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
- 2.2.1.1 Hydrogenation Reactions: Transition Metal Catalysts 19
- 2.2.2 Hydrocarbon Transformation Reactions 22
- 2.2.2.1 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

iii	Contents
-----	----------

2.2.5.1	Steam	Reforming	38
---------	-------	-----------	----

2.2.5.2 NH₃ to NO_x Oxidation 39

2.2.5.3 NO Reduction Catalysis 45

2.3 Summary 48 References 51

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

- 4.6 Alloys and Other Promotors 133
- 4.7 The Working Zeolite Catalysts 136
- 4.8 The State of the Mixed Oxide Surface 139

4.9 Summary 139

References 140

5 Advanced Kinetics: Breakdown of Mean Field Approximation 145

- 5.1 Introduction 145
- 5.2 The Kinetic Monte Carlo Method: RuO₂ Catalyzed Oxidation 146
- 5.3 Single Molecule Spectroscopy 149
- 5.4 Catalytic Self-Organizing Systems 153
- 5.4.1 Introduction 153
- 5.4.2 Heterogeneous Catalytic Self-Organizing Systems 154
- 5.4.2.1 Alternation Between Two Different Surface Phases: Spiral Wave Formation 155
- 5.4.2.2 Competitive Reactive Steps Prevent Reactive Phase Formation 165 References 165

Part IIMolecular Heterogeneous Catalysis167Introduction167References171

- 6 Basic Quantum-Chemical Concepts, The Chemical Bond Revisited (Jointly Written with I. Tranca) 173
- 6.1 Introduction 173
- 6.2 The Definitions of Partial Density of States and Bond Order Overlap Population *174*
- 6.3 Diatomic Molecules that Have σ Bonds 176
- 6.4 Diatomic Molecules with π Bonds 182
- 6.5 Comparison of the Electronic Structure of Molecules and Solids 186
- 6.6 Chemical Bonding in Transition Metals 190
- 6.6.1 The Electronic Structure of the Transition Metals 190
- 6.6.2 The Relative Stability of Transition Metal Structures 199 Appendix 205 References 205

7 Chemical Bonding and Reactivity of Transition Metal

Surfaces 209

- 7.1 Introduction 209
- 7.2 The Nature of the Surface Chemical Bond 210
- 7.2.1 The Electronic Structure of the Transition Metal Surface 210
- 7.2.2 Chemisorption of Atoms and Molecules (This Section has been Jointly Written with I. Tranca.) *213*
- 7.2.2.1 The H Adatom: The Covalent Surface Bond 214

Adsorption of the Carbon Atom: The Surface Molecular
Complex 220
The Oxygen Adatom: The Polar Surface Bond 228
Adsorption Site Preference as a Function of Accessible Free
Valence 233
Chemisorption of Molecular Fragments CH_x , NH_x , and OH_x Species:
Coordination Preference as a Function of Accessible Free
Valence 233
CH_3 and NH_3 Chemisorption: The Agostic Interaction 235
Adsorption as a Function of Coordinative Unsaturation of Surface
Atoms: Relation with d Valence Band Energy Shift 243
Chemisorption of CO: Donative and Backdonative Interactions 249
Lateral Interactions 258
Scaling Laws 259
In Summary: The Adsorbate Chemical Bond 262
The Transition States of Elementary Surface Reactions 264
Adsorbate σ -Bond Activation 265
Activation of Methane 265
The Oxidative Addition and Reductive Elimination Model 268
The Umbrella Effect 269
Activation Entropy 270
σ -Bond Activation of Molecules that Bind Through their Lone Pair
Orbital 270
Dissociation of Diatomic Molecules with π -Bonds 273
Principle of Non-Shared Bonding with the Same Surface Metal Atom 274
Reactivity of Surfaces at High Coverage 274
Decreased Surface Reactivity and Site Blocking 275
Adatom Co-Assisted Activation 276
Hydrogen Activated Dissociation 276
Oxygen Assisted X–H Bond Cleavage 277
Reactivity of the Oxide Overlayers 281
References 286
Mechanisms of Transition Metal Catalyzed Reactions 293
Introduction 293
Hydrogenation Reactions 293
Ammonia Synthesis 293
Heterogeneous Catalytic Reaction 293
Enzyme Catalysis 296
Synthesis Gas Conversion to Methane and Liquid Hydrocarbons 297
Hydroconversion of Hydrocarbons 306
Ethylene 306
Ethylene 306
Ethylene 306 Acetylene 309

x Contents

- 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

- xii 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 Analogs 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

The reliance of hear ogeneous catalysis has idourished for over more than a century, its processes have contributed significantly to our modern wayof life by enabling the production of indispensible commodities such as fael and femilizer to well as materials with pressoesly unknown properties such as the polymers. Both successfy and empirical chemical discovery have physical a part to the development of meny of the catalysis and their scientific formulation by Octoold. Substant, and Haber provided the insights and tools accessary for later developments in this field.

ectential phenomena, the twentieth century can be seen as the century of developing the physical sciences at the molecular level. The formulation of a molecular theory and the development of predictive tools for helerogeneous cetarysis has been a forg and fortuous process that is now reaching a centural level of completion.