Contents

Preface xv
Acknowledgments xix
Arrangement of This Book xxi

Part I Physical Chemistry and Kinetics 1

1 Heterogeneous Catalysis 3
1.1 What is Heterogeneous Catalysis? 3
1.2 Early Developments 4
1.2.1 Early Nineteenth Century Discoveries 5
1.2.2 Later Nineteenth Century Discoveries 7
1.3 The Three Basic Laws of Catalysis 7
1.3.1 Berzelius’ Catalysis Law 7
1.3.2 Ostwald’s Catalysis Law 8
1.3.3 Sabatier’s Catalysis Law 10
References 12

2 Heterogeneous Catalytic Processes 15
2.1 Introduction 15
2.2 Important Heterogeneous Catalytic Reactions and Processes 19
2.2.1 Hydrogenation and Dehydrogenation Reactions 19
2.2.2 Hydrogenation Reactions: Transition Metal Catalysts 19
2.2.2.1 Hydrocarbon Transformation Reactions 22
2.2.2.2 Brønsted Acid Catalysis 22
2.2.3 Oligomerization and Polymerization Catalysis 27
2.2.3.1 Methanol to Ethylene and Aromatics: The Aufbau Reaction 27
2.2.3.2 Fischer–Tropsch Catalysis 29
2.2.3.3 Disproportionation and Metathesis Reaction: Single Site Catalysis 32
2.2.3.4 Polymerization: Surface Coordination Complex Catalyst 35
2.2.4 Hydrodesulfurization and Related Hydrotreating Reactions 36
2.2.4.1 Hydrodesulfurization 36
2.2.4.2 The Biomass Refinery 37
2.2.5 Oxidation and Reduction Reactions 38
## Contents

3 Physical Chemistry, Elementary Kinetics 59
   3.1 Introduction 59
   3.2 Catalyst Characterization 63
      3.2.1 Langmuir Adsorption Isotherm 64
      3.2.2 Measurement of Pore Volume 65
      3.2.3 Porosity 66
      3.2.4 Temperature-Programmed Reactivity Measurements 67
      3.2.5 Spectroscopic Techniques 68
   3.3 Elementary Kinetics 68
      3.3.1 Lumped Kinetics Expressions: Kinetic Determination of Key Reaction Intermediates 68
      3.3.1.1 The Rate Constant of an Elementary Reaction 68
      3.3.1.2 Elementary Catalytic Reaction Kinetics 71
      3.3.2 Sabatier Principle and Volcano Curves: Brønsted–Evans–Polanyi Relations 78
         3.3.2.1 Brønsted–Evans–Polanyi Relations of Elementary Surface Reaction Rate Constants 79
         3.3.2.2 The Sabatier Volcano Curve 84
         3.3.2.3 The Reaction Energy Diagram of the Catalytic Reaction Cycle 90
         3.3.2.4 Electrocatalysis and Sabatier Principle Optimum 94
         3.3.2.5 Temperature Dependence of Catalytic Reaction Rate 96
         3.3.2.6 Summary: The Order of Reaction Rate 101
   3.4 Transient Kinetics: The Determination of Site Concentration 104
   3.5 Diffusion 106
      3.5.1 Concentration Profiles 106
      3.5.2 Effectiveness Factor 107
      3.5.3 Diffusion in Zeolitic Micropores 110
   References 114

