; k_2 , k_{-2}

$$B-S \leftrightarrow B+S$$
 desorption; k_{-3} , k_3

If we let $S = S_V$, $A-S = S_A$, and $B - S = S_B$, then S_V , S_A , and S_B refer to the chemical forms of unoccupied and occupied active surface sites, respectively. Reactant *A* adsorbs on vacant site S_V to form the catalyst–reactant complex S_A which is converted to adsorbed product complex S_B , and finally, adsorbed product desorbs to give gaseous product *B* and also regenerate the vacant active site S_V so that a cyclic reaction pattern repeats itself and a large number of product molecules can be formed by each active

site. The important point is that the vacant site S_V consumed by the first step is regenerated in the third step of the reaction mechanism, leading to a closed sequence.

In order to proceed with the kinetic analysis, the *a priori* assumption that the number of active sites is a constant proportional to the mass of catalyst (S_O) is utilized in writing a "site balance":

$$S_O = S_V + S_A + S_B \tag{2.15a}$$

Considering that the number of active sites on the surface is small compared to the number of reactant molecules in the gas phase, a dynamic steady state is readily established between gaseous and adsorbed species if the intermediate steps are reactive enough. Under conditions where the quasi- or pseudo-steadystate approximation is applicable, the distribution of active sites between occupied and unoccupied forms does not change with respect to time, and thus, surface concentrations of intermediate species can be related to their gas-phase concentrations:

$$\frac{dS_A}{dt} = k_1 C_A S_V - k_{-1} S_A - k_2 S_A + k_{-2} S_B = 0$$
(2.15b)

$$\frac{dS_B}{dt} = k_2 S_A - k_{-2} S_B - k_{-3} S_B + k_3 C_B S_V = 0$$
(2.15c)

Since the net rates of all the consecutive steps in the mechanism are identical under the steady-state approximation, the net steady-state rate for the overall reaction may be evaluated from any one of the steps. However, considering that most reactions involve more than one reactant and/or product, the resulting sizeable rate equations are cumbersome and tend to correlate virtually any set of data with little distinction.

Simplification of the rate expression is possible if the rate constants corresponding to one of the elementary steps in the reaction mechanism can be identified as being small compared to others. This is called the "slow step" or the rate-controlling/rate-limiting/rate-determining step in the overall reaction mechanism. In the limiting case, all elementary reaction steps of the mechanism are essentially at equilibrium except the rate-determining slow step; therefore, the net steady-state rate can be expressed in terms of the slow step, and equilibrium statements can directly be written for all other steps in the mechanism.

The slow step may be any one of the three steps in the reaction mechanism; so, the limiting case may be that of (I) surface reaction controlling, (II) adsorption of reactant controlling, or (III) desorption of product controlling. Since a large majority of heterogeneous reactions are surface reaction controlled, the Langmuir–Hinshelwood approach to kinetics of fluid–solid catalytic reactions [15] based on fractional surface coverages of reactants was restricted only to this particular rate-limiting step. The Langmuir–Hinshelwood formulation is a special case of the comprehensive approach put forward later by Hougen and Watson [16] for deriving rate expressions when adsorption, surface reaction, or desorption is controlling the rate; the latter treatment provides a rational and structured approach to catalytic kinetics, despite the restrictions of the Langmuir isotherm on which it is based [13, 17]. Furthermore, parameters accounting for catalytic activity, catalyst effectiveness as a result of diffusion, and/or activity decay may also be included in the Hougen– Watson derivations. It must, however, be kept in mind that the equations obtained are kinetic models, not mechanistic descriptions, and they will only indicate that the proposed sequence of steps are plausible.

Case I Surface reaction controlling

This limiting case corresponds to the assumption that the adsorption and desorption steps of the reaction mechanism are fast and essentially at equilibrium, while the surface reaction step is slow and far from equilibrium:

$$k_2S_A, k_{-2}S_B \ll k_1C_AS_V, \ k_{-1}S_A, \ k_{-3}S_B, \ k_3C_BS_V$$

 $(-R_A)_{SI} = k_2S_A - k_{-2}S_B$ = net steady-state rate for Case I
(2.16a)

 $S_A = \frac{k_1}{k_{-1}} C_A S_V = K_A C_A S_V = \text{adsorption equilibrium statement for } A$ (2.16b)

$$S_B = \frac{k_3}{k_{-3}}C_B S_V = K_B C_B S_V = \text{desorption equilibrium statement for } B$$
(2.16c)