4 The State of the Working Catalyst 117
   4.1 Introduction 117
   4.2 Surface Reconstruction 119
   4.3 Compound Formation: Activation and Deactivation 123
   4.4 Supported Small Metal Particles 124
      4.4.1 Nature of the Support Material 125
      4.4.2 Reactivity and Stability 127
   4.4.3 Summary 128
   4.5 Structure Sensitivity of Transition Metal Particle Catalysts 129
      4.5.1 Particle Size and Structure Dependence of Heterogeneous Catalytic Reactions 129
      4.5.2 Site Generation 133
   References 138
7.2.2.2 Adsorption of the Carbon Atom: The Surface Molecular Complex 220
7.2.2.3 The Oxygen Adatom: The Polar Surface Bond 228
7.2.3 Adsorption Site Preference as a Function of Accessible Free Valence 233
7.2.3.1 Chemisorption of Molecular Fragments CH_x, NH_x, and OH_x Species: Coordination Preference as a Function of Accessible Free Valence 233
7.2.3.2 CH_3 and NH_3 Chemisorption: The Agostic Interaction 235
7.2.4 Adsorption as a Function of Coordinative Unsaturation of Surface Atoms: Relation with d Valence Band Energy Shift 243
7.2.5 Chemisorption of CO: Donative and Backdonative Interactions 249
7.2.6 Lateral Interactions 258
7.2.7 Scaling Laws 259
7.2.8 In Summary: The Adsorbate Chemical Bond 262
7.3 The Transition States of Elementary Surface Reactions 264
7.3.1 Adsorbate σ-Bond Activation 265
7.3.1.1 Activation of Methane 265
7.3.1.2 The Oxidative Addition and Reductive Elimination Model 268
7.3.1.3 The Umbrella Effect 269
7.3.1.4 Activation Entropy 270
7.3.1.5 σ-Bond Activation of Molecules that Bind Through their Lone Pair Orbital 270
7.3.2 Dissociation of Diatomic Molecules with π-Bonds 273
7.3.2.1 Principle of Non-Shared Bonding with the Same Surface Metal Atom 274
7.4 Reactivity of Surfaces at High Coverage 274
7.4.1 Decreased Surface Reactivity and Site Blocking 275
7.4.2 Adatom Co-Assisted Activation 276
7.4.2.1 Hydrogen Activated Dissociation 276
7.4.2.2 Oxygen Assisted X–H Bond Cleavage 277
7.4.2.3 Reactivity of the Oxide Overlayers 281

8 Mechanisms of Transition Metal Catalyzed Reactions 293
8.1 Introduction 293
8.2 Hydrogenation Reactions 293
8.2.1 Ammonia Synthesis 293
8.2.1.1 Heterogeneous Catalytic Reaction 293
8.2.1.2 Enzyme Catalysis 296
8.2.2 Synthesis Gas Conversion to Methane and Liquid Hydrocarbons 297
8.2.3 Hydroconversion of Hydrocarbons 306
8.2.3.1 Ethylene 306
8.2.3.2 Acetylene 309
8.2.3.3 Hydrogenolysis and Isomerization 310
8.2.4 NH_3 and CH_4 to HCN 314
8.2.5 Electrocatalysis; H_2 Evolution 316
8.3 Oxidation Reactions  321
  8.3.1 Synthesis Gas from Methane  321
  8.3.1.1 Steam Reforming  321
  8.3.1.2 Methane Oxidation  322
  8.3.1.3 NH₃ Oxidation to NO and N₂  323
  8.3.1.4 Selective Oxidation of Ethylene  325
8.4 Uniqueness of a Metal for a Particular Selective Reaction  337
References  338

9 Solid Acid Catalysis, Theory and Reaction Mechanisms  345
  9.1 Introduction  345
  9.2 Elementary Theory of Surface Acidity and Basicity  345
    9.2.1 The Pauling Charge Excess  345
    9.2.2 The Chemistry of the Zeolitic Proton  351
      9.2.2.1 Vibrational Spectroscopy of the OH Bond  352
      9.2.2.2 Quantum Chemistry of the Zeolite Acidic OH Chemical Bond  358
      9.2.2.3 The Proton Transfer Reaction  364
      9.2.2.4 Chemical Reactivity Probes of Proton Donation Affinity: H/D Exchange Reactions  367
    9.3 Mechanism of Reactions Catalyzed by Zeolite Protons  371
      9.3.1 Introduction to Acid-Catalyzed Reactions and Their Mechanism  371
      9.3.2 Elementary Reactions in Acid Catalysis  374
        9.3.2.1 Alkene Protonation  374
        9.3.2.2 Alkane Activation  378
        9.3.2.3 Alkene Isomerization  383
        9.3.2.4 n-Butene Isomerization  386
        9.3.2.5 β-C–C Bond Cleavage  388
        9.3.2.6 The Hydride Transfer Reaction  390
      9.3.3 Catalytic Reaction Cycles and Kinetics  394
        9.3.3.1 Physical Chemistry of Zeolite Catalysis  394
        9.3.3.2 Catalytic Cracking  396
        9.3.3.3 Bifunctional Catalysis  402
        9.3.3.4 Methanol Aufbau Chemistry: Alkylation by Methanol  413
    9.4 Acid Catalysis and Hydride Transfer by Enzyme Catalysts  420
References  421

10 Zeolitic Non-Redox and Redox Catalysis, Lewis Acid Catalysis  429
  10.1 Introduction  429
  10.2 Non-Reducible Cations; The Electrostatic Field  429
  10.3 Catalysis with Non-Framework Non-Reducible Cations  433
    10.3.1 Alkali and Earth Alkali Ions  433
    10.3.2 Non Redox Oxycationic Clusters  437
  10.4 Catalysis by Non-Framework Redox Complexes  440
    10.4.1 NO Reduction Catalysis: Selective Catalytic Reduction  440
    10.4.2 N₂O Decomposition Catalysis  441
## Contents

10.4.3 Selective Oxidation of Benzene and Methane: The Panov Reaction 443
10.5 Related Homogeneous and Enzyme Oxidation Catalysts 446
10.6 Lewis Acid Catalysis by Non-Reducible Cations Located in the Zeolitic Framework 453
10.6.1 Bayer–Villiger Oxidation 454
10.6.2 Meerwein–Ponndorf–Verley Reduction and Oppenauer Oxidation 456
10.6.3 Homogeneous and Biocatalyst Analogos 461
10.6.4 Propylene Epoxidation 461
10.7 Catalysis by Redox Cations located in the Zeolitic Framework: The Thomas Oxidation Catalysts 463
10.7.1 Bayer–Villiger Oxidation with Molecular Oxygen 464
10.7.2 Zeolite Catalysts for Caprolactam Synthesis 464
10.7.3 Alkane Oxidation 467
10.8 Summary of Zeolite Catalysis 468

References 469

11 Reducible Solid State Catalysts 475
11.1 Introduction 475
11.2 Chemical Bonding of Transition Metal Oxides and Their Surfaces 475
11.2.1 Electronic Structure of the Metal Oxide Chemical Bond 475
11.2.2 The Electronic Structure of the Transition Metal Oxides 478
11.2.3 The Electronic Structure of the Transition Metal Oxide Surface 488
11.2.4 Trends in Adsorption Energies of O Adatoms to Transition Metal Oxide Surfaces 490
11.2.5 Reconstruction of Polar Surfaces 492
11.3 Mechanism of Oxidation Catalysis by Group V, VI Metal Oxides 494
11.3.1 Reactivity Trends 494
11.3.2 Selective Oxidation of Propylene and Propane 500
11.3.2.1 Propylene to Acrolein Conversion 500
11.3.2.2 Propane Ammoxidation 502
11.3.3 Methane Conversion to Higher Hydrocarbons 503
11.3.3.1 Direct CH₄ Conversion to Aromatics 503
11.3.3.2 The Mechanism of Oxidative Methane Coupling, the LiO–MgO System 504
11.4 Metathesis and Polymerization Catalysis: Surface Coordination Complexes 507
11.4.1 Alkene Disproportionation and Metathesis 507
11.4.2 Polymerization of Propylene 511
11.4.3 Ziegler–Natta Polymerization versus Metathesis Reaction 514
11.5 Sulfide Catalysts 515
11.6 Electrocatalysis: The Oxygen Evolution Reaction (OER) 520
11.6.1 Trends in OER Reactivity 520
11.6.2 Reaction Mechanism of OER Reaction 522
11.6.3 Summary Mechanism of OER Reaction 531
11.6.4  Comparison with the OER in Enzyme Catalysis  532
11.7   Photocatalytic Water Splitting  538
11.7.1  Device Considerations  538
11.7.2  Mechanism of Photoactivation of Water  540
References  545

Index  553