 $S_O = S_V + S_A + S_B = S_V + K_A C_A S_V + K_B C_B S_V = \text{site balance}$

$$S_{V} = \frac{S_{O}}{1 + K_{A}C_{A} + K_{B}C_{B}}$$

$$(-R_{A})_{SI} = \frac{(k_{2}K_{A}S_{O})(C_{A} - \frac{C_{B}}{K})}{1 + K_{A}C_{A} + K_{B}C_{B}}$$
(2.17)

(2.16d)

$$K = \frac{K_{sr}K_A}{K_B} \tag{2.18}$$

Case II Adsorption of reactant controlling

This case relates to the situation where the adsorption of reactant *A* on a vacant active site to form the active complex S_A is slow, while both the surface reaction converting S_A to adsorbed product S_B and the desorption of *B* are fast:

$$k_1C_AS_V, \ k_{-1}S_A \ll k_{-3}S_B, \ k_3C_BS_V, \ k_2S_A, \ k_{-2}S_B$$

 $(-R_A)_{SII} = k_1C_AS_V - k_{-1}S_A = net steady-state rate for Case II$
(2.19a)

$$S_B = \frac{k_3}{k_{-3}} C_B S_V = K_B C_B S_V = \text{desorption equilibrium statement for } B$$
(2.19b)

$$k_2 S_A = k_{-2} S_B; \quad S_B = \frac{k_2}{k_{-2}} S_A = K_{sr} S_A = \text{reaction equilibrium statement}$$

$$S_A = \frac{K_B}{K_{sr}} C_B S_V \text{ since } S_B = K_B C_B S_V = K_{sr} S_A$$
(2.19c)

$$S_O = S_V + S_A + S_B = S_V + \frac{K_B}{K_{sr}}C_BS_V + K_BC_BS_V = \text{site balance}$$
(2.19d)

$$S_{V} = \frac{S_{O}}{1 + \frac{K_{B}}{K_{sr}}C_{B} + K_{B}C_{B}}$$
$$(-R_{A})_{SII} = \frac{k_{1}S_{O}(C_{A} - \frac{C_{B}}{K})}{1 + \frac{K_{A}}{K}C_{B} + K_{B}C_{B}}$$
(2.20)

The denominator of this equation does not explicitly contain the reactant concentration C_A .

Case III Desorption of product controlling

This is the step where S_B decomposes to give gaseous product *B* and regenerates S_V . Both the adsorption of *A* and the surface reaction converting S_A to S_B are fast:

$$k_{-3}S_B, k_3C_BS_V \ll k_2S_2, k_{-2}S_3, k_1C_AS_1, k_{-1}S_2$$
$$(-R_A)_{SIII} = k_{-3}S_B - k_3C_BS_V = \text{net steady-state rate for Case III}$$
$$(2.21a)$$

$$S_A = \frac{k_1}{k_{-1}} C_A S_V = K_A C_A S_V = \text{ adsorption equilibrium statement for } A$$
(2.21b)

$$S_2S_A = k_{-2}S_B$$
; $S_B = \frac{k_2}{k_{-2}}S_A = K_{sr}S_A$ = reaction equilibrium statement

$$S_B = K_A K_{sr} C_A S_V \tag{2.21c}$$

$$S_O = S_V + S_A + S_B = S_V + K_A C_A S_V + K_A K_{sr} C_A S_V = \text{site balance}$$
(2.21d)

$$S_{V} = \frac{S_{O}}{1 + K_{A}C_{A} + K_{A}K_{sr}C_{A}}$$

$$(-R_{A})_{SIII} = \frac{k_{1}S_{O}K(C_{A} - \frac{C_{B}}{K})}{1 + K_{A}C_{A} + KK_{B}C_{A}}$$
(2.22)

The denominator of this expression does not explicitly contain the product concentration C_B .

2.2.1.1 Langmuir-Hinshelwood-Hougen-Watson rate equations

The intrinsic Langmuir–Hinshelwood–Hougen–Watson (LHHW) rate expressions (Eqs. 2.17, 2.20, and 2.22) derived for various reactions with different or similar postulated slow steps are of the following general form:

$$Rate = \frac{(kinetics term)(driving potential term)}{(adsorption term)^n}$$
(2.23)

Here, the exponent n shows the number of sites involved per catalytic reaction cycle, and its value can be 1 or 2, very rarely 3, for surface reaction-controlling cases. Since one active site is involved per reaction cycle in the example discussed earlier, the exponent of the adsorption term for the surface reaction limiting case is unity.

The individual terms appearing in LHHW rate expressions describing different kinetic schemes were prepared in the form of tables first by Yang and Hougen [18] for four different reactions that cover nearly all possible types of catalytic reactions [5, 13, 19]: